ELECTROSPINNING OF NANOFIBERS AND THEIR APPLICATIONS

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Abstract

Electrospinning is a useful and efficient technique to produce ultrafine polymeric fibers. It has been a process of great scientific and industrial interest due to its versatility, cost-efficiency and potential to be used in a wide range of applications, resulting in an outstanding potential for nanotechnology research. As it is regarded as the most promising approach to produce continuous nanofibers on a large scale, a huge amount of work and study is observed to be carried out in this area both in academic and industrial circles, aiming to utilize the technology in a wide range of applications. The technique has been used with many synthetic and natural polymers. This training material on electrospinning gives detailed information on history of electrospinning, process theory and basic principles, parameters that influence the process and fiber morphology, advantages of superior properties and applications of electrospun nanofibers. In addition, the state-of-the-art, problems and limitations in this technology are evaluated. Recent progresses as well as future trends and challenges are discussed.

1 INTRODUCTION

Electrospinning is a versatile and efficient method to produce continuous nanofibers from submicron diameters down to nanometer diameters by using a high potential electric field. It is possible to produce nanofibers with diameters ranging between a few nanometers to a few
hundred nanometers thanks to the latest developments in electrospinning [1, 2]. The technique can easily be employed in the laboratory and can be scaled up to an industrial process [3]. Electrospinning of nanofibers from polymer solutions or melts has been a focus of interest as they have many potential applications [4]. Electrospun nanofibers have advantages such as higher surface areas than regular fibers. Electrospun nonwoven mats have small pore size, high porosity and high surface area. These porous, nonwoven polymer networks have high fiber interconnectivity. There is also the advantage to control the nanofiber composition to achieve the desired property or functionality, offering more flexibility in surface functionalities. These outstanding properties make the polymer nanofibers to be good candidates for many applications, which extend to filtration, tissue engineering, scaffold constructions, wound dressings, energy conversion and storage, catalysts and enzyme carriers, protective clothing, sensors, drug delivery, cosmetics, electronic and semi-conductive materials. Despite the advantages offered by this process, the throughput has been a serious bottleneck that limits its applications. Electrospinning units with high-throughput speed are expected to offer more opportunities for the use of electrospun nanofibers, [1, 5, 6].

Electrospinning is a direct extension of electrospraying, as both processes are based on the same physical and electrical mechanisms. The main difference is that continuous fibers are formed in electrospinning whereas small droplets are produced in electrospraying [7]. The as-spun fibers are mostly deposited on electrode collectors in the form of nonwoven nanofiber mat. It is also possible to obtain aligned nanofibers by using controlled fiber deposition techniques [8]. Optimal nanofibers can be fabricated by controlling solution, process and ambient parameters, as the characteristics of electrospun fibers are determined by these parameters. It is very important to avoid the occurrence of the beads, especially for smaller nanofibers. Much attention has been directed to control fiber morphology by control of these parameters. It is possible to control fiber diameter and pore characteristics [4].

Electrospinning is applicable to a wide range of materials such as synthetic and natural polymers, metals as well as ceramics and composite systems [9]. The technique can also be used to produce other functional nanostructures, such as nanotubes and nanowires, through the alignment of electrospun nanofibers. In this paper, it is aimed to present detailed information and understanding on electrospinning of nanofibers and applications of the obtained nano materials.

1.1 History of Electrospinning

A number of processing techniques have been used to prepare polymer nanofibers in recent years. Some of these techniques are given below:

i) Drawing: Long single nanofibers can be produced with this process. Viscoelastic materials that have enough cohesion to withstand stresses while going through strong deformations can be formed into nanofibers by drawing process.
ii) Template Synthesis: This process uses a nanoporous membrane to produce nanofibers. Nanometer tubules and fibrils of various materials including carbon, conducting polymers, metals and semi-conductors can be fabricated, but one-by-one continuous nanofibers cannot be made with this method.

iii) Phase Separation: The polymer is transformed into a nanoporous foam with this process. It is a time-consuming process.

iv) Self-assembly: This process involves organization of individual, pre-existing components to desired patterns and functions. It also takes a long period of time.

v) Electrospinning: One-by-one continuous nanofibers can be obtained with electrospinning [1].

The term electrospinning was derived from “electrostatic spinning” and it is an old technique that dates back to 1897 [5]. The electrospinning technique was not commercially adopted due to competition with mechanical drawing process to form polymeric fibers and it remained an obscure method of making fibers until the mid 1990’s. As Formhals patented his invention, the process gained importance. Formhals reported spinning of cellulose acetate fibers in his first patent, where the polymer solution was introduced into an electric field. Polymer filaments were formed from the solution between two electrodes of opposite polarity. One of the electrodes was placed into the solution and the other onto a collector. The charged solution jets evaporated after ejected from the spinnerette and they were collected on the collector as fibers. Farmhals refined his earlier approach in his second patent by altering the distance between the feeding nozzle and fiber collecting device to give longer drying time for the electrospun fibers [1, 10, 11].

In 1960’s, jet forming process were studied fundamentally by Taylor. He studied the cone shape of the polymer droplet at the needle tip when an electric field was applied, leading to the name as ‘Taylor cone’ in subsequent literature [12]. In the following years, research focused on characterization of electrospun nanofibers and understanding the relationship between process parameters and fiber morphology. In 1971, Baumgarten reported electrospinning of acrylic fibers having diameter range between 500 to 1100 nm [13].

Reneker and his colleagues showed the potential of the technique to be used in nanotechnology research as the fibers produced had sub-micron diameter. Additionally, a wide range of polymeric materials could be used in the process in a cost-efficient way, leading to its use in research laboratories [14, 15]. Doshi and Reneker attempted to characterize the electrospinning process and identify the parameters governing it. They studied the structure of polyethylene oxide (PEO) nanofibers obtained by varying solution concentration and applied electric potential. They produced fibers with a variety of cross sectional shapes and variations along their length. The electric potential necessary to start the spinning process and to form a jet was determined. As they also gave some possible applications of electrospun nanofibers, including reinforcing fibers in composite materials, non-wetting surface layers on textiles, nonwoven fabrics, wound dressing materials, etc., their work led to momentum in research on electrospinning [16].

Some milestones for electrospinning are given in Table 1 [5, 14, 17]:

H. Karakaş
Table 1: Important milestones in electrospinning process.

<table>
<thead>
<tr>
<th></th>
<th>Event</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>First observed by Raleigh in 1897</td>
</tr>
<tr>
<td>2</td>
<td>Origins by first patents by Cooley and Morton</td>
</tr>
<tr>
<td>3</td>
<td>Zeleny studied further on electrospraying in 1914</td>
</tr>
<tr>
<td>4</td>
<td>Formhals patented the process in 1934</td>
</tr>
<tr>
<td>5</td>
<td>Between 1934 and 1944, patents were published by Formhals</td>
</tr>
<tr>
<td>6</td>
<td>About 50 patents were taken on electrospinning between 1944 and 2004</td>
</tr>
<tr>
<td>7</td>
<td>Taylor laid the groundwork by his work on electrically driven jets</td>
</tr>
<tr>
<td>8</td>
<td>Vonnegut and Neubauer produced 0.1 mm diameter streams from highly electrified uniform droplets in 1952</td>
</tr>
<tr>
<td>9</td>
<td>In 1966, Simons patented an apparatus for production of nonwovens with different patterns using electrical spinning</td>
</tr>
<tr>
<td>10</td>
<td>Baumgarten built an apparatus to electrospin acrylic fibers having diameter range between 0.05-1.1 micron in 1971</td>
</tr>
<tr>
<td>11</td>
<td>Electrospinning process gained more popularity in 1980’s due to interest in nanotechnology and increase in use of ultrafine fibers and fibers in submicron and nanometer scale</td>
</tr>
<tr>
<td>12</td>
<td>In 1981, Larrondo and Manley investigated electrospinning process using melting polymer</td>
</tr>
<tr>
<td>13</td>
<td>Reneker and Chun proved the probability of electrospinning using different kind of polymer solution</td>
</tr>
<tr>
<td>14</td>
<td>A high number of research activity is going on in this area, especially after the relevance of electrospun nanofibers in applications including tissue engineering, energy storage, composite materials, etc. was shown</td>
</tr>
<tr>
<td>15</td>
<td>Studies and work is also focused on upscaling and on extending the application areas of electrospun fibers and fibrous materials.</td>
</tr>
<tr>
<td>16</td>
<td>Companies such as Donaldson Company and Freudenberg are using electrospinning process in their air filtration products since the last two decades</td>
</tr>
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</table>

Research related to electrospinning process and electrospun nanofibers has started especially beginning from 2000 and it is growing at a tremendous speed. This is mostly due to the fact...
that nanotechnology is gaining more interest and ultrafine fibers in nanoscale can be easily fabricated with electrospinning process. The increase in scientific activity as can be measured from number of publications is a good indicator about the interest in this field. The publication intensity has almost quadrupled from 2005 to 2010. The ultimate aim in almost all of the studies is to utilize this technology in a wide range of applications.

2   FUNDAMENTAL ASPECTS OF ELECTROSPINNING PROCESS

Electrospinning technique can be considered as a variant of the electrostatic spraying (electrospraying) process, as both techniques use high voltage to induce the formation of liquid jets. Small droplets or particles are formed as a result of the break-up of the electrified jet in electrospraying, whereas a solid fiber is formed as the electrified jet is stretched in electrospinning [18]. Electrospinning makes use of electrostatic forces to stretch the solution or melt as it solidifies. The fiber mat is collected as a distribution of continuous nanofibers [19].

A typical electrospinning set-up, as shown in Figure 1, consists of mainly three components:

1) A capillary tube with pipette or needle of small diameter
2) A high voltage supplier
3) A metal collecting screen

![Schematic diagram of set up of electrospinning apparatus](image)

**Figure 1**: Schematic diagram of set up of electrospinning apparatus a) typical vertical set up, b) horizontal set up [5]
Electrospinning is carried out at room temperature with atmosphere condition. There are basically two electrospinning set-ups; vertical and horizontal. Figure 2 shows the schematic of diagram for nanofibers produced by electrospinning process [1]. A high voltage is applied to create an electrically charged jet of polymer solution or melt. The jet undergoes stretching before it reaches the collector and it solidifies on the collector in the form of nanofibers by the evaporation of the solvent [20, 21, 22].

![Figure 2: Schematic diagram for the electrospinning process [1]](image)

In electrospinning, most of the polymers are dissolved in a solvent, forming a polymer solution. The polymer fluid is then fed to the capillary for electrospinning. In the case of polymers molten at high temperature, polymer melt is fed into the capillary. For polymer melts, the electrospinning process must be conducted at vacuum condition. The polymers electrospun in molten form are much less in number compared to polymers electrospun in polymer solution form.

The process principle involves subjecting a polymer solution or melt held at its own surface tension at the end of a capillary to an electric field. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the capillary elongates and forms a conical shape known as the Taylor cone. The electric field reaches a critical value where the repulsive electric force overcomes the surface tension force. At this critical value, a charged jet of the solution is ejected from the tip of the Taylor cone. The solvent evaporates as the jet travels in air. In the case of the melt, the discharged jet solidifies when it travels in the air. The charged polymer fiber is randomly deposited on a collector [1, 5, 16].
A number of theories and simulated modeling techniques were used to explain the electrospinning process [23, 24]. Generally, it is agreed that there are four different regions (Figure 3) within electrospinning process:

1) The base region: the charged surface of the solution at the nozzle end,
2) The jet region: where the solution travels along a straight line
3) The splay region: where the jets split into many nanofibers
4) The collector region: where nanofibers eventually settle [23, 25].

![Different regions within electrospinning extrusion](image)

**Figure 3:** Different regions within electrospinning extrusion [23]

The behavior of the electrospun jet can be divided into three main stages: the formation of the Taylor cone, the ejection of the straight jet and the unstable whipping jet region. Figure 4 shows the behavior of the electrospun jet. The interactions of the electrical charges on the polymer solution with the external electric field result in Taylor cone. As a very strong electric field is applied to the Taylor cone, the droplet becomes unstable, leading to drawing of a single fluid jet. After a straight path, the ejected liquid jet becomes unstable [26]. It is triggered by the electrically driven bending instability, alternatively referred to as whipping instability [27].
Hamzeh et al used classic electrostatic theory to explain fiber formation from nozzle to collection point and to make a good understanding of electrospinning process. Step-by-step schematic of electrospinning process is shown in Figure 5. The electro-field lines and their distribution when a positively charged solution is attracted by a negatively charged collector plate.

**Figure 4:** Behaviour of the electrospun jet [26]

**Figure 5:** Step-by-step schematic of electrospinning process [23]
When the solution is subjected to high voltage electric field, the concentration of net positive charges at the tip of the nozzle are very high and so the solution is forced out of the nozzle. Taylor cone is a direct result of this force of attraction surrounded by the solution surface tension. The polymer divides into fine strands as the surface tension reaches a limit. The repulsive forces between these strands cause them to split into nanofibers and collected on the negatively charged collector plate [23].

Hsu et al have shown the nature of the jet at various stages during electrospinning of poly(ε-caprolactone) nanofibers [28].

![Sequential photographs showing the nature of the jet at various stages during the electrospinning process. The numbers correspond to time (s) elapsed after the application of the voltage](image)

**Figure 6**: Sequential photographs showing the nature of the jet at various stages during the electrospinning process. The numbers correspond to time (s) elapsed after the application of the voltage [28]
3 ELECTROSPINNING PARAMETERS

It is very important to understand the electrospinning working parameters, as they effect fiber morphologies. It is much easier and more possible to obtain desired fiber diameters and morphologies through control of these parameters. The ideal targets in electrospinning of a polymer into nanofiber are:

a) The diameters of the fibers must be consistent and controllable
b) The fiber surface must be defect-free or defect-controllable
c) Continuous single nanofibers must be collectable

Fiber diameter is among the most important quantities in electrospinning. Another challenge is the uniformity of the fiber diameters. The occurrence of defects such as beads and pores is a major problem [1]. Figure 7 shows the pores in Poly-L-lactide (PLLA) fibers. The beaded fiber structure can be observed in Figure 8.

![Figure 7: Poly-L-lactide (PLLA) nanofibers with different diameters and pores [29]](image)

![Figure 8: Electrospun polyurethane (PU) nanofibers with beads [30]](image)
The parameters governing electrospinning process are given in Figure 9.

**Solution Parameters**—viscosity, conductivity, molecular weight, molecular weight distribution, surface tension, polymer structure, solution properties

**Process Parameters**—applied electric field, tip to collector distance, feeding or flow rate, hydrostatic pressure in the capillary, plate movement

**Ambient Parameters**—humidity and temperature of the surroundings, solution temperature, air flow rate

**Figure 9**: Electrospinning process parameters

The characteristics of electrospun nanofibers are determined by electrospinning parameters and this has been widely investigated by researchers. The effects of various electrospinning parameters are summarized below:

a) **Solution parameters:**

i) Concentration

When a solid polymer is dissolved in a solvent, the solution viscosity is proportional to the polymer concentration. As higher viscosity leads to larger fiber diameter, higher polymer concentrations will also result in larger nanofiber diameters.

A minimum concentration is required in the electrospinning for fiber formation to occur. At very low concentrations, electrospray occurs instead of electrospinning. This is due to the low viscosity and high surface tensions of the solution [31]. At low solution concentrations, a mixture of fibers and beads are obtained. As the concentration increases, the shape of the
bead changes from spherical to spindle-like. Finally, uniform fibers with increased diameters are formed [5].

An optimum solution concentration must be obtained, as at very low concentrations beads are formed, whereas at very high concentrations the formation of continuous fibers is prohibited due to inability to maintain the flow of the solution [32]. In his study, Fong found that higher polymer concentrations led to a structure with less beads. Figure 10 shows the structure of PEO nanofibers obtained by solution concentrations ranging between 1 wt. % and 4 wt.% PEO concentration. The beads did not completely disappear at high concentrations, but their shape changed from spherical to spindle-like [33].

![Figure 10: SEM photographs of electrospun nanofibers from different polymer concentration solutions [33]](image)

Liu et al [4] studied electrospinning of Poly(butylene succinate) (PBS) in seven different polymer concentrations between 11% to 17%. The number of beads decreased as polymer concentration increased and finally no beads were observed. They explained this by lower surface tension leading to more beads. As polymer concentration increases, surface tension also increases, leading to fewer beads.

Demir et al showed that the diameter of the electrospun nanofiber was proportional to the cube of the polymer concentration [34].

Beachley et al studied the effect of different electrospinning parameters on maximum fiber length, average fiber diameter, diameter uniformity and fiber quality of PCL nanofibers. They observed that fiber formation was sometimes impeded by the high viscosity of the solution at very high polymer concentration [35].
ii) Molecular weight

Molecular weight is another important parameter that affects the electrospun nanofiber morphology, as it effects viscosity, surface tension and conductivity. In principle, molecular weight reflects the entanglement of polymer chains in solutions, namely the solution viscosity. Keeping the concentration fixed, using a polymer with too low molecular weight leads to formation of beads rather than fibers, increasing the molecular weight will give smooth fibers, whereas a very high molecular weight results in electrospun fibers having very large diameters [5, 36, 37]. Structures for various molecular weights can be seen in Figure 11.

![Figure 11: SEM photographs showing typical structure in the electrospun polymer for various molecular weights](image)

Long and McKee obtained oligomer-sized phospholipid fiber nonwoven membranes from lecithin solutions via electrospinning. This showed that high molecular weights are not always needed as long as sufficient intermolecular interactions can provide a substitute for the interchain connectivity obtained through chain entanglements [38].

iii) Solution viscosity

Optimal solution viscosity is required for electrospinning, as very low viscosity leads to no fiber formation and very high viscosity results in difficulty in ejection of jets from polymer solution. Also, viscosity is very critical for fiber morphology. Viscosity, polymer concentration and polymeric molecular weight are related with each other. Generally, the solution viscosity can be adjusted by changing the polymer concentration of the solution. Different solution viscosities result in different structures (Figure 12). The viscosity range for different polymers for electrospinning are different from each other. Increasing solution viscosity or concentration results in electrospun nanofibers with larger and more uniform diameter. Surface tension is the dominant factor in low viscosities, with the result of beads or
beaded fibers [5, 37]. Researchers have studied nanofiber formation in different viscosities for a number of polymers.

Figure 12: SEM images of electrospun PAN products with different solution viscosities by adjusting the concentration of polymer solution (1.3 wt. % vs. 15 wt. %, PAN molecular weight: 150,000 g/mol) [37]

The morphologies obtained at different solution viscosities obtained by Fong et al [39] in electrospinning of PEO are given in Figure 13.

(a) 13 centipoise

(b) 74 centipoise
iv) Surface tension

Different surface tensions are obtained by using different solvents. Reducing the surface tension contributes to the formation of nanofibers without beads as suggested by Doshi and Reneker [16], but low surface tension will not always offer ideal electrospinning conditions. It is critical in determining the upper and lower boundaries provided that other parameters are constant. Yang et al investigated the effect of surface tensions on poly(vinyl pyrrolidone) (PVP) electrospun nanofiber morphology using ethanol, DMF and MC as solvents and they showed that different solvents may contribute different surface tensions. They obtained smoother nanofibers by reducing the surface tension and keeping the concentration fixed, rather than beaded structure at higher surface tensions [40].

v) Conductivity/surface charge density

Solution conductivity is mainly determined by the polymer type, solvent used and the presence of ionisable salts. Generally, solutions with higher conductivity lead to electrospun nanofibers with smaller diameter. Addition of salts to the polymer solution increases the conductivity of the solution and the surface charge density of the solution [5, 35]. The addition of salt in order to increase the solution conductivity has been used by many
polymers such as polyacrylic acid, polyamide 6, polyethylene oxide (PEO), collagen type I-PEO, etc. Zong et al have produced beadless and smaller diameter poly(D-L-lactic acid) (PDLA) nanofibers ranging between 100 to 200 nm by the addition of ionic salts such as KH$_2$PO$_4$, NaH$_2$PO$_4$ and NaCl and they showed the effect of ions on the structure compared to fiber structure obtained without salt addition [41]. The effects of three kinds of salts on the structure of electrospun membrane are shown in Figure 14.

Figure 14: SEM images of PDLA membranes fabricated by electrospinning of a 30 wt% solution at voltage of 20 kV, feeding rate of 20 ml/min and with 1 wt% of A) KH$_2$PO$_4$, B) NaH$_2$PO$_4$ and C) NaCl [41]

b) Processing parameters

i) Applied voltage

Applied voltage is the crucial factor in electrospinning as the threshold voltage must be exceeded for the charged jets to be ejected from Taylor cone. After the threshold voltage is
reached, fiber formation occurs, inducing the necessary changes on the solution along with the electric field and starting the electrospinning process [5, 37].

The effect of applied voltage on electrospinning process has been extensively studied and there are different arguments. Reneker et al have shown that applied voltage does not have a significant effect on fiber diameter in electrospinning of polyethylene oxide [15]. Zhang et al showed that there is more polymer ejection at higher voltages, facilitating the formation of larger fiber diameter. They studied the effect of voltage on fiber morphology and diameter distribution with poly(vinyl alcohol) (PVA)/water solution [42]. The results can be observed in Figure 15.

![Figure 15: Morphology and fiber diameter distribution with 7.4 wt% PVA/water solution at varying voltages (a) 5 kV, (b) 8 kV, (c) 10 kV and (d) 13 kV](image) (tip-target distance = 15 cm, flow rate= 0.2 ml/h) [42]
Some other researchers observed that increase in applied voltage favoured the narrowing of fiber diameter and they showed that fiber diameter decreased with increasing voltage due to the increase in electrostatic repulsive force on the charged jet. Bead formation was also more observed at higher voltage [34, 35].

It was also stated by Yördem et al. that applied voltage influenced fiber diameter and that the level of significance varies with polymer solution concentration and tip to collector distance [43].

ii) Feed rate/flow rate

The flow rate of the polymer in the syringe is another process parameter as the material transfer rate and jet velocity are directly effected. A slower feed rate is recommended in order to offer enough time for the evaporation of the solvent. A minimum flow rate must be present. High flow rate also resulted in beaded fiber structure [5].

iii) Distance between the tip and the collector (tip-to-collector distance)

Tip-to-collector distance is among the effecting parameters, though its effect is less significant on fiber morphology when compared with other process parameters. An optimum distance must be selected in order to obtain evaporation of the solvent from the polymer solution.

iv) Collectors

The function of a collector is also forming a conductive substrate for the collection of nanofibers. Aluminum foil is mostly used [Figure 16], whereas rotating rod, wire mesh, conductive paper or cloth, parallel or grided bar are also used [5]. Figure 17 shows SEM images of electrospun nanofibers collected on different targets [37].

**Figure 16**: Schematic illustration of the electrospinning process with aluminum collector [44]
PEO fibers were deposited on a rotating multi frame structure as shown in Figure 18. Deposition target geometry is important. Different deposition targets have also been designed for various applications. For example, aligned micro and nanofibers are of particular interest for nerve tissue engineering. Secasanu et al [45] have developed a new collector that combines the benefits of standard parallel electrodes and the spinning wheel with a sharpened edge. This new design made deposition possible on a larger cross-sectional area and the yield of uniaxially aligned fibers (Figure 19).

Figure 17: SEM images of different electropun products with different types of collectors [37]

Figure 18: Continuous as-spun nanofibers deposited on a rotating multiframe structure [1]
Figure 19: (a) side view image and (b) top view image of aligned fibers on the standard parallel electrode; (c) side view image and (d) top view image of the aligned fibers on the new sharpened parallel electrode. All scale bars are 1 mm. The sharpened parallel electrode allowed the fibers to deposit through a larger cross-sectional area (a vs c), increasing the yield of parallel fibers [45]

c) Ambient parameters

Ambient parameters such as humidity and temperature also effect the fiber diameter and morphology. Increased temperature leads to yield of fibers with decreased diameter, while lower humidity may dry the solvent completely. Also, increased humidity results in appearance of small pores on the fiber surface.

4 APPLICATIONS

Nanofibers promise diverse applications including biotechnology, drug delivery, wound healing, tissue engineering, microelectronics, environmental protection, energy harvest and storage due to their very large surface area to volume ratio, flexibility in surface functionalities and superior mechanical performance [20].

A comprehensive summary of polymers that have been successfully electrospun has been given by Z.M. Huang et al [1]. In Table 2, some examples from these polymers, solvents used and their perspective applications are given. Table 3 gives a list of some polymers that have been electrospun in melt form.
<table>
<thead>
<tr>
<th>Polymers electrospun in solution form</th>
<th>Solvent</th>
<th>Perspective Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamide 6,6, PA 6,6</td>
<td>Formic acid</td>
<td>Protective clothing</td>
</tr>
<tr>
<td>Polyurethanes, PU</td>
<td>Dimethyl formamide</td>
<td>Protective clothing</td>
</tr>
<tr>
<td></td>
<td>Dimethyl formamide</td>
<td>Electret filter</td>
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<tr>
<td>Polybenzimidazole, PBI</td>
<td>Dimethyl acetamide</td>
<td>Protective clothing</td>
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<td></td>
<td></td>
<td>Nanofiber reinforced composites</td>
</tr>
<tr>
<td>Polycarboate, PC</td>
<td>Dimethyl formamide:tetrahydrofuran (1:1)</td>
<td>Protective clothing</td>
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<tr>
<td></td>
<td>Dichloromethane</td>
<td>Sensor, filter</td>
</tr>
<tr>
<td></td>
<td>Dimethyl formamide:tetrahydrofuran (1:1)</td>
<td>Electret filter</td>
</tr>
<tr>
<td>Polycrylic acid, PAN</td>
<td>Dimethyl formamide</td>
<td>Carbon nanofiber</td>
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<tr>
<td>Polyvinil alcohol, PVA</td>
<td>Distilled water</td>
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<tr>
<td>Polylactic acid, PLA</td>
<td>Dimethyl formamide</td>
<td>Membrane for prevention of surfer-induced adhesion</td>
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<tr>
<td></td>
<td>Dichloromethane</td>
<td>Sensor, filter</td>
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<tr>
<td></td>
<td>Dichloromethane</td>
<td>Drug delivery system</td>
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<tr>
<td>Polyethylene oxide, PEO</td>
<td>Distilled water: ethanol (3:2)</td>
<td>Microelectronic wiring, interconnects</td>
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<td></td>
<td>Isopropyle alcohol + water</td>
<td>Electret filter</td>
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<tr>
<td>Collagen, PEO</td>
<td>Hydrochloric acid</td>
<td>Wound healing, tissue engineering, hemostatic agents</td>
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<tr>
<td>Polyaniline (PANI) / PEO blend</td>
<td>Chloroform</td>
<td>Conductive fiber</td>
</tr>
<tr>
<td></td>
<td>Camphorsulfonic acid</td>
<td>Conductive fiber</td>
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<tr>
<td>Polyaniline (PANI) / Polystyrene (PS)</td>
<td>Chloroform</td>
<td>Conductive fiber</td>
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<tr>
<td></td>
<td>Camphorsulfonic acid</td>
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<td>Polymers</td>
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<td>Polyvinylcarbazole</td>
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<td>Dichloromethane and trifluoracetic</td>
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<td>Polystyrene, PS</td>
<td>Tetrahydrofuran, dimethylformamide, carbon disulfide, toluene, methylethylketone Tetrahydrofuran</td>
<td>Enzymatic biotransformation Catalyst, filter</td>
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<td>Cellulose acetate, CA</td>
<td>Acetone, acetic acid, dimethylacetamide</td>
<td>Membrane</td>
</tr>
<tr>
<td>Polycaprolactone, PCL</td>
<td>Chloroform : methanol (3:1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Toluene /methanol (1:1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dichloromethane / methanol (1:1)</td>
<td></td>
</tr>
<tr>
<td>Poly(vinylidene fluoride), PVDF</td>
<td>Dimethylformamide/dimethylacetamide (1/1)</td>
<td>Flat ribbons</td>
</tr>
<tr>
<td>Polyacrylonitrile (PAN) / TiO₂</td>
<td></td>
<td>Photovoltaic and conductive polymers</td>
</tr>
</tbody>
</table>
**Table 3:** Examples for polymers electrospun in melt form [1]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Processing temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene, PE</td>
<td>200 – 220</td>
</tr>
<tr>
<td>Polypropylene, PP</td>
<td>220 – 240</td>
</tr>
<tr>
<td>Polyamide 12, PA 12</td>
<td>220</td>
</tr>
<tr>
<td>Polyethylene terephthalate, PET</td>
<td>270</td>
</tr>
<tr>
<td>Polyethylene naphthalate, PEN</td>
<td>290</td>
</tr>
<tr>
<td>PET/PEN blends</td>
<td>290</td>
</tr>
</tbody>
</table>

Melt electrospinning is an alternative method as problems such as solvent removal, recycling, environmental issues and toxicity due to the use of solvents are eliminated. The polymer in melt form is fed into the capillary tube. The process has to be carried out in vacuum condition, therefore the capillary tube, the travel of the charged melt fluid jet and the metal collector has to be encapsulated within a vacuum. Despite the advantages offered by melt electrospinning, the method has not gained more popularity and has not been widely used in comparison with electrospinning from a polymer solution. This is mainly due to high viscosity, high process temperatures and failure to achieve fibers in nanometer range. The use of such high temperatures have restricted their use in tissue engineering or drug delivery applications [5].

Due to the diversity of applications in electrospinning, especially from polymer solutions, a considerable amount of work and research & development is going on in this area. Work is mainly focused on extending the applications and end-uses. The state-of-the-art applications of nanofibers and the materials used are summarized below:

**1. Environmental protection**

Electrospun nanofibers can be used to collect pollutants through physical blocking or chemical adsorption as they have a high specific surface area. Therefore, they can be solution to protect our environment.

Use of electrospun nanofibers in filtration applications have a history and companies such as Donaldson, Amsoil and DuPont have developed nano-fiber based filters for various uses including consumer, defense, automotive, apparel applications. Figure 20 shows the air filter developed by Donaldson. It consists of layered nanofiber nonwoven material. Electrospun nanofiber mats offer considerable increases in filtering capability [46, 47].
Nanofiber mats proved to be efficient in filtering

- airborne particles,
- tiny liquid droplets within liquid-liquid immiscible systems,
- ultrafiltration for oil/water emulsion separation [48, 49, 50]

Another application is **metal ion adsorption and recovery**. Presence of high level of metal ions is a serious pollution in water resources and may be a risk for human health and the environment. Electrospun nanofibers can be used to collect metal ions from a solution thanks to their high specific surface area, high porosity and controllable surface functionality. The adsorption of metal ions on electrospun nanofibers can be improved by introduction of functional materials to fiber surface using surface chemistry or coating techniques and by increasing surface area to improve adsorption capability [46].

### 2. Biomedical

A wide range of biodegradable biopolymers can be electrospun into mats with specific fiber arrangement and structural integrity. Nanofiber surface can be functionalized to display specific biochemical characteristics.

Electrospinning method is very suitable to process natural polymers and synthetic biocompatible or bioabsorbable polymers for biomedical applications [2]. Almost all of the tissues and organs are deposited in nanofibrous forms or structures. Therefore, electrospun nanofibers find promising applications in this area. **Tissue engineering** is among the most promising and mostly studied application areas. The purpose of tissue engineering is to repair, replace, maintain or enhance the function of a particular tissue or organ, with the basic principle shown in Figure 21.
Electrospun nanofibers were suggested to be used in soft tissue prostheses such as blood vessel, vascular, breast and also to be deposited on hard tissue protheses as porous film.

Design of scaffolds that mimic the structure and biological functions of natural extracellular matrix is an important challenge in tissue engineering [1]. Electrospun nanofibrous scaffolds have exhibited great performance in cell attachment, proliferation and penetration both in vivo and in vitro trials. There is a wide range of material choices for preparation of electrospun scaffolds for tissue engineering applications and they may be in natural and synthetic polymer categories. Electrospun fibrous scaffolds prepared from natural polymers, for example from collagen, alginate, silk protein, hyaluronic acid, fibrinogen, chitosan, starch, are mostly preferred. Among synthetic polymers, poly (ε-caprolactone) (PCL), poly(lactic acid) (PLA), poly(glycolic acid) (PGA) and their copolymers are extensively used for biomedical applications due to their biocompatibility and biodegradability [3]. Biodegradable scaffolds are used as temporary templates for cell seeding, invasion, proliferation and differentiation prior to the regeneration of biologically functional tissue or natural extracellular matrix (ECM) [5].

Electrospun scaffolds with biomolecule delivery delivery capacity can be fabricated with various technique. Thereby, the biomolecules can be loaded into electrospun scaffolds. Physical adsorption is based on dipping the scaffolds into an aqueous phase. In blend electrospinning, biomolecules are mixed within the polymer solution and the mixed solution is used in electrospinning process to fabricate a hybrid scaffold. Core-shell fibers produced with coaxial electrospinning have great potential in preserving proteins, offering popularity to the use of coaxial electrospinning in protein delivery field. Biomolecules are immobilized onto the fiber surface via chemical bond in covalent immobilization. The fabrication techniques are illustrated in Figure 22 [3].
Bilayered electrospun nanofiber architectures were fabricated to mimic native blood vessel scaffold. The mechanical properties of bilayered scaffold were comparable with native vessels [46]. Zhang et al studied the tissue engineering of vascular grafts with genetically modified bone marrow mesenchymal stem cells (MSC) on poly(propylene carbonate) graft. They seeded MSCs onto the electrospun fibrous grafts and cultured. The integration of seeded cells with the microfiber scaffolds formed a three-dimensional cellular network. A tubular scaffold (Figure 23) with a diameter of 2 mm was fabricated by electrospining of poly(propylene carbonate) [51].
Electrospun nanofibers are also effective guidance substrates for **nervous tissue repair**. The effects of fiber diameter on cell culturing have been investigated. Lee et al have grown polypyrrole (PPy) on random and aligned PLGA nanofibers, thereby incorporating electrical stimulation during cell growth and they prepared conductive nanofibrous scaffolds. Electrically stimulated nanofibers offered longer neuritis and more neurite formation than without stimulation [52].

Nanofibers from PCL were extensively studied for **bone tissue engineering** [53]. Electrospun polymer nanofibers were also produced to be used as cosmetic **skin care mask** for skin healing, skin cleansing and other therapeutical properties [1].

Sun et al reported the formation of core-shell nanofibers by **coaxial electrospinning**. This technique proved to be a very versatile method for encapsulation of biorelevant molecules and nanocomposites [54]. Zhang et al [55] encapsulated a model protein within PCL nanofibers with coaxial electrospinning (Figure 24).
Electrospun nanofiber mat is also a good candidate for **wound dressing** due to the highly porous structure and well interconnected pores for exuding fluid from the pores, high specific surface area to inhibit the exogenous microorganism invasions. An open wound healing test using electrospun collagen nanofiber showed that early stage healing was faster than normal cotton gauze. Nanofibers of biodegradable polymer can be directly sprayed on the injured location of skin (Figure 25).

Electrospun nanofibers also exhibited many advantages as potential **drug delivery** carrier, as drug loading is very easy with electrospinning[46].

**3. Protective clothing**

Electrospun nanofiber membranes are considered as potential clothing applications due to their lightweight, large surface area, high porosity (breathable nature), great filtration efficiency, etc., which are also desirable characteristics of protective clothing. Electrospun nanofibers laid down in a layer with high porosity but small pore size provide resistance to the chemical harm agents in aerosol form [56].

**4. Electrical and optical application:**
Conductive nanofibers find use in applications such as sensors, actuators, batteries, etc. There are studies to impart sensing capability to nanofibers. Electrical conductivity is an important property for sensing devices. Conductive polymers are interesting with this respect. Insulating polymers were also used, but ions or nano fillers were added to improve conductivity. Several approaches have been used to impart nanofibers sensing capability. A polymeric sensing material can be used to electrospin nanofibers, sensing molecules can be incorporated into nanofibers, sensing material can be applied on the nanofiber surface by coating/grafting [46].

5. Composite application:

Nanofibers are promising to find applications in nanocomposites. Nanofibers will have better mechanical properties than micro fibers of the same material, therefore nanocomposites will have superior structural properties. Current literature contains a great deal of work on carbon nanofiber or nanotube reinforcements [1]. There are also nanocomposites reinforced with electrospun polymer nanofibers. Electrospun nanofibers of polybenzimidazole (PBI) were used as reinforcement in epoxy and rubber matrix [57]. Bergshoef et al produced nanocomposite with electrospun Nylon-4,6 nanofiber membranes and an epoxy matrix. Stiffness and strength of this nanocomposite was measured to be significantly higher than those of the reference matrix film [58]. Rojas et al incorporated cellulose whiskers in electrospun polystyrene–based microfibers. Nanoparticles of cellulose whiskers were used to reinforce electrospun polystyrene micro and nanofibers (Figure 26). The manufactured nanocomposite fibers and respective nonwovens will be used in high-performance applications due to their highly porous structure and large surface areas [6].
Electrospinning of nanofibers and their applications

Figure 26: SEM micrographs of PS/CNW electrospun microfiber composites loaded with 6% CNW a) in the absence of surfactant b) with surfactant added [6].

6. Energy harvest and storage applications:

Polymeric conductive membranes are also considered to have potential use in electromagnetic interference shielding, photovoltaic device, electrostatic dissipation, production of tiny electronic devices, sensors, actuators, etc. [5].

Nanofibrous materials were found to have higher energy conversion and storage efficiency than their bulk counterparts. Electrospun anofibers have shown great application potential in dye-sensitized solar cells.

In fuel cells, electrospun nanofibers have been prepared as alternative catalyst to the Pt nanoparticle catalyst, which is the main component in the fuel cell. They have high catalytic efficiency and good durability.

As for mechanical energy harvesters, different piezo electric materials can be made into nanofibrous structure by electrospinning and these electrospun nanofibers proved to have energy scavenging capability.

Carbon nanofibrous mats produced by electrospinning are used in supercapacitors and they offer high capacitive behavior.
Nanofiber mats of various polymers were studied as lithium battery separator in lithium ion batteries. Electrospun PAN mat displayed high ion conductivity and electrochemical stability [46].

The applications of electrospun fibers is briefly shown in Figure 27.

![Figure 27: Applications of electrospun fibers in different sectors](image)

**Future trends and challenges**

In the beginning of 2000, the main concerns on electrospinning were fabrication of nanofibers from natural or synthetic polymers and looking for application areas. A great deal has been achieved in understanding and controlling the electrospinning process through a very good understanding of the parameters and their interaction, resulting in ability to obtain desired fiber diameter and morphology. Electrospinning has begun to be extended for fiber formation based not only on synthetic or natural polymers, but also on metals, ceramics and organic/inorganic, inorganic/inorganic composite system. Incorporation or entire use of functional electrospun nanofibers in micro size electronic devices is among the major targets [59]. It is expected that high-throughput electrospinning units will open further opportunities for electrospun nonwovens [6]. Also, the increase in applicability of the electrospun nanofibers are extensively tried to be improved. For that purpose, new innovations take place including coaxial electrospinning, mixing and multiple electrospinning, core shelled electrospinning, blow assisted electrospinning, etc. Future applications are tried to be
broadened. Therefore the efforts are focused on up-scaling and also improving the nanofiber properties.

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