

Optimization of solutions of polyamide for AC electrospinning

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3. T. Kalous, *Improved spinnability of PA 6 solutions*, Elsevier, 2020, DOI: 10.1016/j.matlet.2020.128761

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Abstract

Nowadays, nanofibers and nanoparticles have become the attraction of study for researchers. Due to the unique physical properties such as ultra-thin fiber diameter. The electrospinning manufacturing technique produces nanofibers that have potential applications in the electronic, biomedical, and filtration industries. Until today, plenty of polymers has been electrospun into nanofibers. Researchers are trying to find the finest nanofibers with excellent spinnability on electrospinning.

This study's goal was to optimize the solution for polyamides on alternating current (AC) electrospinning. The polymers PA 6 and PA 6,12 have been chosen for the study. These polymers were dissolved in the mixture of formic acid and dichloromethane at a weight ratio of 1:1 with an increasing concentration of sulfuric acid. All the solutions were electrospun on the alternating and direct current electrospinning systems. The solubility and spinnability of polyamides were investigated. The scanning electron microscope was used for nanofiber diameter measurement. The solution parameters, such as surface tension, conductivity, and viscosity, were measured to see the impact of acid content on the mixture.

All the prepared polyamide solutions were spun on both AC and DC electrospinning systems. The sulfuric acid concentration influences the spinnability, nanofiber diameter, and solution properties. AC and DC electrospun polyamide nanofibrous structures are different in terms of bulkiness or thickness.

Keywords: Nanofibers, electrospinning, polyamide, AC and DC electrospinning, solution, additive.

Abstrakt

V současné době se nanovlákná a nanočástice staly lákadlem pro studium. A to například v jedinečným fyzikálním vlastnostem jako je ultratenký průměr vlákna. Technika výroby elektrostatického zvlákňování produkuje nanovlákná, která mají potenciální uplatnění v elektronickém, biomedicínském a filtračním průmyslu. Do dnešního dne byla spousta polymerů elektrostaticky zvlákňována do nanovláken. Vědci se snaží najít nejjemnější nanovlákná s vynikající zvlákňovatelností při elektrostatickém zvlákňování.

Hlavním cílem této studie bylo optimalizovat řešení pro polyamidy na elektrostatické zvlákňování střídavým proudem (AC). Pro studii byly vybrány polymery PA 6 a PA 6,12. Tyto polymery byly rozpuštěny ve směsi kyseliny mravenčí a dichlormethanu v hmotnostním poměru 1:1 se zvyšující se koncentrací kyseliny sírové. Všechny roztoky byly elektrostaticky zvlákňovány na systémech střídavého a stejnosměrného elektrického zvlákňování. Byla zkoumána rozpustnost a spřádatelnost polyamidů. Pro měření průměru nanovláken byl použit rastrovací elektronový mikroskop. Parametry roztoku, jako je povrchové napětí, vodivost a viskozita, byly měřeny, aby se zjistil vliv obsahu kyseliny na směs.

Všechny polyamidové roztoky byly připraveny jak na střídavém, tak stejnosměrném elektrostatickém zvlákňování. koncentrace kyseliny sírové ovlivňuje průměr nanovláken a vlastnosti roztoku. Bylo zjištěno, že AC a DC elektrostaticky zvlákňované polyamidové nanovláknenné struktury se liší co do objemnosti nebo tloušťky.

Klíčová slova: Nanovlákná, elektrostatické zvlákňování, polyamid, AC a DC elektrostatické zvlákňování, roztok, aditivum.

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1 Introduction

In the lives of humans, fibers have become a fundamental element since civilization began. The first fiber was captured as a spider web. That web of spiders is constructed of silk fibers. Over the years, humankind studied and developed many fibers. The fibers such as wool, cotton, silk, viscous rayon, and nylon. These fibers have a generally limited diameter. The diameters of these fibers range from 10 micrometers to 100 micrometers (μm).[1]

To break the limitation of the diameter of fibers, ultrathin fibers with nanometer diameters arrived in the world. This concept evolved mainly due to the electrospinning production technique. Electrospinning produces continuous nanofibers with a diameter ranging from 10 nanometers (nm) to several micrometers.[1]

Along with electrospinning, there are other methodologies also present to produce nanofibers. From these methods, electrospinning showed versatility over other methods [2]. Electrospun nanofibers have shown promise in a variety of applications, including filtration, biomedical, and electronic industries. On the other hand, the production scale of electrospinning had a high degree of potential to take into consideration. Where the electrospinning machine can be made more simplistic in design. Talking about polyamides (nylon). Nylon was the first synthetic fiber created by humans, and it is mostly used as a polymer across the globe until today. Polyamide is available as biocompatible, biodegradable, hydrophilic, and chemically resistant. Polyamide can form a nanofiber, which makes it useful in the filtration and medicine industries. Over the years, polyamides have been electrospun into nanofibers, which adds extra benefit to the application area of the polyamides. Studies are evolving to produce polyamide nanofibers to fulfill the needs of industries. Until now, many studies on the electrospinning of polyamide with different

solvent systems and with different electrospinning set-ups have been investigated. Whereas the studies said that electrospinning can produce polyamide nanofibers with a nanofiber diameter ranging from 80 nm to 200 nm on average. Also, studies have been conducted to get finer nanofiber via changing the solvent systems and their properties. By changing the solvent properties, researchers tried to achieve finer fiber diameter and scalable production of polyamide nanofibers [10–14]. But until now, the study has been done only on direct current (DC) system electrospinning. Although DC electrospinning has drawbacks compared to alternating current (AC) system electrospinning, for example, a thin layer and bulky layer of nanofibers structure.

Considering the facts mentioned in the above points, the primary goal of the study is to optimize the solution of the polyamide on an AC electrospinning system with a given solvent system. To characterize the nanofibers, fiber diameter has been investigated in this study. The solution's properties such as surface tension, conductivity, and viscosity were measured.

2 Theoretical part

The theoretical part consists of basic terminologies of electrospinning, types of electrospinning, and parameters in the electrospinning. The AC electrospinning system is compared with the DC electrospinning system. The theoretical part has shown the studies on the electrospinning of polyamides with different solvents.

2.1 Nanofibers

The word "nanofiber" includes two components, nano, and fiber. Geometrically, fiber is defined as an elongated thread object or a structural strand. A nano is defined as a billionth of the unit reference. Nanometer, nanosecond, nanogram, and so on.[2]

For producing nanoscale polymeric fiber, different techniques are available. Some of the best techniques are listed as follows -

1. Drawing [8]
2. Template synthesis [8]
3. Phase separation [9]
4. Self-assembly [10]
5. Electrospinning [11]

Each of the process techniques has its advantages and disadvantages. The above-listed numbers 1 to 4 techniques are only made for laboratory purposes. Where only electrospinning techniques can be used in the laboratory as well as at the industrial level.[2]

The principle and apparatus setup of electrospinning is simple to understand and versatile for any researcher. Products produced from electrospinning have applications in the areas of smart mats, filtration membranes, storage components, biomedical scaffolds, and electronic devices.[1]

The electrospinning systems facilities produce a range of polymer electrospinning. It can produce nanoscale diameter fiber with several centimeters to several meters of fiber length. Electrospinning is becoming a stronger candidate among other techniques because of its cost-effectiveness, long continuous fiber formation can be done, and it can be used at the industrial level.[2]

2.2 Electrospinning

The history of fibers starts over 140 million years ago. Until now, fibers have become a fundamental element of human life since the start of civilization. In the year 1880, Rayon was introduced as the first synthetic fiber and fabric. In the year 1938, the first synthetic fiber, nylon, was developed by Dupont.[1]

Synthetic fibers can be produced via different methods. Some of the leading methods are wet, dry, melt, and gel spinning. In these spinning techniques, jets are created due to shearing and or by mechanical drawing when they are coming out of the spinneret. These techniques have a limited fiber diameter range. The diameter of fibers produced by these techniques ranges from 10 μm to 100 μm . [1]

The electrospun fibers have diameters of 10 nm to several micrometers. Even the nanofiber diameters are below 1 nm. Electrospinning is known as a versatile production technique because of its plain design construction and the availability of a range of polymer processing. Electrospinning technology comes with a wide range of production methods, which include needle, needleless, electro blowing, melt, multijet, centrifugal, direct current source, and an alternating current source electrospinning method. All these methods have advantages and disadvantages in comparison to one another. Needle-based electrospinning systems have

lower production as compared with needleless electrospinning due to needle blocking problems [12]. Where needleless shows lower control of the electrospinning solutions as compared with needle-based electrospinning. The type of power source for electrospinning also changes the production of electrospinning and the processability of polymers in electrospinning. This describes electrospinning as a versatile technology and has the potential for many developments.

William Gilbert was the first person who described the electrostatic attraction of liquid in the year 1600 [13]. The process of manufacturing nanofibers was described by Charles Vernon's boys. In the year 1900, the first patent came onto the board by John Francis Cooley. In 1914, John Zeleney studied the liquid droplet behavior at metal capillaries, which helped to start the mathematical model study for fluids under electrostatic forces.[14]

Around 22 patents on electrospinning were given in the period between 1933 and 1944 by Anton Formhals. He designed a prototype machine with a saw-toothed rotating blade and a fiber emitter. The circular saw blade was partially submerged in a spinnable liquid. On the wet tip of the saw, electrical charges are concentrated, which will cause the generation of fibers. Those created fibers fly off from the saw tip to a rotating disc. It was the first trial done by Formhals. After this, he kept researching the topic. Between 1964 and 1969, the mathematical modeling of electrospinning was done by Geoffery Ingram Taylor. After 1995, there were enough research papers published, mostly by Reneker. He advertised the electrospinning process. Through this advertisement, electrospinning comes into the light for studies. [13]

2.2.1 Principle of Electrospinning

The chapter introduces the working principle of electrospinning and elaborates on the electrospinning parameters and their importance.

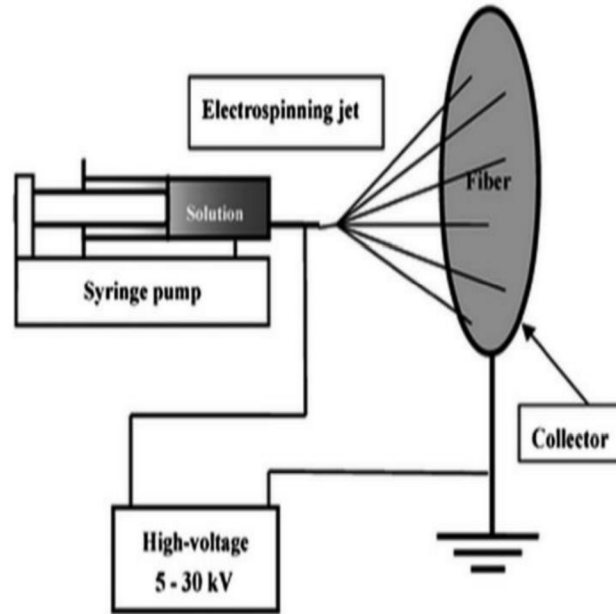


Figure 1: Basic electrospinning setup.[15]

The basic setup, or a framework of electrospinning, is shown in Figure 1. The electrospinning setup consists mainly of three parts: a syringe filled with the polymer solution, a high voltage supply, and a grounded plate. These three parts provide individual objects in the electrospinning process. A high voltage supply is used to impart the required electric force on the polymer solution. By introducing electric force to the solution, the solution becomes unstable. The solution is attracted by the grounded collector. The stretching of the polymer solution occurs between the syringe tip and the collector. This phenomenon is called Taylor cone formation. While the collector work to collect the produced nanofibrous mat. The polymer solution is electro spinnable when it can carry the electrical charges and an optimum amount of viscosity to be stretched out without resulting in droplets. The high voltage supply is connected to the electrode. The collector is placed

counter to the electrode. The electrical field is created between the electrode and the ground collector. A solution or melt is filled into a capillary tube. A drop suspended from a needle of polymer solution becomes electrified when the intensity of the electrical field is increased. When electric charges are induced into the liquid surface, the deformation of the liquid drop occurs into a conical shape on the liquid surface. This conical shape is termed the "Taylor cone" When electrical force surpasses the surface tension of the solution, a charged jet of solution appears. Then this polymer jet is ejected from the tip of the Taylor cone and travels towards the collector. A polymer jet needs to be a stable jet from a continuous fiber. If the polymer jet is unstable, it will result in whipping. The polymer jet, after leaving the stable zone, experiences a series of bending instabilities. The polymer solution is transferred from the solution surface to the collector, the polymer solution leads to fiber elongation and solvent evaporation occurs in the air.[15]

The electrospinning process gives continuous and long fibers with an uneven fiber diameter distribution along the length. The nanofibers that are created are internally solid and have a smooth surface. While different nanofiber structures have been developed, such as multichannel, tubular, core/shell, porous, hollow, necklace, and ribbon structures nanofibers.[24 – 29]

2.2.2 Parameters in electrospinning

While talking about the spinnability of polymer and properties of produced nanofibers highly dependent on the parameters of electrospinning. The electrospinning parameters are divided into two main types: solution parameters and process parameters. Where solution parameters include solution viscosity, conductivity, and surface tension of the solution, the process parameters can be changed with applied current voltage, tip to collector distance, feeding

flow rate, etc. Process parameters and solution parameters are both quite important because the morphology and diameter of nanofibers depend on them. The ambient conditions used during the electrospinning can affect the diameter of the produced fibers. Ambient conditions, such as surrounding temperature and humidity.[21]

In the electrospinning process, the applied voltage to the solution is one of the crucial parameters. After reaching a threshold voltage, fiber formation occurs. The voltage introduces a required number of charges into the solution of the electrospinning process. As the supply voltage increases, the nanofibers are elongated in the electrospinning up to a certain point of voltage, if the applied voltage exceeds the optimum value, bead formation (small spherical objects) will occur in the fiber. For that purpose, the supply voltage should be optimum for each polymeric solution.[30,31]

The flow rate of the solution in the electrospinning also affects the final nanofiber characteristic. The flow rate of the solution influences the velocity of the jet and the mass transfer rate of the solution. While the smallest amount of flow rate results in finer fiber formation due to exposure to high evaporation time for the solvent. The low flow rate of the solution is suitable for electrospinning. An increase in the flow rate results in the growth of the fiber diameter up to a certain limit. While a higher flow rate leads to bead formation due to less time of evaporation for the solvent. The distance between the spinning electrode and the collector affects the morphology of the fiber. Because the distance between electrode and collector affects the time of deposition of fiber on the collector. The evaporation of the solvent is affected by this distance. A small distance will not give enough time for evaporation of solvents, which results in a thick fiber formation, and a longer distance will result in an elongated fiber due to added evaporation time.[32–34]

Solution concentration and viscosity of solution change the electrospinning process. An optimum amount of solution concentration is needed during electrospinning. Lower solution concentration results in bed formation and a higher concentration gives thicker fiber formation. The concentration of the solution must be optimized [26]. The molecular weight of the polymer also has a significant impact on the rheological and electrical properties of the solution. Generally, larger molecular weight polymers are used for electrospinning. The large molecular weight of polymer supplies a minimum amount of viscosity for electrospinning. The low molecular weight of polymer leads to bed formation, and a higher weight can also result in a larger fiber diameter [27]. The viscosity of the solution should be controlled. The lower viscosity of the solution causes problems during fiber formation. The increased viscosity shows the difficulty in the ejection of a jet from the tip of the needle during electrospinning [28]. The solution conductivity is affected by polymer type, solvent type, and the feasibility of ionizable salt in the solution. An increase in the solution conductivity results in a reduction in the fiber diameter. If the conductivity of the solution is low, the elongation of the jet will be low during electrospinning, which can lead to bed formation.[29]

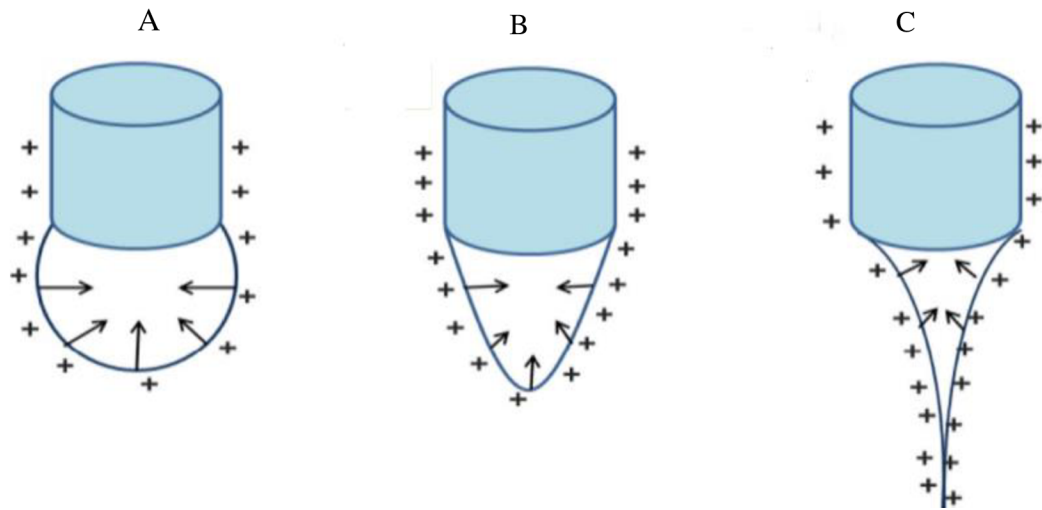


Figure 2: Formation of Taylor cone according to the conductivity of a solution. A- at the start, B - destabilization of the droplet, C- in Taylor cone formation.[30]

Figure 2 shows the droplet shape changes during the electrospinning process. The plus sign in the figure shows the charges on droplets and arrows characterize the capillary force acting on the liquid surface. Due to the contest between the electrical forces and capillary force jet formation occurred during the electrospinning. Whereas the choice of solvent depends on the boiling point and surface tension of the solvent. A lower boiling point will cause higher evaporation and a higher boiling point will cause less evaporation. The process of solidifying fibers depends on the humidity and temperature provided in the environment. If we increase the temperature and humidity, the fiber surface becomes porous. The elevated temperature will cause more evaporation of the solvent, and high humidity will cause condensing of water vapor.[21]

During the production of nanofibers, electrospinning is characterized by

- Diameter of fiber
- Continuity
- Surface (should be defect-free and porosity of nonfibrous structure if needed)

The diameter should be equal throughout the length. The surface shouldn't hold any beads and pores in it, affecting the fiber properties. Continuity of fiber is important to collect the fiber on the collector.[21]

2.2.3 Types of electrospinning

The conventional electrospinning technique uses a needle as a spinneret. Because of that, it is known as "needle electrospinning". Conventional electrospinning is a versatile technique, but it has some drawbacks. Conventional electrospinning has a limited amount of productivity and sometimes uses toxic solvents that are concerned for the environment. Due to this drawback, electrospinning comes in unique designs.[15]

2.2.3.1 Melt electrospinning

The polymers that cannot be dissolved in common solvents. For those polymers that melt electrospinning is the way of manufacturing nanofibers. A suitable temperature is used for the melting of the polymer in this process. Larrondo and Manley applied electrostatic force to a molten polymer to spin out the nanofibers. The whole setup of the machine is conventional. A polymer heater is used to melt the polymer. This setup comes with many advantages, such as no need for solvent, a high throughput rate, and ease of fabricating polymeric fiber blends. It has limitations such as a complex configuration due to the heater plantation in the design, the requirement of an elevated temperature melting system, electric discharge problems associated with the melt, and low conductivity of the melt polymer.[31]

2.2.3.2 Multijet electrospinning

To increase the production of nanofibers, and to form multi jets from solution, multiple needles are used instead of a single needle in electrospinning. Multijet electrospinning comes

with different configurations of several needles, needle designs, and needle gauges. The main problem with multijet is a jet deviation between the needles, which creates instability in the process. Instability includes the dripping of polymer solution and difficulty in the collection of the fibers on the collector. Multijet electrospinning devices are tried in industrial plants with 1000 nozzles, the trial found an issue related to industrialization requires large working spaces. Regular needle cleanup makes for much more complex work.[15]

2.2.3.3 Electro blowing or gas jet electrospinning

This technique uses two simultaneous forces to produce nanofiber. It uses electric force and air-blowing shear force. The same design as conventional electrospinning with an added air blower. This design is mainly used for a highly viscous solution, where electric force has less power to overcome surface tension.[15]

2.2.3.4 Centrifugal electrospinning

This type of electrospinning uses a combination of centrifugal and electrical force to produce nanofiber. This design provides a higher orientation of polymer chains and gives higher production with less electrical energy. This design is expensive compared with others. The main drawback is that the produced fibers may be non-continuous.[15]

2.2.3.5 Needleless electrospinning

Needle-based electrospinning has its problems that can be resolved by a needleless electrospinning setup. The needleless electrospinning supplies solutions to problems such as needle clogging and makes it easy to scale up the production of the electrospinning process. The setup configuration is easy and simple to construct. Needleless electrospinning design

manufactures nanofibers directly from the open liquid surface. In 1979, the first needleless electrospinning attracted researchers to focus on it [32]. In needleless electrospinning unique designs of the electrodes are present, which include air bubble [33], conical wire aided by the act of gravity [34], metal plate [35], splashing spinneret [36], rotary cone [37], bowl edge [38], toothed wheel [39], linear flume [40], and shear added spinneret [41]. In needle spinning, polymeric jet formation occurred due to capillary action, but in needleless electrospinning, polymeric jet formation occurred on a free liquid surface. The needleless electrospinning, it is hard to control the jet formation, which is one of the tasks in needleless electrospinning that needs to be focused on.[42]

2.2.4 AC electrospinning

In the year 2004, the first study was done on AC electrospinning. Kessick, the researcher, conducted a study on AC electrospinning. Recent studies say that AC electrospinning can produce nanofiber at a high production rate with a bulky structure. Due to its bulky structure, AC electrospinning is used for the fabrication of nanofibers. This fibrous structure is used in fibrous scaffolds and drug delivery systems. [43]

In conventional electrospinning, capillary pressure is an important term for jet formation for nanofibrous formation. When electric pressure is suppressed on capillary pressure, jet formation occurs. Studies state that AC electrospinning imparts higher hydrodynamic instability into the polymer solution, which leads to fiber formation.[44]

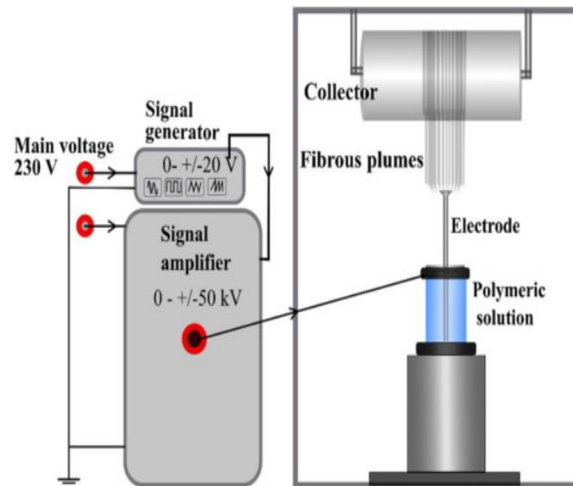


Figure 3: Basic schematic for AC electrospinning system.[44]

The DC electrospinning system and the AC electrospinning system work in a comparable way. In both systems, electrical charges are introduced to the solution and the rest of the things are different from each other. While the main difference between AC and DC is the type of power supply for electrospinning and collector used in both systems. The DC electrospinning uses a constant charge in the solution and an electrically active collector, which must be grounded. In the case of AC electrospinning, the collector does not require to be electrically active due to charge neutralization. AC electrospinning works on positive and negative polarities for the formation of nanofiber. It uses a function having both positive and negative “half steps” in the form of a sign wave, step function, or other. The AC electrical field shows attraction and repulsion of the Coulombic forces, due to the opposite polarities. This polarity of AC electrospinning generates the virtual collector and electrical wind simultaneously. This wind and virtual collector were generated due to the ionization between the air and electrode. At every half cycle of current, the ionized gas makes a connection with the emerging charged jets from the solution. The collector is provided by the previously emitted fiber, and the ionic wind is produced continuously. Concurrently, negative, and positive charges attract together and neutralize the net charge. Because of this phenomenon,

AC electrospinning gives a reduced amount of whipping and starching instability during the jet formation.[44]

This produced plume moves vertically away from the electrode, and electrical wind allows the fibers to collect on the collector. The nanofibrous structure is inactive. The collection of nanofibers is easier in AC electrospinning due to the self-bundling tendency of the plumes produced by AC electrospinning.[44]

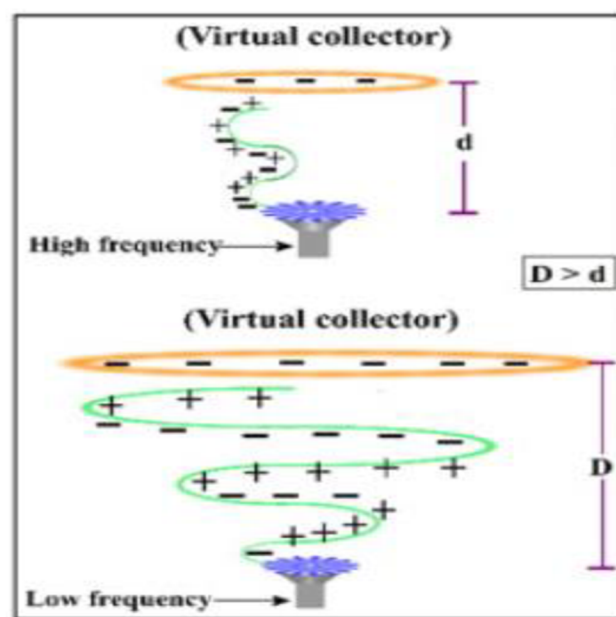


Figure 4: Electrical wind due to the polarity results in a virtual collector.[44]

Studies show that the AC electrospinning system depends on the AC electricity source, electricity properties (voltage, frequency), type of electrode, solution properties, and relative atmosphere during the electrospinning. Electrical parameters such as voltage and frequency play the main roles during fiber formation. According to some studies, voltage ranges ranging from 5 kV to 30 kV were used for AC electrospinning with a needle [51,53,54,55]. The AC electrospinning system can be designed as a needle or needleless system as per our product and producer requirements. [47]

2.2.5 AC and DC electrospinning

Electrospinning can be broadly classified into systems using an alternating current source (AC) and a direct current source (DC). The most widely accepted technique across the globe is direct current electrospinning.[56–58]

The AC and DC electrospinning systems work on different electrical supply sources and design constructions. Because of that, they have their advantages and disadvantages which need to be compared. Presently, several electrospinning machines can mass-produce nanofibers at the industrial level. Machines such as Nanospider™ NS 8S1600U by Elmarco and Nanospinner 416 by Inovenso can produce nanofibers at the industrial level.

The DC electrospinning system has a DC power supply, syringe pump, needle, and grounded collector. The needle and collector are connected to an opposite charge. Taylor cone formation occurred due to the accumulation of the same charges on the liquid surface. The jet is extended by the movement of the electrical field towards the collector. In DC electrospinning, the potential difference between the needle and the collector causes nanofiber formation.[1]

An AC electrospinning system has four main components: an AC power supply, pump, needle, and collector (electrically inactive). In AC electrospinning, due to a change in the polarity of charge, a nanofiber flume is produced from the polymer solution and the movement of the nanofibers towards the collector occurs due to the electrical wind.[51, 53, 55]

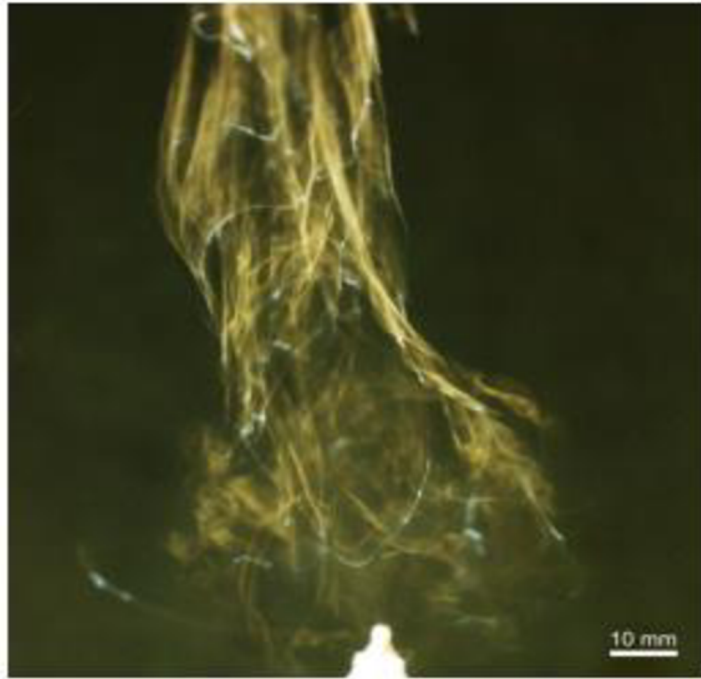


Figure 5: Nanofibrous creates a smoke-like structure on the AC electrospinning without a grounded collector.[51]

In Figure 5, basic AC electrospinning nanofiber generation has been shown. In the picture, it is seen that the produced nanofibers are creating a smoke-like, bulky nanofibrous structure during the spinning. That smoke-like formation of nanofibers is also called a plume. A charged electrode is typically covered in a polymer solution in the form of a thin film in both AC and DC electrospinning systems. The DC electrospinning needs to charge the collector with electrodes or grounded to attract the generated fibers to accumulate on them. Where AC electrospinning doesn't need an electrically active collector, it works on a virtual collector due to the ionization in air. In DC electrospinning, the electrically active collector-produced nanofiber layers are collected at a certain area and dense nanofiber layers are formed at the collector. Whereas AC electrospinning produces bulkier nanofiber structures.[56–59]

Studies state that AC electrospinning has a higher throughput rate than DC electrospinning because AC electrospinning produces multiple jets of polymer continuously with charged and discharged drops. The DC electrospinning produces a single jet from a drop of the liquid surface, due to the high amount of jet formation from AC electrospinning showing higher nanofibrous production than the DC system, the production can be 20 times higher [52]. The collector less electrospinning results in savings on capital equipment and production costs. An AC system doesn't require a grounded collector. In the AC, electrospinning plumes are attracted to the collector due to the electrical wind. In the DC electrospinning system, produced fibers are charged with a single charge. Due to the single charge formation on fibers, fibers tend to repel each other and cause problems during accumulation on the collector. In the case of the AC system, it's achievable easily. Also, AC system electrospinning supplies a bulky nanofibrous layer and it can cover any material.[48–50, 53]

The production of both charged fibers leads to the neutral product at the end of production, and due to the bulkiness of the nanofiber layer, these layers can be used in the filtration industry, tissue engineering, and composites. A recent study paper shows that there is still potential in the development of AC electrospinning, areas such as the improvement in the optimization of the shape or frequency of AC signals and the modification of electrospinning solutions.[48–50]

2.3 Polyamides

Polyamides are formed by joining amine and carboxylic groups (-CO-NH-). Polyamides are generated via synthetic and natural means [54]. Synthetic polyamides are formed by condensation polymerization, and synthetic polymers include aliphatic polyamides (Nylon),

aromatic polyamides (Aramids), and polyphthalamides. Natural polyamides include silk and wool.[55]

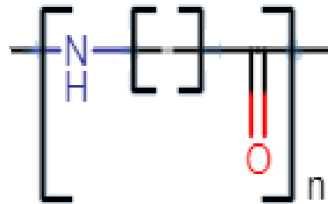
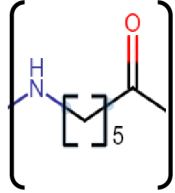
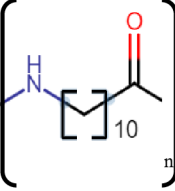
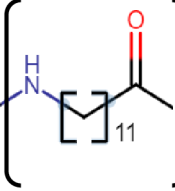
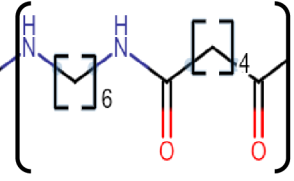
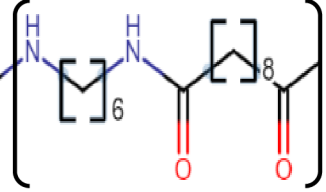
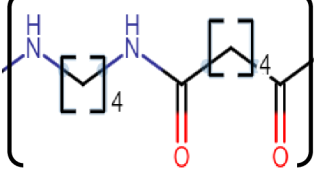


Figure 6: Basic unit structure of polyamide.

In the year 1930, the invention of nylon was made by Dupont, who put nylon on the market for practical use. In 1938, Dupont used nylon fibers to make toothbrush bristles for the first time. During the second world war, polyamide became popular in synthetic textiles due to its unique properties such as chemical resistance, lightweight, excellent elastic recovery, and high mechanical strength. They were first commercially used for waterproof tents and parachute fabrics.[56]

Table 1: Chemical structures of monomers of polyamide.[57]

Polyamide	Repeating unit
6	
11	
12	
6,6	
6,10	
4,6	

The filaments are known for their fineness. The polyamide can produce a fine filament with a long length. Filaments of polyamide can have a length equal to the distance between New York (NY) and London (LON) cities. For this reason, aliphatic polyamide is famously known as nylon. There are two types of nylon: nylon XY and nylon Z. X and Y represent the carbon atoms connected to diamine and diacid, and Z stands for carbon atoms in the repeating unit. There are several types of polyamides present in the current market. Polyamides such as nylon 6 and nylon 6,6 are the most used, and other polyamides such as nylon 4,6, nylon 6,10, nylon 6,12, nylon 11, and nylon 12 are used for special purposes. Nylon 6,6 raw material is hexamethylene diamine and adipic acid. A polycondensation reaction happens when these materials react together. Nylon 6 is a polyamide polymer of the Z type. For nylon 6, caprolactam is used as the raw material. Caprolactam needs a catalyst to start polymerization. A catalyst such as water can be used during the reaction. The catalyst converts a small amount of caprolactam to ϵ -aminocaproic acid. This acid helps the polymerization process.[58]



Polyamides come in the semicrystalline polymer category. Nylons are known for their extensibility, high abrasion resistance, high strength, and excellent resistance to most chemicals. Due to this property, nylon is used in dress materials, hosiery products, outerwear, and floor coverings. Nylons are used in technical textiles such as carpet fibers, parachute fabrics, car safety belts, hoses, and lightweight canvas for luggage, tyer cords, ropes, cordages, fishing nets, and printer ribbons, bolting cloths, and sutures.[59]

2.4 Polyamides as nanofibers

Polyester, polyvinyl alcohol, polyvinylidene fluoride, and polyamides are thermoplastic polymers that are commonly used for the electrospinning of nanofibers. Most of these thermoplastic polymers are synthetic. Some PA can be made from natural materials, and PA is the most utilized polymer around the globe as compared with other synthetic polymers.[68,69]

Table 2: Properties of polyamide.[62]

Properties	PA 6	PA 11	PA 6,12
Melting point (K)	342	461	218
Molecular weight (g/mol)	113	183	328
Density (g/cm ³)	1.13	1.15	1.05
Dielectric constant	3.80	3.15	3.90

Polyamide nanofibers proved a fiber diameter range of 100 nm to 300 nm on electrospinning. Silicon dioxide nanoparticles are used during electrospinning with polyamide to form a composite to get better biocompatibility, tunable size of fiber diameter, and filtration properties, and it will also have an antimicrobial effect on the material. which shows added benefits to textile structures. So, PA 6 is light in weight, easy to electro spin, and widely used as membranes for filters, and polyamide nanofibers have immense potential in various applications.[68,69]

In recent days and into the future, the world has faced a scarcity of oil, gases, and plastic problems. This points to a better future for PA 11 because it can be produced from castor beans and is a biodegradable polymer. PA 11 nanofibers can be used in water filters, textiles, and sound absorbers. The electrospun PA 11 nanofibers have an average fiber diameter of

130 nm to 800 nm. In the case of PA 6,6, electrospun nanofibers showed a 65 nm to 220 nm average fiber diameter range. It can be electrospun with formic acid and dichloromethane solvent, which is inexpensive and can be produced at large-scale production.[10,70–72]

The polyamide 6,12 polymer is made from dodecanedioic acid (DDDA) and hexamethylene diamine. The polyamide 6,12 does not have adipic acid in the polymer chain, due to which it is more thermally stable than polyamide 6,6. PA 6,12 shows properties such as stable mechanical property, resistance to abrasion, and excellent chemical resistance. It has low moisture absorption, better dimensional stability, and ductility. It has applications in the areas of automobile manufacturing, electric and electronic appliances, and aerospace engineering.[66,67]

2.5 Electrospinning of polyamides

This chapter shows, both the AC and DC electrospinning of polyamides. Diverse types of solvents and additives are being used to improve the spinnability of polyamides in electrospinning, which is highlighted in this chapter.

2.5.1 Solvent systems and additives for polyamide electrospinning

Until now, most of the studies on polyamide nanofiber have focused on the DC electrospinning system. From the year 2000, AC electrospinning started to attract attention for research. In 2014, AC electrospinning has shown can produce nanofibers without an electric active collector [43]. In specific cases, not all the solutions spin well on the DC system, but they can spin on the AC system and vice versa. The solution parameters affect the processability of electrospinning, the diameter of nanofibers, and the shape of the nanofibers. The electrospinning solution parameters include solvent, polymer concentration,

viscosity, surface tension, and solution conductivity. These solution parameters are interconnected with each other. The viscosity of the solution depends on the concentration, molecular weight, and weight distribution of the polymer. While the surface tension and conductivity of the solution also depend on the concentration of solute, they can be altered by the addition of additives (ionic salts or surfactants) into the solution.[60]

Electrospinning depends on the type of solvent or mixture of solvents and the concentration of the solution used for electrospinning. Due to the semicrystalline structure and amide group linkages present in polyamide, the polyamide polymer is difficult to dissolve in any solvent. Polyamide can dissolve in formic acid (FA), cresol, or fluoric solvents.[7]

The polyamide can be electrospun using different solvent systems. Solvents used for the electrospinning of polyamides are mentioned in Table 3. Some of the polyamides are electrospun with a single solvent system and others with a mixed solvent system. Each solvent has individual properties such as density, boiling point, dipole moment, and dielectric constants that affect the electrospinning of polymers and average fiber diameter. Overall, solvent properties play a leading role during electrospinning. The dipole moment of the solvent results in the cohesive energy between the solvent and the polymer chain, which means it describes whether the solvent is good or bad for the polymer in the whole entanglement of polymer chains. The dielectric constant of the solvent measures net charge deposition on the spherical droplet, which helps to measure the ease of fiber formation. Mostly, during the choice of solvent, high dipole moment and dielectric constant are preferred. The boiling point of the solvent should be perfected. Because of the lower boiling point, the solvent evaporates quickly, which can cause the needle to clog. Where the high boiling point of the solvent requires a longer evaporation time during electrospinning there is no period available for evaporation during electrospinning.[6,68]

Table 3: Solvents for electrospinning of the polyamides.[12,13]

Solvents	Density (g/cm ³)	Boiling point(°C)	Dipole moment (Debey)	Dielectric constants
Ethanol	0.78	78	1.7	24.6
Dimethylformamide (DMF)	0.94	153	3.8	37.0
m-cresol	1.03	203	1.4	11.8
Acetic acid	1.04	117	1.7	6.2
Dimethyl sulfoxide (DMSO)	1.09	189	3.9	46.7
Formic acid	1.22	101	1.4	51.1
Chlorophenol	1.26	175	1.1	8.2
Dichloromethane	1.32	40	1.6	8.9
Trifluoroacetic acid	1.53	73	2.2	8.4
Hexafluoroisopropanal	1.59	58	2.0	16.7
Sulfuric acid	1.83	117	1.5	101.0

2.5.1.1 Single solvent system for electrospinning of polyamides

Mit-Uppatham et al, electrospun the polyamide 6 with different solvent systems. He used PA 6 resin of 20,000 molecular weights (Da) with a 32 % (w/v) concentration for all trials and solvents used as, 85 wt. % formic acid, m-cresol, 96 wt. % glacial acetic acid, sulfuric acid ethanol N, N -dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). During the solution preparation, it was seen that formic acid, m-cresol, and sulfuric acid are good solvents. Formic acid takes the shortest time (6 hours of stirring for the dissolution of PA 6) for solution preparation. While m-cresol and sulfuric acid take one day to get a transparent solution. The acetic acid, ethanol, DMF, and DMSO solvents are unable to dissolve PA 6.[69]

The electrospinning of PA 6 with formic acid, sulfuric acid, and m-cresol-based solutions, results in a state where the continuous jets of polyamide are formed from the formic acid solution system. The m-cresol solution shows discrete jet formation during electrospinning. A sulfuric acid solution electrospinning resulted in droplet formation. Diluted sulfuric acid (20 and 40 wt. %) seemed to have better solution formation than 100 wt. % of sulfuric acid.

But the diluted sulfuric acid solution system did not electrospin. The reason behind the failure of spinnability of polyamide with the sulfuric acid solution could be due to a sudden reduction in molecular weight of polyamide that results in a drop in the viscosity of the solution. The average fiber diameter of about 83.5 nm and the smooth circular cross-section of PA 6 nanofibers results in a formic acid solution system. While the fused fibers were seen with an m-cresol solution system. The low dielectric constant and high boiling point of m-cresol caused the fused fiber formation.[69]

R, Nirmala et al, studied the electrospinning of PA 6 with different solvent systems. The solvent system in these studies includes formic acid, dichloromethane, chlorophenol, acetic acid, hexafluoroisopropanol, and trifluoroacetic acid. These solvents are used as single and in mixed solvent systems. During this study, other parameters were kept constant, and they performed the electrospinning of polyamide with a different solvent system. The electrospinning of polyamide in a single solvent system, the formic acid solvent system, is spinnable. The polyamide fibers produced with formic acid solution show an 80 nm to 100 nm average fiber diameter with a uniform distribution of fibers. Formic acid is a polar protic solvent that can attack lactam to generate a series of oligomers. The solution of polyamide with formic acid shows polyelectrolytic behavior. Unlike the acetic acid single solvent system, the polyamide does not dissolve. The reason said in the studies is that the high evaporation rate of the solvent causes an improper mixture of solutions. [5]

The chlorophenol single solvent system for polyamide is a good solvent and can electrospin the polyamide. Chlorophenol has low conductivity, but it produces polyamide nanofibers with a size ranging from 100 nm to 220 nm. The nanofibers are unable to produce a high aspect ratio with this solution system, while the uniformity of fibers can be adjusted by varying the solution concentration and voltage.[5]

Hexafluoroisopropanol is acidic alcohol with a strong hydrogen bonding solvent that is used for different polymers. In the hexafluoroisopropanol single solvent system, polyamide is electro spinnable, but the solution has a high viscosity, which results in thicker fiber formation. The fiber diameters range from 900 nm to 1200 nm. While trifluoro single solvent polyamide is electro spinnable up to the mark, the viscosity of trifluoro is extremely high. Fibers produced with this solution are thick and film structures.[5]

2.5.1.2 Mixed solvent system for electrospinning of polyamides

Mit-Uppatham used mixed solvents systems to electrospun the PA 6 while keeping the formic acid as one of the main solvents in the mixture. He used various mixtures of solutions and measured the viscosity, surface tension, and conductivity of the solutions given in Table 4.

Mit- Uppatham tried to spin the PA 6 with a solvent mixture of formic acid and m-cresol, with different ratios. As the content of m-cresol with formic acid increases, the viscosity, and conductivity of the solution increase. Where the surface tension of the solution decreases. The content of 10 % to 30 % of m-cresol with formic acid, showed discrete fiber formation and increased fiber diameter from 100 nm to 200 nm. While 40 wt. % content of m-cresol solution created fused fibers. The solution of formic acid with 20 wt. % or 40 wt. % sulfuric acids it's not electro-spinnable. The reason behind this is that sulfuric acid is a strong acid, which can hydrolyze PA 6 molecules. Resulting in lower viscosity and higher conductivity of the solution.[69]

Table 4: Solution systems used by Mit-Uppatham in the study.[69]

Solvent system	(% v/v)	Viscosity (Pa*s)	Surface tension (mN/m ²)	Conductivity (ms/cm)
Formic acid + m-cresol	90/10	1.70	42.44	2.93
	80/20	2.10	41.35	2.11
	70/30	3.12	40.65	1.39
	60/40	4.07	39.88	0.82
Formic acid + 20 wt. % Sulfuric acid	90/10	1.29	43.85	7.31
	80/20	0.83	44.53	14.94
	70/30	0.79	44.53	24.00
	60/40	0.51	44.73	41.31
Formic acid + 40 wt. % Sulfuric acid	90/10	1.38	42.83	10.37
	80/20	1.09	43.43	20.32
	70/30	0.93	43.83	34.80
	60/40	0.68	44.23	59.10
Formic acid + Acetic acid	90/10	1.45	42.83	10.37
	80/20	1.56	41.13	2.55
	70/30	1.76	39.83	1.82
	60/40	2.03	39.73	1.28
Formic acid + Ethanol	90/10	1.11	42.32	3.10
Formic acid + Dimethylformamide	90/10	1.29	43.63	3.63
Formic acid + Dimethyl sulfoxide	90/10	1.75	43.61	3.09

A solvent system of formic acid with acetic acid in compositional ratios of 10 % to 40 % (v/v) of acetic acid is electro spinnable for PA 6. Results show that an increasing amount of acetic acid leads to an increase in the viscosity of the solution and a decrease in the conductivity and surface tension of the solution. The average fiber diameter also increased with an increased amount of acetic acid in the solution. The average fiber diameter ranges from 93.6 nm to 235.6 nm.[69]

Ethanol is known for its low boiling point and low surface tension for electrospinning. The ethanol and formic acid solutions are capable of electrospinning the PA 6, but it shows a problem during the solution formation. According to SEM image analysis, the 10 % ethanol content had an average fiber diameter of 90.9 nm, and the 20 % ethanol had an average fiber diameter of 115 nm.[73,74]

DMF and DMSO solvents are known as higher dielectric constant and high dipole moment compounds. The DMF and DMSO with formic acid up to 10 % (v/v) can be electrospun into the polyamide. At 20 % (v/v) DMF or DMSO with formic acid, it is not capable of dissolving 32 % (v/v) PA 6. The solution becomes inhomogeneous. The PA 6 can be electrospun with this solution. An increase in DMF and DMSO content causes a decrease in the fiber diameter. In general, the study states that the average fiber diameter is increasing with an increasing amount of the second solvent for the solvent system, m-cresol, sulfuric acid, acetic acid, and ethanol. While DMF and DMSO with increased formic acid content showed a decrease in the fiber diameter.[73,74]

While R, Nirmala, tried to spin polyamide on DC electrospinning with a mixture of different solvents. The study kept formic acid as a constant solvent in different mixed solvent trials. The following mixtures of solvents are used to electrospun the polyamide.[5]

Table 5: Solvents and their properties used for electrospinning polyamides.[5]

Solvent system	Solvent ratio (%)	Viscosity (Pa*s)	Conductivity (mS/m)
Formic acid	100	1.37	412
Formic acid + Dichloromethane	69:40	2.33	157
Formic acid + Acetic acid	60:40	2.37	112
Formic acid + Acetic acid	80:20	1.92	210
Formic acid + Chlorophenol	50:50	1.33	60

Used solvent mixtures such as formic acid with dichloromethane or acetic acid or chlorophenol. The formic acid with dichloromethane showed a thick mixture of flat ribbon-like fibers and cylindrical fibers. It showed uniform fiber distribution and a fiber diameter ranging from 150 nm to 300 nm. The reason behind the ribbon formation is given as faster evaporation of the solvent. While formic acid and acetic acid solvents with 3:2, 4:1, and 3:2 ratio solvents showed smooth fiber surface morphology with fiber diameters from 100 nm to 200 nm. In the case of a 4:1 ratio of formic acid and acetic acid, polyamide nanofiber showed fiber diameters of 135 nm to 165 nm. During the electrospinning, some flake generations also occurred. For both ratios, it is possible to electrospun polyamide due to the lower dielectric constant and surface tension of the solvents. Formic acid and chlorophenol solvent systems with a 1:1 ratio can be electrospun, but they show thicker nanofiber formation compared to other solvent systems, with a fiber diameter ranging from 120 nm to 220 nm. R, Nirmala said that formic acid in a single solvent system results in fine and uniform fiber distribution over another solvent system.[5]

To see the effect of the solution conductivity on the solution, salt is used to alter the solution conductivity. Sodium chloride (NaCl) was used as a salt, from 1 to 5 wt.% concentration. An increase in concentration results in droplet formation during electrospinning. The reason behind the droplet formation is due to coulombic force, viscoelastic force, and surface

tension. Coulombic force comes into play when the viscosity of the solution is extremely low. When the solution has a high viscosity, the viscoelastic force is much higher than the coulombic force due to which higher chain length entanglement occurs. It will result in preventing droplet formation. While the conductivity of the solution increased with an increased amount of salt, the addition of salt gave a flat fiber structure and increased fiber diameter with increased salt content.[73,74]

Kris et al. study the new solvent systems for polyamide 11 and 12 electrospinning. This solvent system should fulfill the requirements of electrospinning and should be practical economically. In his study, it is seen that one of the researchers, named Mr. Stephens, used 1,1,1,3,3,3-hexafluoro-2-propanol solvent for the electrospinning of polyamide 12, and it was a successful trial of electrospinning. The drawback of this experiment was that the solvent was expensive, and the solvent is flammable. Which limits this trial to use in industrial applications.[3]

The study used formic acid and dichloromethane (DMC or DCM) as a solvent. Formic acid and DMC are cheap solvents and are widely used in the electrospinning of different polymers. During the experiment, the polyamide dissolved properly and electrospun with a controlled diameter. For the preparation of the solvents, he used hydrophilic solvents such as acetic acid, nitric acid, formic acid, and sulfuric acid. Where hydrophobic solvents like tetrahydrofuran, dichlorobenzene, DMC, and toluene solvents were used. The study used all possible combinations of these solvents. The study found out that only formic acid and DMC combinations can dissolve polyamide well. The study tried to electrospun the polyamides with different volume ratios of formic acid and DMC. The 1:3 ratio of FA and DCM leads to a cloudy suspension, and the 3:1 ratio of FA and DCM results in unchanged pellets of polyamide in the solution. Just swelling of pellets happened. In the end, a 1:1 ratio of FA

and DMC solvent can properly dissolve the polyamide. According to the study, all the polyamide structures can dissolve in a 1:1 ratio of FA and DCM. So, the study said that this solvent system is a universal solvent for polyamides.[3]

Kris used 2 % to 5 % wt. % of PA 11 for the DC electrospinning with a 1:1 of FA and DCM solvent system. The results show that an increase in the concentration of polyamide from 2 % to 5 % causes an increase in the average fiber diameter and a change in the shape of the fiber from cylindrical to ribbon. While fiber diameter distribution also varied. But at a 2 % concentration level, the polyamide was not able to achieve continuous fiber production on electrospinning. While the fiber diameter ranges can be altered from 130 nm to over 900 nm with a 2 % to 5 % concentration ratio.[3]

PA 6 easily dissolves in formic acid, while PA 11 doesn't dissolve in a formic acid solvent system. PA 11 and PA 12 show resistance to the dissolution in common solvents such as strong oxidizing agents, organic acids, and strong mineral acids due to the long hydrocarbon chains in PA 11.[3]

Tomas Kalous et al. electrospun the PA 6 using AC electrospinning, and he tried to improve the spinnability of the polyamide solutions by using oxoacids. The electrospinning of the polyamide on the AC electrospinning is difficult with ordinary solutions such as formic acid and acetic acid solution systems. To improve the spinnability of the solutions, a set of oxoacids with different concentration levels was used. The used solution systems are based on formic acid and acetic acid with a 1:1 wt. % ratio and with the oxoacids. The oxoacids include sulfuric acid (H_2SO_4), methane sulfonic acid (CH_3SO_3H), nitric (HNO_3), p-toluene-sulfonic monohydrate (para- $TsOH \cdot 2H_2O$), and phosphoric acid (H_2PO_4). For the electrospinning, he used a setup of 34 kV (50 Hz) for all the trials. During the trials,

promising results have been seen that the basic solvent systems result in flake formation, which is bad electrospinning. The enhanced solutions with oxoacids can be spinnable with collectible cohesive nanofibers on AC electrospinning. The flakes have a fiber diameter of under 100 nm, while the oxoacid solution has a 200 nm to 300 nm fiber size with a bulky structure.[4]

Table 6: AC electrospinning of polyamides with additives by Tomas et al.[4]

Additive	Conc.(mol/l)	Spinning	Additive	Conc.(mol/l)	Spinning
H ₂ SO ₄ (96%)	0.07	Bad	CH ₃ SO ₃ (99%)	0.19	Bad
	0.14	Bad		0.29	Good
	0.2	Good		0.37	Good
	0.27	Bad		0.46	Good
	0.32	Bad		0.55	Bad
H ₂ PO ₄ (85%)	0.46	Bad	HNO ₃ (65%)	0.17	Bad
	0.67	Bad		0.28	Bad
	0.86	Good		0.39	Good
	1.05	Good		0.44	Good
	1.23	Bad		0.55	Bad
Para- TsOH- H ₂ O	0.10	Bad		-	-
	0.20	Bad		-	-
	0.30	Good		-	-
	0.40	Good		-	-
	0.50	Bad		-	-

Oxoacids are used at different concentration levels as mentioned in Table 6. The sulfuric acid-based solution systems show that the viscosity of the solution increases with the increasing amount of sulfuric acid concentration up to a certain limit. After reaching a critical point of sulfuric acid concentration, the viscosity of the solution was drastically reduced. While the diameter of fibers increased with an increased level of sulfuric acid, the highest level of sulfuric acid showed a fiber diameter of 1.3 μm. The addition of sulfuric acid causes hydrolysis of the polyamides. The hydrolysis can be neutralized by the addition of a low

concentration of sodium chloride (NaOH) and ammonia vapor in the solution. The viscosity of the solution increases as the concentration of methane sulfonic acid in the solution increases. While fiber diameter also increases with the increased amount of acid content.[4]

Pavel et al. studied the DC and AC electrospinning of PA 6, PA 4,6, PA 6,6, PA 11, and PA 12 with formic acid and a dichloromethane solvent system. The study used a 1:1 weight ratio of formic acid and dichloromethane as solvent. The mixture of the solution is formed by the magnetic stirring of the mixture for 24 hours at room temperature in the closed containers. The study states that each polyamide is dissolvable in a mixture of formic acid and dichloromethane solution. The PA 11 and PA 12 have limited solubility in this mixture. The solubility is limited to up to 12 % wt. and 10 % wt. for PA 11 and PA 12, respectively. The solution leads to rapid precipitation on their surfaces. The proactive evaporation of dichloromethane in solution causes precipitation on the surface. Precipitation causes a halt in electrospinning. To overcome this problem, the study substituted tetrachloroethane instead of dichloromethane, but it is also not suitable for PA 11 and PA 12. The rest of the polyamides can dissolve in the solvent. The DC electrospinning of all polyamides proves that the increase in length of the aliphatic chain in the repeating of polyamides results in decreased solubility of solution. While lower concentration levels result in a compact structure with less distinctive fiber formation. In the AC electrospinning, the impact of concentration was not as clear as in DC electrospinning. The AC spun fibers result in a bulky and sticky product.[71]

Table 7: Suitable concentration levels for DC and AC electrospinning for polyamides.[71]

Polyamides	PA 4 (18,000 g/mol)	PA 4 (2,80,000 g/mol)	PA 4,6	PA 6	PA 6,6	PA 6,10	PA 6,12	PA 11	PA 12
DC	22 %	3 %	8 %	10 %	6 %	10 %	10 %	6 %	4 %
AC	22 %	3 %	8 %	10 %	8 %	12 %	10 %	8 %	4 %

The fiber diameters of polyamides are increasing with an increase in the concentration of polyamides for both AC and DC electrospinning and vice versa. The dynamic viscosity of solutions increases with increased concentration. The conductivity of the solution remained majorly unchanged. The study states that there is no correlation found between DC and AC electrospinning with fiber diameters, which means that both systems produce similar qualities of the fiber layer. [71]

Over the years, polyamides have been extensively used in textiles and other industrial applications. Polyamides supply unique properties that make them different from other polymers. Researchers are investigating the electro spinnability of polyamides. Trying to get the finest nanofibers of polyamide with large-scale production. The DC electrospun polyamide nanofibers have shown satisfactory results. While the AC electrospinning system needs to be studied, Studies show that solvents and their properties have an impact on the solubility and electrospinning processability of polyamides. In the single solvent system until now formic acid is the best solvent for the PA 6 and PA 6,6 electrospinning. While the rest of the solvents have problems such as improper dissolution, bad electrospinning, and thicker fiber formation results. In the mixed solvent systems, studies kept the mixture of formic acid as a constant solvent with all other solvents. The addition of salt or acids in the solutions also causes the change in spinnability and fiber diameter of polyamide. Behler et al and Pavel et al, studied that formic acid and DMC solvent system is capable of electrospun

most of the polyamides. Pavel et al supplied a suitable concentration of polyamides for electrospinning on AC and DC electrospinning. Both tried to change the solution composition to achieve the goal. Overall, the studies show that there is still potential research for a suitable solvent system for the spinnability of different polyamides.

2.5.1.2.1 Sulfuric acid

H₂SO₄ is made from sulfur, pyrite, and hydrogen sulfate. Sulfur dioxide is known as the blood of the chemical industry. It is the most used chemical in industry. The main uses of sulfuric acid are in fertilizer production, chemical synthesis, metal extraction, refining, and pulp and paper industries. Where the reactivity of sulfuric acid is high, it dissolves most of the metals and is a non-flammable chemical.[72]

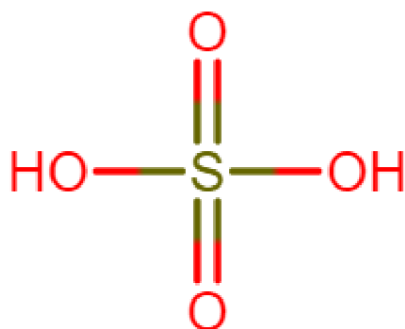


Figure 7: Sulfuric acid chemical structure.

3 Experimental part

The theoretical part concludes that a solution made from formic acid and dichloromethane shows comparatively better results rather than other solutions of the polyamides. Along with that, the spinnability of the polyamide solutions affects by the additives. The experimental part was devoted to the electrospinning of PA 6 and PA 6,12, with AC and DC electrospinning. A single solution system with different concentrations of additive is used. Further produced samples were tested for the different properties such as the morphology of nanofiber, viscosity, surface tension, and conductivity of the solutions under the standard testing method.

3.1 Materials and solution preparation

The polymers used for the experiment are PA 6 and PA 6,12. The PA 6 Ultramid B27 01 was purchased from BASF, Ludwigshafen, Germany. The average molecular weight of PA6 is 21.050 g/mol and its polydispersity index is 3.2. Where PA 6,12 CAS 26098-55-5 is supplied by Sigma Aldrich, Praha, Czech Republic. The solution is prepared from the formic acid (p.a., CAS 64-18-6) and dichloromethane (p.a, CAS 75-09-2), which was purchased from Penta, Praha, Czech Republic. The additive 96 % concentrated sulfuric acid (20450-11000) was used.

The solvent used for the experiment holds formic acid and dichloromethane at a 1:1 weight ratio. Where the polymer concentration of PA 6 and PA 6,12 was a 10 % weight ratio for all mixtures. To form the uniform solution magnetic stirring process was used for 2 hours to 3 hours at room temperature. Heidolph magnetic stirrer was used for two to three hours of a stir.



Figure 8: Polyamide solutions.

After the solution preparation, the additive sulfuric acid was added to the solution in a weight ratio (wt. %). The weight ratios are used as 0 %, 0.6 %, 1.3 %, 1.8 %, 2.4 %, and 2.9 % of sulfuric acid. A micropipette is used for the addition of sulfuric acid to the solution. A total of six solutions for each polyamide were prepared. After adding the sulfuric acid, the prepared solutions were electrospun on AC and DC electrospinning followed by stirring. Table 8 shows the final calculated amount of sulfuric acid for the solution preparation.

Table 8: Addition of sulfuric acid to the solution on a weight basis.

Percentage of Sulfuric acid	Weight of solution (grams)		Wight of Sulfuric acid addition(grams)	
	PA 6	PA 6,12	PA 6	PA 6,12
0.00 %	32.03	30.48	0.00	0.00
0.60 %	30.50	30.25	0.18	0.18
1.30 %	33.64	30.83	0.44	0.40
1.80 %	29.16	20.55	0.53	0.37
2.40 %	30.38	25.09	0.74	0.61
2.90 %	33.83	24.48	1.01	0.73

3.2 Electrospinning setups

In the experiment total of 12 different solutions were prepared and all solutions were electrospun on AC and DC electrospinning systems.

3.2.1 DC electrospinning

Figure 9 shows the DC electrospinning setup used for the experiment. The AU-60P0.5-L (Matsusada Precision, Otsu, Japan) power source was used. A constant power of 30 kV was applied to the electrode and 0 V for the collector. A current of 0.1mA to 0.3 mA was used for all trials. The length of the electrode is 100 mm and the diameter 10 mm. The electrode is provided with a hole at the bottom to connect a high voltage power source. The power source is supplied by the shielded conductor. The setup was discharged after each trial by ground wire.

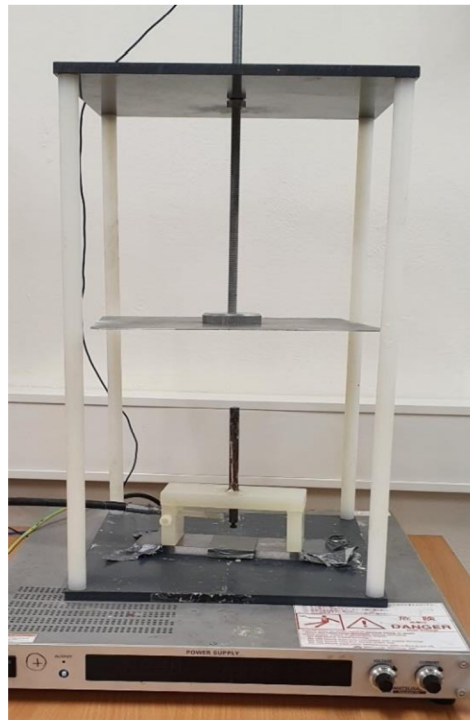


Figure 9: DC electrospinning setup.

The grounded collector was made up of a 1 mm thick steel plate with rounded corners and dimensions of 250 x 250 mm². The spinning distance between the electrode surface and the collector surface was 100 mm. The prepared solutions were fed onto the electrode surface by hand. The electrospinning was started from a single drop until a sufficient layer of nanofibers was obtained. The black card sheet paper is used to collect the nanofibers on it.

3.2.2 AC electrospinning



Figure 10: AC electrospinning setup.

Figure 10 shows the AC electrospinning setup, which is made only for laboratory uses. The setup was connected to a transformer to get the required voltage supply for the electrospinning. The voltage supply of 30 kV and a 50 Hz frequency with a sinus-shaped signal were set for the process. The electrode was 100 mm long and 10 mm in diameter. To

avoid the effect of the environment on the whole AC electrospinning system was isolated by a plastic shield. The collection of fibers is done on the insulated target. The rectangular plastic solid was used as a collector. Both the AC and DC electrospinning are done at room temperature and relative humidity of 40 %.

3.3 Testing

The testing focused on solution parameters and nanofiber morphology. The solution parameters such as viscosity, surface tension, and conductivity were tested. For the nanofiber morphology, fiber diameter was measured.

3.3.1 Scanning electron microscope

The morphology of the nanofibrous structure was tested by measuring the nanofiber diameter. The nanofiber diameter of all samples was measured using a Vega 3 scanning electron microscope (TESCAN, Brno, Czech Republic). The 20 kV accelerated voltage was used to capture the images. The images were taken using different resolutions, ranging from 1000 X to 5000 X. The optimal resolution image was used for measuring the fiber diameter with the Image J software. For every sample, 250 readings have been recorded.

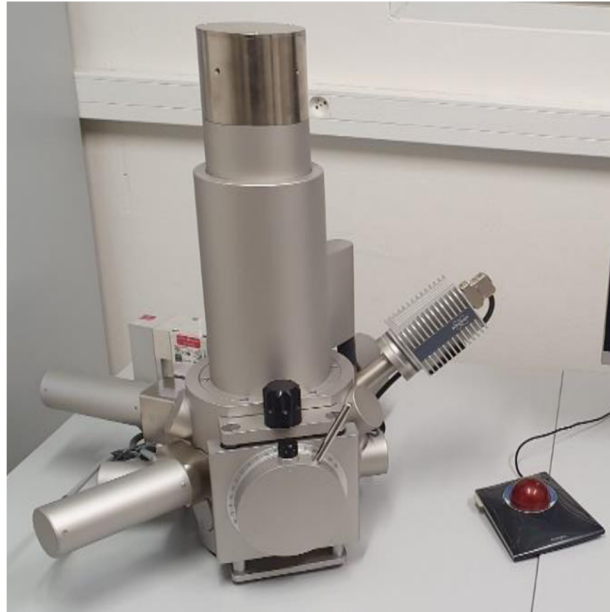


Figure 11: Scanning electron microscope (SEM).

3.3.2 Conductivity

The Eutech CON 510 (Thermo Scientific Eutech Instruments, Landsmeer, The Netherlands) machine was used to test the conductivity of the solutions. The instrument uses a K10/6MM8 probe for conductivity measurements. Each solution sample was tested three times at 21 °C.

The testing equipment gives results in micro siemens (μs) per centimeter (cm). Before the start of each test, the probe was cleaned with a basic solvent. The probe consists of a platinum plate inside the glass rod, which measures the conductivity of the solution.



Figure 12: Conductivity testing equipment.

3.3.3 Surface tension

The surface tension of all solutions was measured by the KRUSS surface tension measurement device. The device works on the bubble pressure principle. The maximum internal pressure of a gas bubble is formed in a liquid using capillary force, then it is measured. The average life span for each bubble was approximately 190 microseconds(μs). For each solution, 10 readings were done. For each solution test, the new Teflon tube was used, and the rod was cleaned with paper.



Figure 13: Surface tension measurement device.

3.3.4 Viscosity

The viscosity of the solution was derived by viscometry analysis. For viscometry analysis, the HAAKE Rotovisco (Thermo Fisher Scientific, Praha, Czech Republic) rheometer was used. The rheometer consists of a C35/1°Ti L cone and a gap distance of 0.1 mm. During the test, the shear rate increased from 300 to 3000 linearly in a period of 30 s. All the tests were conducted at a temperature of 23 °C. Each sample was tested three times. By comparing the dynamic viscosity of the solutions, the concentration dependence of each solution was evaluated. For each reading, 0.2 ml of solution was used on the fixed surface of the viscometer.



Figure 14: Viscosity measurement device.

4 Result and Discussion

In the result and discussion part of this thesis, the observations from solution preparation, the nanofiber testing, and solution testing results are discussed.

4.1 Material and Solution preparation

A set of six solutions for each polyamide was prepared. The solutions have an increasing concentration of sulfuric acid., The solution with the polymer was prepared primary, then sulfuric acid was added to the solution. Both polyamides were successfully dissolved in formic acid and the dichloromethane mixture without any difficulty. In the case of PA 6, at the highest concentration of sulfuric acid, the solution precipitated and needed extra time for solution preparation than other solutions. The PA 6,12, solutions show clear solution formation without any precipitation at every concentration level of sulfuric acid. The higher concentration sulfuric acid solution settles down after some time in both types of solution sets, which again needs to be stirred.

Where dichloromethane is highly volatile, the solvent evaporation rate was high, which needs to be controlled. It can be controlled by tetrachloromethane or by finding another suitable mixture. For better control of spinning and storage of the solution, which will lower the volatility of the solution.

4.2 The AC and DC electrospinning

Both sets of polyamide solutions were electrospun on both AC and DC electrospinning systems. Each solution of polyamide was successfully electrospun on both electrospinning systems.

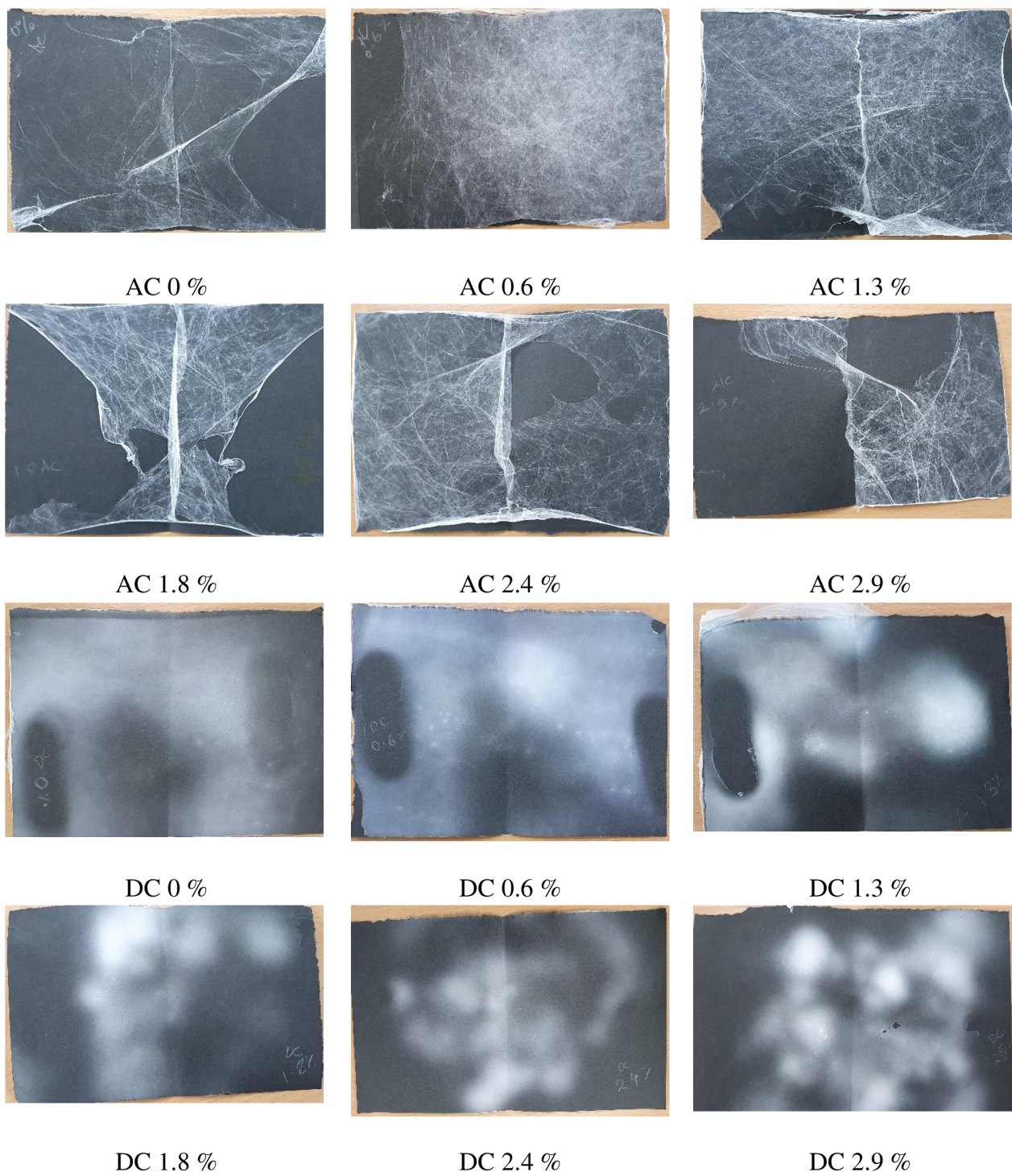


Figure 15: Visual pictures of AC and DC electrospun fibers of PA 6 polyamide with different concentrations.

Figure 15 has the pictures of the AC and DC electrospun fibers of PA 6. During the experiment, the spinnability of the solutions of PA 6 on each electrospinning was significantly improved with the increase in the amount of sulfuric acid.

The images in Figure 15 show the difference between the AC and DC electrospun fiber layers of PA 6 nanofibers. The DC electrospinning layers of PA 6 were thin and had a compact fibrous structure. On the other hand, the AC electrospinning nanofibrous layer was bulky and easily separable from the collector, like a spider web.

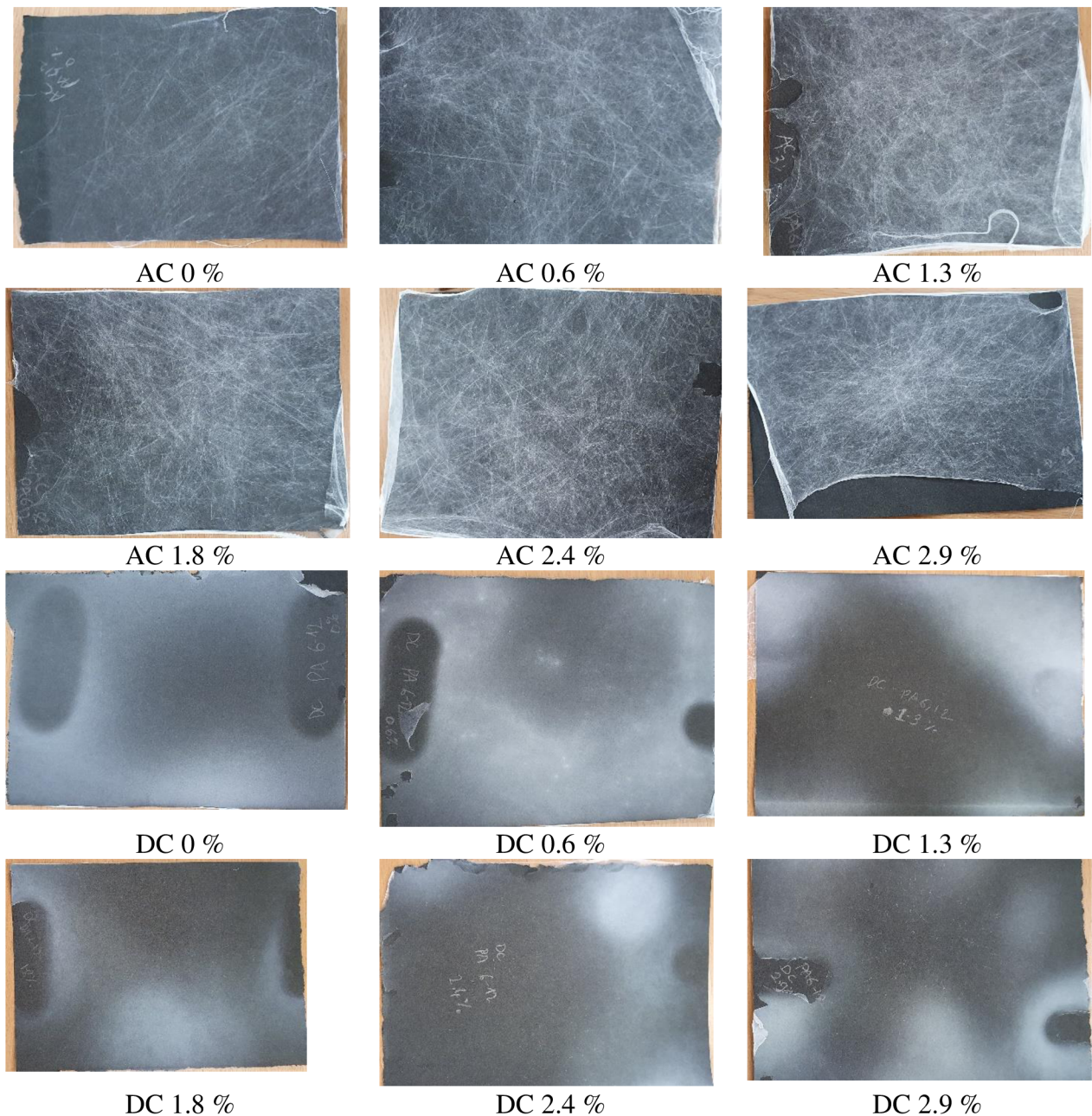
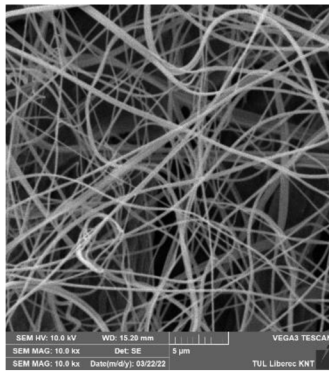


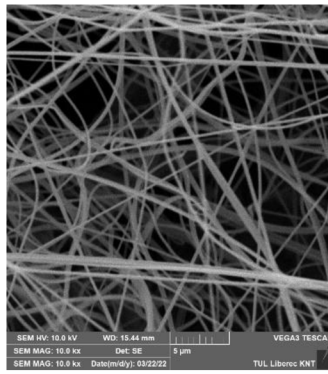
Figure 16: Visual pictures of AC and DC electrospun fibers of PA 6,12 polyamide with different concentrations.

The AC and DC electrospinning of PA 6,12, nanofiber structures are presented in Figure 16. Where PA 6,12 also behaves the same as PA 6, on the AC and DC electrospinning. The spinnability was increased with the growing content of additive.

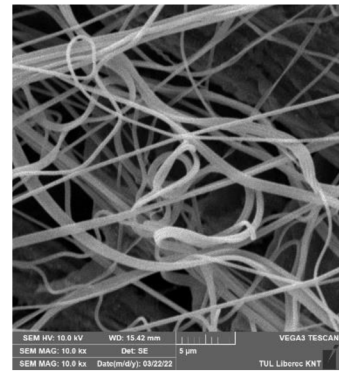
The SEM images have been used to measure the fiber diameters and present the fibrous structure. Figures 17 and 18 show all SEM images for PA 6 and PA 6,12 for each solution set. As the sulfuric acid content is increasing in the solutions of both polyamides, the fiber diameter uniformity within the fibrous structure is changing. The high dose of the additive led to a fibrous layer of faintly distinguishable fibers of higher diameters.



AC 0 %



AC 0.6 %



AC 1.3 %



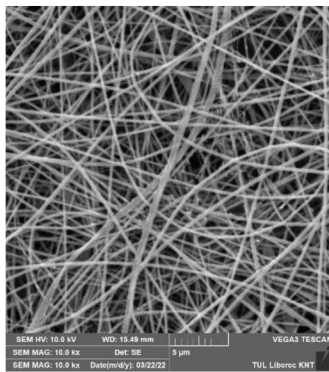
AC 1.8 %



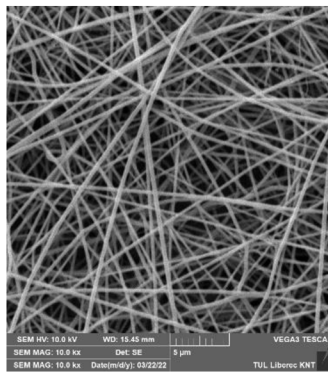
AC 2.4 %



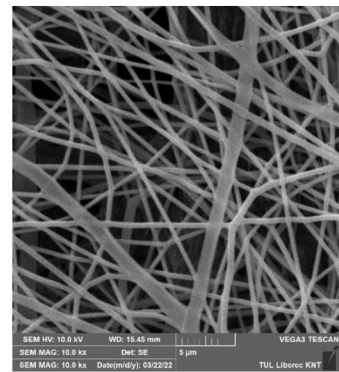
AC 2.9 %



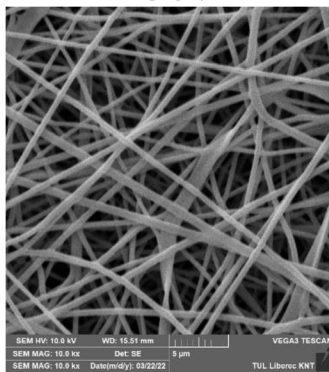
DC 0 %



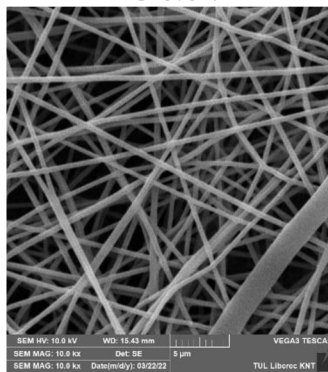
DC 0.6 %



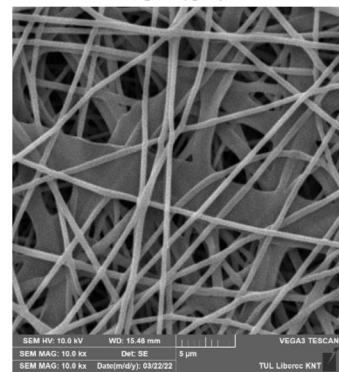
DC 1.3 %



DC 1.8 %

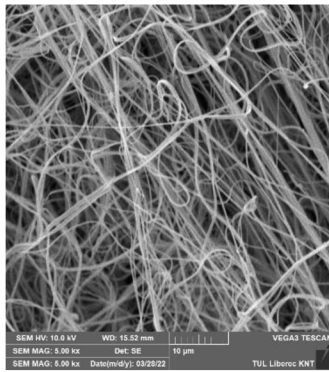


DC 2.4 %

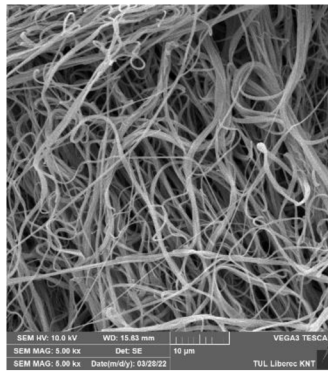


DC 2.9 %

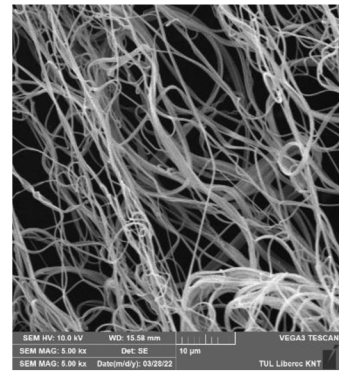
Figure 17: SEM images of PA 6 nanofibers for AC and DC electrospinning.



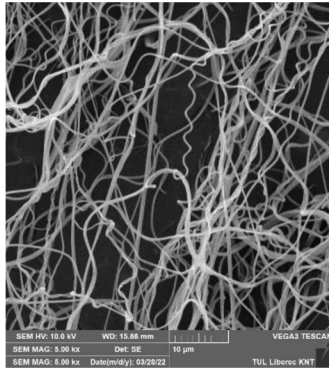
AC 0 %



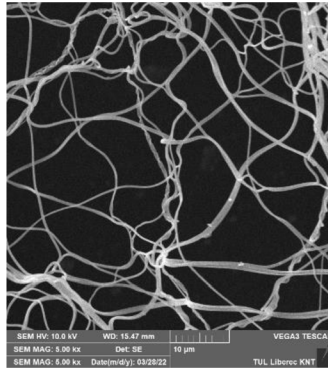
AC 0.6 %



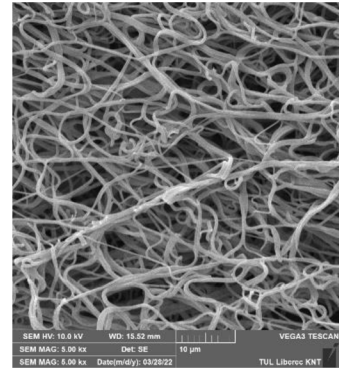
AC 1.3 %



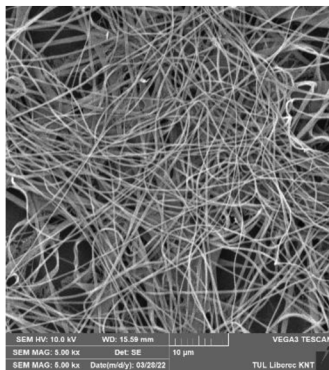
AC 1.8 %



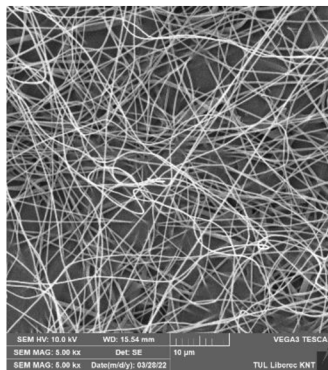
AC 2.4 %



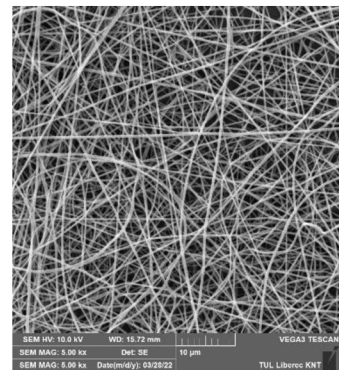
AC 2.9 %



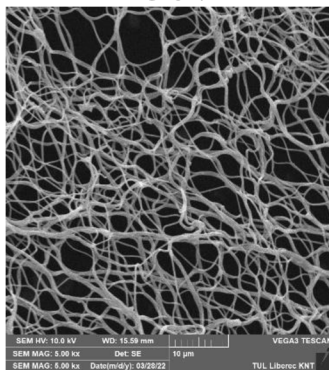
DC 0 %



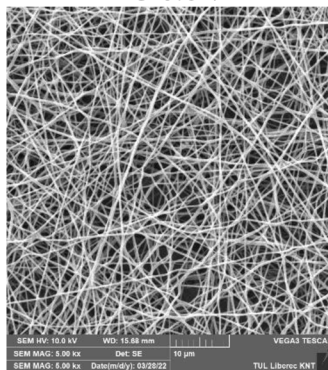
DC 0.6 %



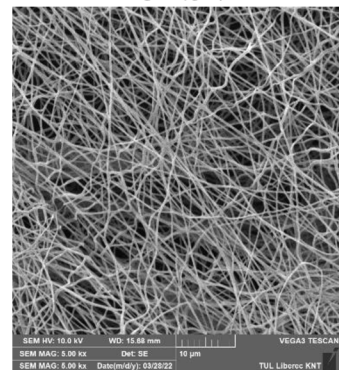
DC 1.3 %



DC 1.8 %



DC 2.4 %



DC 2.9 %

Figure 18: SEM images of PA 6,12 nanofibers for AC and DC electrospinning.

Table 9: Average fiber diameter for polyamide solutions.

Sulfuric Acid	PA 6				PA 6,12			
	AC		DC		AC		DC	
	Average diameter (nm)	Standard deviation	Average diameter (nm)	Standard deviation	Average diameter (nm)	Standard deviation	Average diameter (nm)	Standard deviation
0.00 %	196	39.71	193	31.11	215	43.73	250	44.84
0.60 %	198	39.93	220	33.77	254	43.38	229	28.84
1.30 %	314	76.22	338	59.32	224	52.84	260	45.95
1.80 %	425	87.07	417	97.33	311	66.62	254	48.03
2.40 %	433	80.75	369	45.93	312	53.12	250	36.03
2.90 %	556	168.39	413	67.92	342	90.60	259	42.05

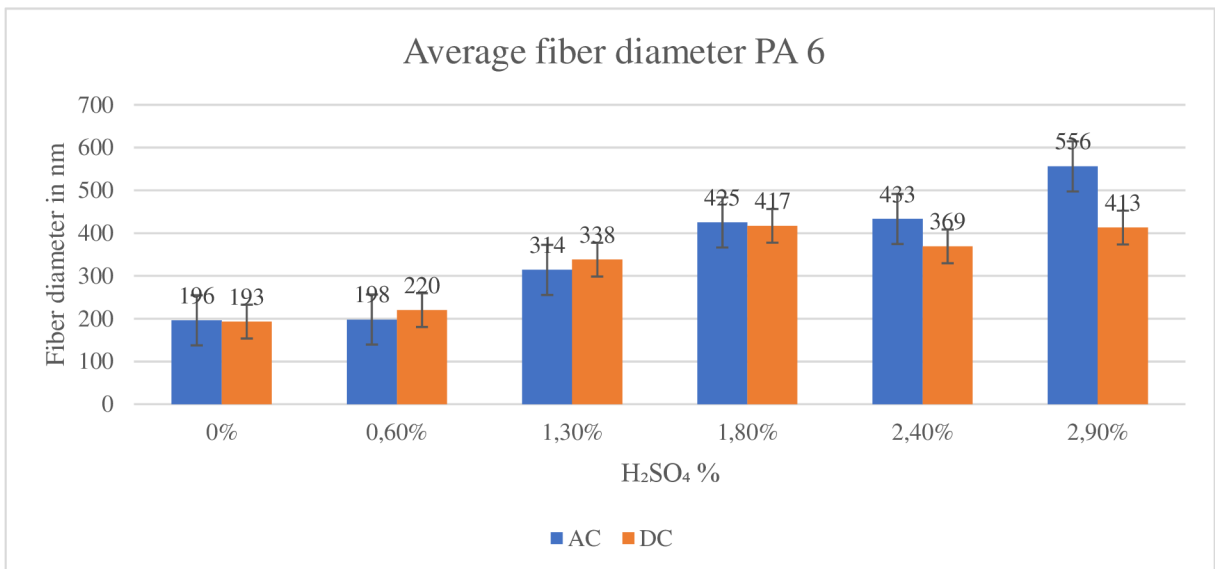


Figure 19: Column diagram for PA 6 nanofibers.

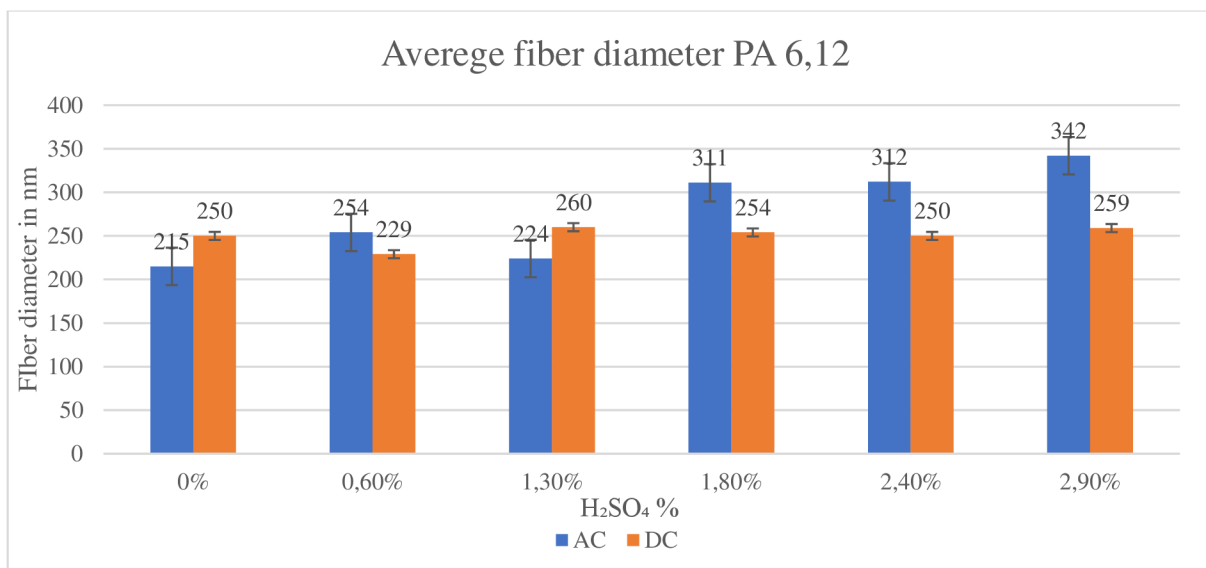


Figure 20: Column diagram for PA 6,12 nanofibers.

The fiber diameters of both PA 6 and PA 6,12 have been shown in Figure 19 and Figure 20. In the PA 6 solutions on AC electrospinning, the average fiber diameter was increased with the rising amount of sulfuric acid in the solution. Where DC electrospinning of PA 6 showed, the fiber diameter was increased by up to 1.8 % of additive content. A slight drop in fiber diameter has been seen after this content of additive. The AC electrospinning of PA 6 shows, a linear increment in fiber diameter with increased additive in solution

The average fiber diameters of PA 6,12 also increased with an increased amount of sulfuric acid for AC and DC electrospinning. In each case, AC electrospun fibers had a higher fiber diameter than DC electrospun fibers. The DC electrospun fibers of PA 6,12 had no major impact after exceeding the dose of 1.8 % of acid.

The fiber diameters of PA 6 in both electrospinning ranged from 193 nm to 556 nm. Whereas for PA 6,12 the range was 215 nm to 342 nm. It's clearly shown that sulfuric acid has more impact on PA 6 solution compared with PA 6,12. But overall, the spinnability of the

solutions was significantly improved and the nanofiber diameter raised with an increase in additive content for both polyamides on each electrospinning.

4.3 Solution

The solution testing results help to evaluate how solution parameters change the spinnability and morphology of polyamide fibers.

4.3.1 Surface tension

The initiation of electrospinning requires the charged solution to overcome the surface tension to start the jet from the solution. Table 10 shows the average value of surface tension for all solutions of polyamides.

Table 10: Surface tension values for polyamide solutions.

Surface tension (mN/cm), Life span 190ms				
solutions	PA 6		PA 6,12	
	Average	Standard deviation	Average	Standard deviation
0.00 %	33.46	0.22	29.07	0.09
0.60 %	33.92	0.25	36.20	0.22
1.30 %	38.25	0.06	37.45	0.25
1.80 %	38.82	0.38	39.52	0.26
2.40 %	39.80	0.17	39.53	0.21
2.90 %	38.33	0.27	40.34	0.36

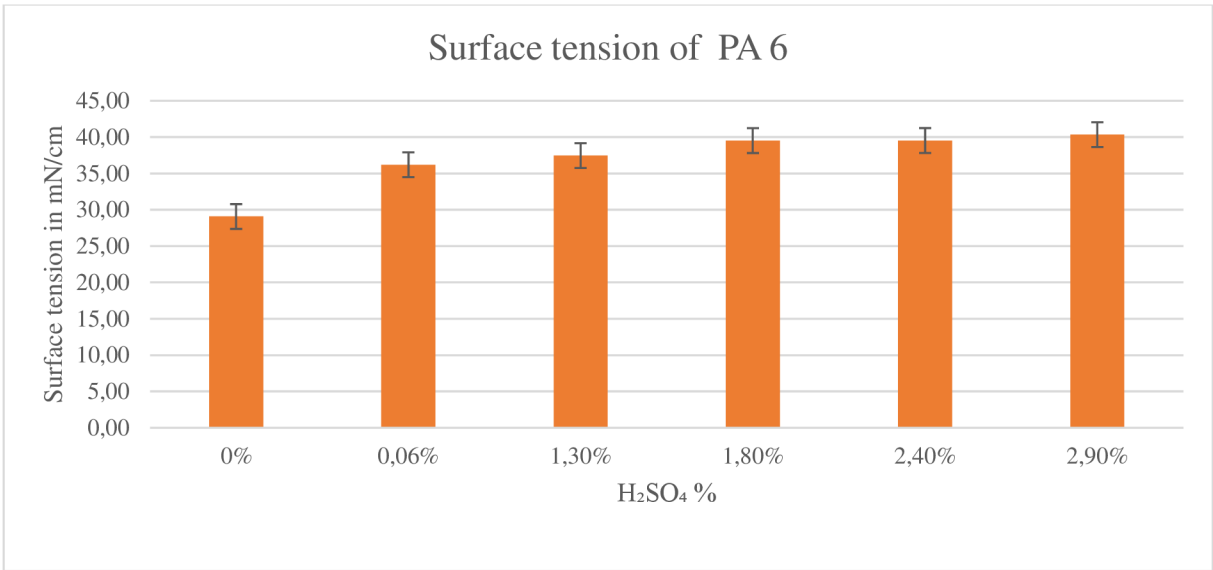


Figure 21: Surface tension of PA 6 solutions.

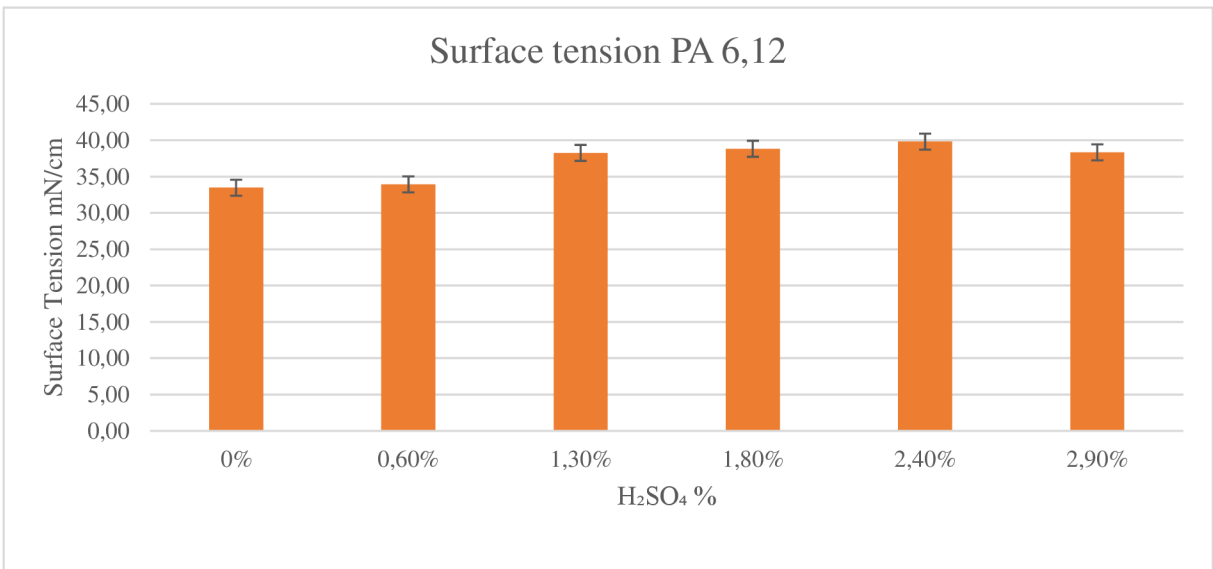


Figure 22: Surface tension of PA 6,12 solutions.

Both solutions behaved similarly about surface tension with the addition of sulfuric acid. The surface tension was raised with the increasing amount of sulfuric acid. The higher surface tension means greater interaction between the solvent and polymer molecules, which may cause thicker fiber formation.

4.3.2 Conductivity

In the electrospinning process, stretching of the solution is caused due to the repulsion of charges at the surface of the solution. The increased conductivity results in more charges carried by jet. The addition of ions causes an increase in the conductivity of the solution. Sulfuric acid was used to increase conductivity.

The graphs in Figure 21 clearly show that, as the sulfuric acid content in each solution increases, the conductivity of the solutions increases. The conductivity of PA 6,12 solution was more than PA 6 solutions. This shows that acid has an extra effect on PA 6,12 solution

Table 11: Conductivity for polyamide solutions.

Conductivity (μS)				
solutions	PA 6		PA 6,12	
	Average	Standard deviation	Average	Standard deviation
Without Polymer	17	0.22	17	0.11
0.00 %	1353	77.33	1342	55.21
0.60 %	1660	22.01	1858	23.11
1.30 %	1816	33.93	2027	69.01
1.80 %	1991	129.15	2307	136.12
2.40 %	2153	35.13	2810	156.23
2.90 %	2416	140.11	2973	64.33

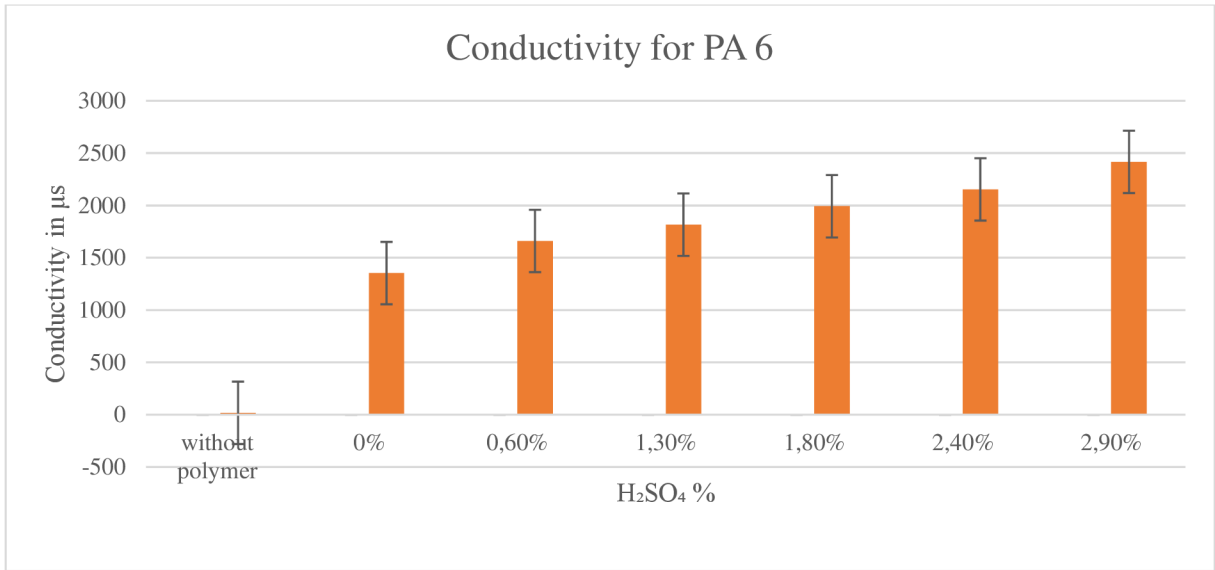


Figure 23: Conductivity for PA 6 solutions.

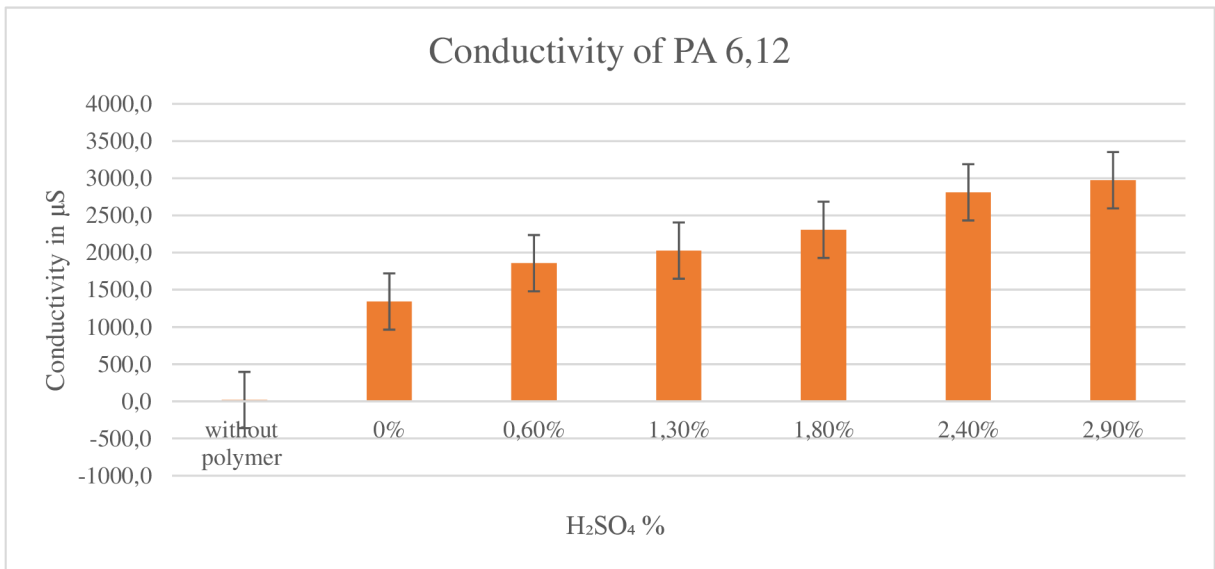


Figure 24: Conductivity for PA 6,12 solutions.

4.3.3 Viscosity

The viscosity of the solution plays a vital role in achieving continuous fiber formation during electrospinning. The viscosity depends on the molecular weight of the polymer and the concentration of the polymer. Table 12 shows the viscosity of all solutions.

Figure 22 shows the viscosity of all solutions of polyamides. The increase in sulfuric acid content increased the viscosity of polyamide solutions. The general cause of the increment in viscosity is the higher number of chain interactions in the solution. The trend of viscosity is followed by the fiber diameters. An increase in viscosity resulted in thicker fiber formation.

The viscosity of PA 6 solution was greater than the viscosity of PA 6,12 solution for each concentration of additive.

Table 12: Viscosity of polyamide solutions.

Viscosity (η) in Pas				
solutions	PA 6		PA 6,12	
	Average	STD	Average	STD
0.00 %	0.166	0.012	0.1445	0.014
0.60 %	0.190	0.005	0.1623	0.004
1.30 %	0.243	0.003	0.1727	0.002
1.80 %	0.247	0.020	0.2497	0.030
2.40 %	0.242	0.008	0.2207	0.005
2.90 %	0.296	0.011	0.2171	0.018

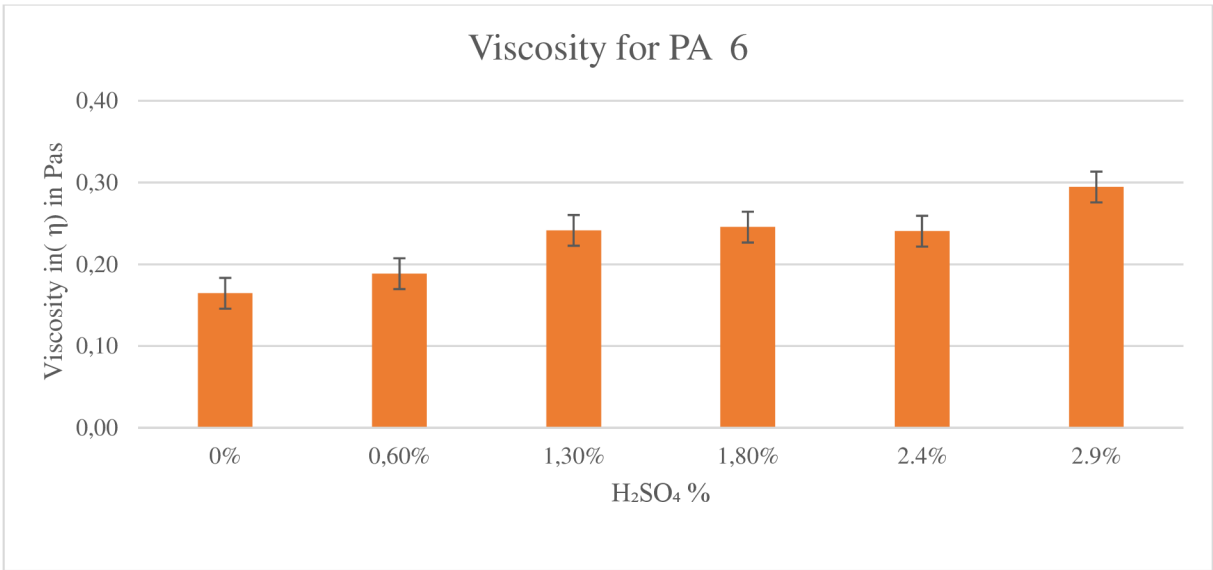


Figure 25: Viscosity for PA 6 solutions.

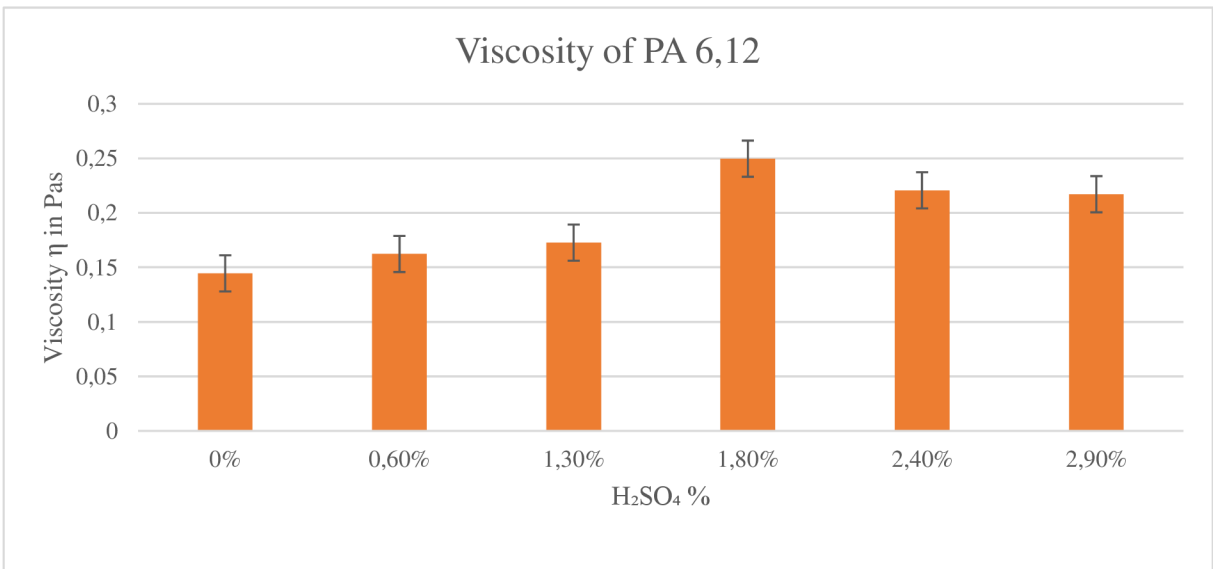


Figure 26: Viscosity for PA 6,12 solutions.

5 Conclusion

The thesis aims to optimize the solutions of polyamides for AC electrospinning. The polyamides, PA 6 and PA 6,12 made clear mixtures of solution with the given solvent and additive. All prepared solutions of polyamide were successfully electrospun on AC and DC electrospinning. Additive sulfuric acid has an impact on the spinnability of both AC and DC electrospinning of both the polyamides. The increased amount of the additive showed a rise in spinnability and nanofiber diameter of polyamides. The polyamide nanofibrous layers from AC and DC electrospinning have immensely different means of bulkiness. AC electrospun layers are bulkier than DC electrospun layers. The layer of nanofibrous is easy to withdraw from the collector. The electrospinning of polyamides on AC electrospinning is easier than DC electrospinning due to the simplicity of design and ease of operation.

Solution parameters such as conductivity, surface tension, and viscosity are influenced by the addition of sulfuric acid into the solution. The increased amount of sulfuric acid caused a slight increment in surface tension for all solutions. Where the conductivity and viscosity are increased with the addition of sulfuric acid. The increased viscosity of the solution may be due to improved interaction between molecular chains increased due to the acid ions. Sulfuric acid may cause an increase of free ions in the solution, which can result in a rise in the conductivity of the solution.

The solvent system will be thoroughly studied in the future to figure out the root cause of how the additive changes the solution properties of polyamide.

6 Reference

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