Review of Polymer Solutions for Near-Field Electrospinning with Spatial Control

Antonio Osamu Katagiri Tanaka, Héctor Alán Aguirre Soto

Abstract

Near-field electrospinning (NFES) is identified to be a technique able to fabricate polymer nano and micro fibers with accurate placement. In the past years (2006-2019), several polymer solutions have been successfully electrospun into fibers through several variants of the conventional NFES process. Each NFES variant intents to tailor the process parameters in order to improve the fibers' properties. This paper presents a review on the research and related development of electrospun fibers, emphasizing the used polymers, solvents, and fiber characteristics. Relevant summary of polymer solutions and near-field electrospinning processing conditions is provided in this paper.

Keywords: polymer, solvent, near-field electrospinning, NFES, fibers, spatial control

1. Introduction

Even though electrospinning is an old invention [1], it is currently a trending topic among researchers [2–4]. One of the reasons electrospinning is to be studied is its potential to fabricate polymer nano-fibers from a variety of polymers. The technique allows the production of thin continuous fibers with ease, with diameters down to 3 nm in some cases, which is something difficult to achieve by other techniques. Furthermore, the basic setup can be modified with ease to fabricate different fibers with diversified functionalities with different materials. The produced fibers can be aligned or unaligned. Besides, the electrospinning equipment is inexpensive and of small size, compared to the equipment of standard spinning techniques. On the other hand, the understanding of the electrospinning process has improved in the last years [5].

The main components of the electrospinning technique are the fluid control unit (e.g. syringe pump) and a voltage power supply. The process also requires a target electrode or combination of electrodes on which the fibers can be collected. Figure 1 describes a typical near-field electrospinning set-up [5]. Two sub-techniques can be derived from electrospinning depending on the distance between the dispensing electrode and the collector. The process in which the electrospun jet can be controlled near the tip is called NFES or near-field

Email addresses: oskatagiri@gmail.com (Antonio Osamu Katagiri Tanaka), alan.aguirre@tec.mx (Héctor Alán Aguirre Soto)

electrospinning [6]. Moreover, if the distance between the collector and the dispensing needle is greater, the configuration is known as FFES or far-field electrospinning [7]. Near-field electrospinning is considered to be an outstanding technique to fabricate polymer fibers with spatial control and it has suffered several modifications to improve the precision and accuracy of the fiber deposition. This paper intents to collect the NFES variants of electrospunable polymer solutions with spatial control in recent research.

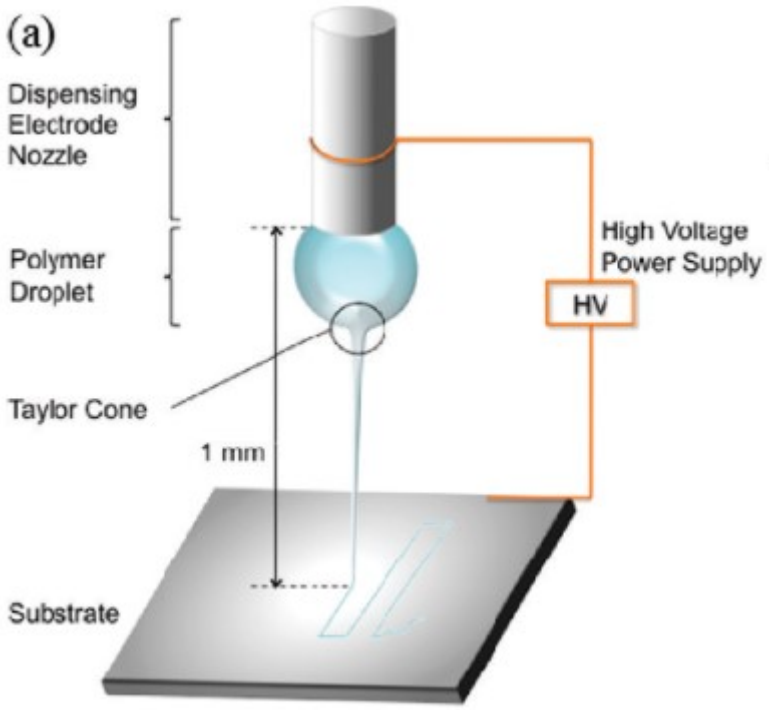

Figure 1: Typical near-field electrospinning set-up [8] .

2. Polymer Solution

In electrospinning, it is generally agreed that with higher concentration, the diameter of the fibers increased due to greater viscosity which resist stretching. In near field electrospinning, similar observations have been reported where concentration increases, fiber diameter increased [Chang et al 2008; Zheng et al 2012]. However, in separate studies by Pan et al (2014) using poly(γ-benzyl α, l-glutamate) and Pan et al (2015) using polyvinylidene fluoride (PVDF) reported reduction in fiber diameter with increasing concentration. Pan et al (2015) attributed this to a higher charge accumulation in higher concentration PVDF solution. However, more studies need to be carried out to verify this.

2.1. Polymers

2.2. Solvents

3. NFES Parameters

To spin nano fibers at close distances, the initial diameter of the jet is required to be as small as possible since stretching of the thread is limited. Kameoka et al (2003) demonstrated that a small initial spinning radius can be achieved using an atomic force microscope tip with a small polymer solution drop at the tip. Near-field electrospinning, has exhibited to be capable fabricate nano fibers over and nano fiber patterns (Sun et al 2006). Nevertheless, having a small polymer solution drop at the nozzle tip limits the length of the fibers that can be fabricated in a continuous manner. Using a spinneret with a reservoir (e.g. syringe) of solution generally produces fibers with diameter of a few micrometers [Gupta et al 2007; Xue et al 2014] since it creates a limit to which the nozzle inner diameter can be reduced to allow the solution to flow through. Coppola et al (2014) have showned a NFES variant that allows polymer nano fibers to be deposited directly from a polymer drop, averting the issue of nozzle clogging. The fibers are also prone soaking after deposition thus giving the fibers a semi-circular cross-section as depicted in Xue et al's (2014) work. The thinnest nozzles in literature so far are about 100 μm in diameter, for instance Chang et al (2008) used a 100 µm inner diameter needle tip to electrospin poly(ethylene oxide) (PEO) and Camillo et al (2013) used a µm-diameter tip Tungsten spinneret in a 26 gauge needle to electrospin co-polymer, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) with poly(ethylene oxide) (PEO).

3.1. Applied Voltage

Further development in the near field electrospinning spinning process have attempted to improve fiber deposition precision and reducing fiber diameter. Camillo et al (2013) was able to fabricate 100 nm diameter fiber at an applied voltage of 1.5 kV and a tip to collector distance of 500 µm using a modified fine tip spinneret. Separate reports by Chang et al (2008) and Bisht et al (2011) have shown that higher voltage leads to a significant increase in the fiber diameter (in the micrometer range) and loss of jet stability. The remedy is to significantly reduce the voltage used in the electrospinning process to about 200 to 600 V with tip to collector distance at about 0.5 to 1 mm. However, the charges on the solution drop at the tip of the needle were insufficient to break free from the surface tension to initiate electrospinning without assistance. Chang et al (2008) used a tungsten probe tip and Bisht et al (2011) used a glass microprobe tip (1 to 3 µm tip diameter) to mechanically draw the solution at the tip of the needle to initiate electrospinning. In the study by Chang et al (2008), reduction of electrospinning voltage from 1.5 kV (at tip to collector distance of 500 µm) to 600 V reduces the fiber diameter from 3 µm to 50 nm. Using a lower voltage of 200 V with tip to collector distance of 1 mm, Bisht et al (2011) was able to pattern nanofibers (polyethylene oxide) with diameter below 20 nm. Similar to electrospinning with longer tip to collector distance, it is likely that there is an optimum voltage which the fiber diameter obtained will be at its finest. Voltage higher or lower than this value will see an increase in the fiber diameter. Song et al (2015) showed that when the voltage for electrospinning

polystyrene was increased from 400 to 500V, at a tip to collector distance of 20 µm, the fiber diameter reduced from close to 160 nm to about 60 nm. Such fiber diameter response to voltage is due to a balance of stretching of the jet and the speed at which it hit the collector. While increasing voltage causes greater stretching which reduces the fiber diameter, this also causes greater jet acceleration where the stretching terminates when the jet hit the collector.

To use a low working voltage in near field electrospinning while eliminating the need to use a physical object to initiate electrospinning, an alternative is to use a higher voltage for initiation of electrospinning and switch to a lower voltage once the jet has erupted from the nozzle. Huang et al (2014) used this concept with a movable stage collector to produce ordered patterns with interfiber pitch of 50 µm. By controlling the height between the nozzle tip and the collector stage and the speed of stage, fibers with different orientation and cross-sectional shape can be obtained. Generally, closer distance between nozzle tip and collector (ranging from 0.5 mm to 2 mm) results in flat fibers due to impaction of the electrospinning jet. A limitation of the setup is that the landing point at electrospinning jet initiation cannot be determined although subsequent adjustment can be made after the jet has landed or the structure can be built up based on the displacement relative to the landing point. To control the landing point of the electrospinning jet, a target point may be set.

Low voltage, near field electrospinning has shown characteristics that differ from conventional near field electrospinning using higher voltage. Fiber diameter has already been shown to be smaller using this technique. With low voltage, near field electrospinning, the fiber diameter was found to be sensitive to the collector stage movement due to mechanical stretching; low velocity giving rise to larger fiber diameter and vice versa [Bisht et al 2011]. Instead of very fine spinneret tip, Bisht et al (2011) showed that it is possible to spin fibers with diameter less than 100 nm using a 27 gauge needle (approx. 200 µm inner diameter).

3.1.1. Electric field

Electrospinning jet can be very sensitive to variation in electric field. Thus a target with electric field profile that attracts the jet may be used to guide the electrospinning jet towards the desired landing point. Bisht et al (2011) demonstrated the precision and accuracy of low voltage, near field electrospinning by suspending fiber across carbon post with diameter of 30 µm and interpostal distance of 100 µm. Min et al (2013) used near field electrospinning to deposit semiconducting poly(3-hexylthiophene) (P3HT):PEO-blend organic nanowire over multiple field-effect transistors on a flexible polyarylate substrate at a speed of 13.3 cm/s with regular spacing of 50 µm and fiber diameter of 289 nm. They have also demonstrated the ability to spin highly aligned nanowires from other materials such as poly(9-vinyl carbazole) (PVK) and poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)}.

The combination of near-field electrospinning and a guiding electrode has the potential to obtain precise and accurate fiber deposition. Xu et al (2014) used a guiding electrode behind the collector to create a direct line from the nozzle tip to it. This significantly dampens the deviation of the electrospinning jet from its original path as a result of electrostatic repulsion from the preceding deposited nano fiber. Without the guiding electrode, the near-field elec-

trospun fibers have a spread of 74 µm. With the guiding electrode, the spread was reduced to just 7 µm. This raises the possibility of building up 3D structures using electrospinning. Kim et al (2018) used inkjet printing with conductive Ag nanoparticles loaded ink to form patterns on a paper as a target for near field electrospun fibers. The conductive printed pattern served as a guiding electrode for the electrospinning jet. Poly(vinylidene fluoride) (PVDF) solution was electrospun from a height of 750 µm and a 150 µm offset from the edge of the pattern. The sensitivity of the electrospinning jet towards the electric field can be seen as the fibers are stacked on the edge of the conductive pattern where the relative electric field was much higher at the edge than at its center. When the pattern lines formed acute angle, right-angle or obtuse angle, the accuracy of the deposited fibers are influenced by slight changes in the relative electric field. From acute angle to right-angle, the electric field singularity increases from the edge to the intersection between the lines. In this case, the fibers were stacked directly on the edge of the line and to the middle of the intersection. For lines forming obtuse angle, the deposited fibers followed the edge of the lines by veered off the line at the intersection.

3.2. Substrate

In near field electrospinning, one of the risks is electrical shorting due to the proximity of the charged needle tip to the grounded collector. Any electrical shorting will disrupt the electrospinning process and result in discontinuous fiber. While using a lower voltage may reduce this risk, an alternative is to use a less conductive collector. Liu et al (2014) used a rotating glass tube with a copper foil lining at the inner surface of the tube for the collection of electrospun oriented polyvinylidene fluoride (PVDF) fiber. While initial fiber alignment was excellent, the alignment starts to deteriorate after prolonged fiber deposition which can be attributed to the presence of residual charges.

The influence of residual charges on the precision of fiber deposited is more pronounced when an insulating surface and a conductive surface were used as collectors. Choi et al (2017) used a hydrophobic and insulating acrylic substrate as collector. To increase conductivity of selected region of the collector, plasma treatment was carried out to render those region hydrophilic. The collector was placed in a high humidity environment such that the hydrophilic region will be slightly conductive due to the presence of water molecule attached to it. Near field electrospinning of polyurethane showed that on the insulating hydrophobic surface, the fibers were twisted and curved due to weak electric field profile between the emitter and the collector surface and the inability of charges to escape. In contrast, on the hydrophilic region, the fiber were placed in accordance to the movement of the emitter relative to the collector. This shows that electrical charges on the electrospinning jet needs to escape for precise deposition and even an insulating substrate with slight conductivity is crucial for ordered fiber arrangement.

Table 1: Electrospun Polymer Solutions - Solution and Process Parameters

Polymer(s)	Solvent(s)	NFES Variant	Process Parameters and Fiber Characterization	Ref.
Poly(ethylene oxide) (PEO; MW = 4,000,000)	Deionized water	Low-Voltage NFES (LV NFES)	**Solution Concentration:** 1, 2, and 3 $wt\%$ PEO **Nozzle:** 27 gauge type 304; stainless steel needle **Solution deposition rate:** lower than $1\mu L/h$ **Nozzle-to-substrate distance:** $1mm$ **Substrate composition:** Pyrolyzed SU-8 carbon and Si **Applied voltage:** polymer jet initiated at 400-600 V and dispensed at 200-400 V **x-y stage velocity:** 10-40mm/s **Fiber Diameter:** 50-425nm **Distance between adjacent fibers:** *Not determined*	[8]
Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV; MW = 380,000) with Poly(ethylene oxide) (PEO; MW = 300,000)	acetonitrile toluene mixture (65/35); acetic acid toluene (17/83); pure toluene	Typical NFES process	**Solution Concentration:** $10mg$ of MEH-PPV in $2mL$ of toluene; $500mL$ of MEH-PPV solution with $250mg$ of PEO in $3.5mL$ of acetonitrile; $500mL$ of MEH-PPV solution with $250mg$ of PEO in $3mL$ of acetic acid / toluene (17 / 83). The resulting MEH-PPV/PEO concentration is 1:100 **Nozzle:** mm-diameter tip Tungsten spinneret in a 26 gauge needle **Solution deposition rate:** $50\mu L/h$ **Nozzle-to-substrate distance:** $500\mu m$ **Substrate composition:** SiO2/Si (oxide thickness = 800 nm) **Applied voltage:** around $1.3kV$ **x-y stage velocity:** $50cm/s$ **Fiber Diameter:** $100nm$ **Distance between adjacent fibers:** around $100\mu m$	[9]

Continued on next page

Table 1 continued

Poly(ethylene oxide) (PEO)	Water	Scanning Tip Electrospinning and NFES	**Solution Concentration:** $7wt\%$ PEO **Nozzle:** Needle outer diameter of $200\mu m$ and inner diameter of $100\mu m$ **Solution deposition rate:** $0.1\mu L/h$ **Nozzle-to-substrate distance:** $500\mu m$ **Substrate composition:** *Not determined* **Applied voltage:** polymer jet initiated at 1.5 kV and dispensed at $600V$ **x-y stage velocity:** $120mm/s$ **Fiber Diameter:** $709\pm131nm$; 49-$74nm$ when applied voltage is $800V$ **Distance between adjacent fibers:** *Not determined* **Notes:** $108m$ yield in $15min$ with a fiber diameter of $709\pm131nm$	[10]
Poly(vinylidine fluorid) (PVDF)	N,N Dimethylformamide (DMF)	Helix Electrohydrodynamic Printing (HE-printing)	**Solution Concentration:** $1.8g$ PVDF in $4.1g$ of DMF and $4.1g$ of acetone. The resulting concentration is 18% PVDF. **Nozzle:** Needle outer diameter of $510\mu m$ and inner diameter of $260\mu m$ **Solution deposition rate:** $400nL/min$ **Nozzle-to-substrate distance:** 10-$50mm$ **Substrate composition:** Poly(dimethylsiloxane) (PDMS) on Ecoflex **Applied voltage:** 1.5–$3kV$ **x-y stage velocity:** 0-$400mm/min$ **Fiber Diameter:** about 1.5-$3\mu m$ **Distance between adjacent fibers:** *Not determined*	[11]

Continued on next page

Table 1 continued

Polyhedral Oligomeric Silsesquioxane-Poly(Carbonate-Urea)Urethane (POSS-PCU) and Polyhedral Oligomeric Silsesquioxane Poly(Caprolactone-Poly(Carbonate-Urea)Urethane) (POSS-PCL-PCU)	Dimethyl acetamide (DMAC) and 1-Butanol	Electrohydrodynamic 3D Print-patterning or Electrohydrodynamic Jetting	**Solution Concentration:** POSS-PCU and POSS-PCL-PCU used in 20%w/w concentration in DMAC **Nozzle:** needle of 750 μm in diameter **Solution deposition rate:** less than 1$\mu L/min$ **Nozzle-to-substrate distance:** about between 500μm to 2mm **Substrate composition:** *Not determined* **Applied voltage:** 8.0-10.0kV **x-y stage velocity:** 10mm/s **Fiber Diameter:** 5-50μm **Distance between adjacent fibers:** 250μm	[12]
Poly(ethylene oxide) (PEO)	Distilled water	Electrohydrodynamic Writing or Mechano-electrospinning (MES)	**Solution Concentration:** 6wt% PEO **Nozzle:** *Not determined* **Solution deposition rate:** 1200nL/min **Nozzle-to-substrate distance:** 7.5mm **Substrate composition:** *Not determined* **Applied voltage:** polymer jet initiated at 2 kV and dispensed at 0.8-1kV **x-y stage velocity:** around 400mm/s **Fiber Diameter:** 200-350nm **Distance between adjacent fibers:** 5μm	[13]

Continued on next page

Table 1 continued

Poly(ethylene oxide) (PEO)	Deionized water and the ethanol with a volume ratio of 3:1	Airflow-assisted Electrohydrodynamic Direct-writing (EDW)	**Solution Concentration:** $8wt\%$ PEO **Nozzle:** Outer airflow passage diameter: $1mm$ Airflow gas pump pressure: $25kPa$ Inner liquid passage diameter: $0.21mm$ **Solution deposition rate:** $30\mu L/h$ **Nozzle-to-substrate distance:** $2mm$ **Substrate composition:** Silicon **Applied voltage:** about $2kV$ **x-y stage velocity:** 1-$20mm/s$ **Fiber Diameter:** $3.73 \pm 1.37\mu m$ **Distance between adjacent fibers:** $5.13 \pm 6.67\mu m$	[14]
Poly(Vinylidene Fluoride) (PVDF)	Acetone and Dimethyl Sulfoxide (DMSO)	3D Electrospinning	**Solution Concentration:** $17wt\%$ PVDF; $1.7g$ of PVDF, $5g$ of acetone, $0.5g$ of Capstone FS-66, $5g$ of DMSO **Nozzle:** Needle inner diameter of $100\mu m$ **Solution deposition rate:** $14\ nL/min$ **Nozzle-to-substrate distance:** $750\mu m$ **Substrate composition:** A4 size commercial printing paper (Double A) **Applied voltage:** $1.9kV$ **x-y stage velocity:** $10mm/s$ **Fiber Diameter:** *Not determined* **Distance between adjacent fibers:** *Not determined*	[15]

Continued on next page

Table 1 continued

Poly(9-Vinyl Carbazole) (PVK)	Styrene	Typical NFES process	**Solution Concentration:** 3.96wt% PVK in styrene **Nozzle:** Needle inner diameter of 100μm **Solution deposition rate:** 500nL/min **Nozzle-to-substrate distance:** around 2.5mm **Substrate composition:** Si/SiO2 **Applied voltage:** 3-4kV x-y stage velocity: 13.3cm/s **Fiber Diameter:** 289.26 $\pm$ 35.37nm **Distance between adjacent fibers:** 50μm **Notes:** 15m yield in 2min	[16]
Polystyrene (PS)	1,2,4-Trichloro benzene	Electrohydrodynamic (EHD) jet printing	**Solution Concentration:** 1 to 5wt% PS **Nozzle:** Glass nozzle inner diameter of 2μm and outer diameter of 2.66μm **Solution deposition rate:** Si **Nozzle-to-substrate distance: 20, 30, 40**μm **Substrate composition:** **Applied voltage:** 500 to 400V in 25V increments **x-y stage velocity:** 0.01-10mm/s **Fiber Diameter:** about 60-170μm **Distance between adjacent fibers:** *Not determined*	[17]
Poly(ethylene oxide) (PEO)	*Not determined*	Typical NFES process	**Solution Concentration:** 3wt% PEO **Nozzle:** *Not determined* **Solution deposition rate:** *Not determined* **Nozzle-to-substrate distance:** 500μm **Substrate composition:** Si **Applied voltage:** 1000V **x-y stage velocity:** 20cm/s **Fiber Diameter:** 300nm **Distance between adjacent fibers:** 25μm	[18]

Continued on next page

Table 1 continued

Poly(ethylene oxide) (PEO)	Distilled water	Multinozzle NFES	**Solution Concentration:** $5wt\%$ **Nozzle:** four-nozzle and six-nozzle array with needle spacing changes from $1.5mm$ to $3.5mm$ **Solution deposition rate:** 1-3$\mu L/min$ **Nozzle-to-substrate distance:** $2mm$ **Substrate composition:** *Not determined* **Applied voltage:** 1.7-2.7kV **x-y stage velocity:** *Not determined* **Fiber Diameter:** $5.47\mu m$ **Distance between adjacent fibers:** 3-5 mm	[19]
Poly(ethylene oxide) (PEO)	Distilled water	Multinozzle NFES	**Solution Concentration:**$5wt\%$ **Nozzle:** Dual-28G-needle array with needle inner diameter of $0.18mm$ and outer diameter of $0.36mm$; with needle spacing changes from $2.0mm$ to $3.0mm$ **Solution deposition rate:** $0.2\mu L/min$ **Nozzle-to-substrate distance:** 3.0-4.0mm **Substrate composition:** *Not determined* **Applied voltage:** 2.0-3.0kV **x-y stage velocity:** $20mm/s$ **Fiber Diameter:** *Not determined* **Distance between adjacent fibers:** 218-326μm	[20]

Continued on next page

Table 1 continued

Poly(ethylene oxide) (PEO)	Distilled water	Multinozzle NFES	**Solution Concentration:**5 $wt\%$ **Nozzle:** Dual-28G-needle array with needle inner diameter of 180μm and outer diameter of 360μm; with needle spacing changes of 2.0mm **Solution deposition rate:** 0.2$\mu L/min$ **Nozzle-to-substrate distance:** 4.0mm **Substrate composition:** chromium-plated glass **Applied voltage:** 2.5kV **x-y stage velocity:** 20mm/s **Fiber Diameter:** *Not determined* **Distance between adjacent fibers:** 2.3002-2.7224mm	[21]
Poly(ethylene oxide) (PEO)	*Not determined*	Typical NFES process	**Solution Concentration:** 2$wt\%$ **Nozzle:** G30 needle with inner diameter of 0.15mm **Solution deposition rate:** *Not determined* **Nozzle-to-substrate distance:** 1-3mm **Substrate composition:** Silicon **Applied voltage:** 1250V **x-y stage velocity:** *Not determined* **Fiber Diameter:** *Not determined* **Distance between adjacent fibers:** 20μm	[22]

Continued on next page

Table 1 continued

Gelatin (porcine skin)	Acetic Acid and Ethyl Acetate	Typical process	NFES	**Solution Concentration:** $11wt\%$ gelatin, $30wt\%$ water, $35.4wt\%$ acetic acid, $23.6wt\%$ ethyl acetate **Nozzle:** 19G needle tip with outer diameter of $1.08mm$ **Solution deposition rate:** *Not determined* **Nozzle-to-substrate distance:** $1.25mm$ **Substrate composition:** Poly(Dimethylsiloxane) (PDMS) films **Applied voltage:** $1000V$ **x-y stage velocity:** *Not determined* **Fiber Diameter:** around 2-3μm **Distance between adjacent fibers:** $40\mu m$	[23]
Poly(ethylene oxide) (PEO)	Water/Ethanol (v/v = 60/40)	Typical process	NFES	**Solution Concentration:** PEO concentrations of 16% adn 18% **Nozzle:** $40\mu m$ **Solution deposition rate:** **Nozzle-to-substrate distance:** $1mm$ **Substrate composition:** Planar silicon **Applied voltage:** $1.7kV$ **x-y stage velocity:** $0.36m/s$ **Fiber Diameter:** $5.15\mu m$ **Distance between adjacent fibers:** *Not determined*	[24]

Continued on next page

Table 1 continued

Poly(ethylene oxide) (PEO)	Water/Ethanol (v/v = 3/1)	Electrohydrodynamic Direct-Write (EDW)	**Solution Concentration:** $14wt\%$ PEO **Nozzle:** Stainless needle with inner diameter of $210\mu m$ and outer diameter of $400\mu m$ **Solution deposition rate:** $50\mu L/h$ **Nozzle-to-substrate distance:** $2mm$ **Substrate composition:** Poly(ethylene terephthalate) (PET) **Applied voltage:** $3kV$ **x-y stage velocity:** $700mm/s$ **Fiber Diameter:** 15-35μm **Distance between adjacent fibers:** $70\mu m$	[25]
Poly(ethylene oxide) (PEO)	Deionized water	Mechano-Electrospinning	**Solution Concentration:** $3wt\%$ PEO **Nozzle:** Stainless steel nozzle with inner diameter of $160\mu m$ and outer diameter of $310\mu m$ **Solution deposition rate:** $50nL/min$ **Nozzle-to-substrate distance:** 2-5mm **Substrate composition:** Silicone **Applied voltage:**polymer jet initiated at $2kV$ and dispensed at $1kV$ **x-y stage velocity:** 200-400mm/s **Fiber Diameter:** from 344±32 to 214±27nm **Distance between adjacent fibers:** *Not determined*	[26]

Continued on next page

Table 1 continued

Poly(co-Glycolic) acid (PLGA)	Dimethyl Carbonate (DMC)	Tethered Pyro-Electrohydro-dynamic Spinning (TPES)	**Solution Concentration:** *Not determined* **Nozzle:** nozzle-free **Solution deposition rate:** The drop reservoir is placed directly on a flat substrate **Nozzle-to-substrate distance:** Taylor's cone is focused and put in direct contact with the collector **Substrate composition:** Poly(tetrafluoroethylene) (PTFE) coated glass slide **Applied voltage:** pyro-electric field of between 2.7 $x10^7$ V/m and 5.5$x10^7$ V/m **x-y stage velocity:** *Not determined* **Fiber Diameter:** 304.7nm **Distance between adjacent fibers:** *Not determined*	[27]
Poly(ethylene oxide) (PEO) with Tetrabutylammonium tetrafluoroborate (TBF) and SU-8 2002	N,N Dimethyl-formamide (DMF)	Typical NFES process	**Solution Concentration:** SU-8/PEO/TBF blend with 0.75wt% PEO, 1wt% TBF; the blend is diluted with 30vol% DMF $\mu m \mu m$ **Solution deposition rate:** *Not determined* **Nozzle-to-substrate distance:** *Not determined* **Substrate composition:** Brass disk with a diameter of 38mm **Applied voltage:** 980V **x-y stage velocity:** *Not determined* **Fiber Diameter:** *Not determined* **Distance between adjacent fibers:** *Not determined*	[6]

Continued on next page

Table 1 continued

Poly(ethylene oxide) (PEO)	Water:Ethanol (3:2)	Suspension NFES	**Solution Concentration:** $14wt\%$ PEO **Nozzle:** stainless steel needle (25 G) with inner diameter of $0.25mm$ **Solution deposition rate:** $3nL/s$ **Nozzle-to-substrate distance:** between 0.5 and $10mm$ with $0.5mm$ increments **Substrate composition:** Planar silicon electrodes **Applied voltage:** $1.6kV$ **x-y stage velocity:** 50, 150, and $250mm/s$ **Fiber Diameter:** $300nm$ **Distance between adjacent fibers:** 0.1 and $0.5mm$	[28]
Poly(ethylene oxide) (PEO)	Deionized water	Typical NFES process	**Solution Concentration:** $10wt\%$ PEO **Nozzle:** 32G metal needle **Solution deposition rate:** (Jet impact speed of $5mm/s$) **Nozzle-to-substrate distance:** $0.5mm$ **Substrate composition:** p-type silicon wafer **Applied voltage:** $400V$ **x-y stage velocity:** $5mm/s$ **Fiber Diameter:** **Distance between adjacent fibers:** $50\mu m$	[29]

4. NFES Variants

Low-Voltage NFES (LV NFES) [8]
Scanning Tip Electrospinning [10]
3D Electrospinning [15]
Electrohydro-dynamic 3D Print-patterning or Electrohydro-dynamic Jetting [12]
Multinozzle NFES [19–21]
Electrohydro-dynamic Writing or Mechanoelectrospinning (MES) [13]
Electrohydro-dynamic Direct-Write (EDW) [25]
Mechano-Electrospinning [26]
Suspension NFES [28]
Helix Electrohydro-dynamic Printing (HE-printing) [11]
Electrohydro-dynamic (EHD) jet printing [17]
Airflow-assisted Electrohydro-dynamic Direct-writing (EDW) [14]
Tethered Pyro-Electrohydro-dynamic Spinning (TPES) [27]

5. Conclusion

Lorem ipsum dolor sit amet, consectetur adipiscing elit, sed do eiusmod tempor incididunt ut labore et dolore magna aliqua. Ut enim ad minim veniam, quis nostrud exercitation ullamco laboris nisi ut aliquip ex ea commodo consequat. Duis aute irure dolor in reprehenderit in voluptate velit esse cillum dolore eu fugiat nulla pariatur. Excepteur sint occaecat cupidatat non proident, sunt in culpa qui officia deserunt mollit anim id est laborum.

References

[1] F. Anton, Process and apparatus for preparing artificial threads (1930). doi:https://patents.google.com/?q=D01D5%2f0076.

[2] Z.-M. Huang, Y. Z. Zhang, M. Kotaki, S. Ramakrishna, A review on polymer nanofibers by electrospinning and their applications in nanocomposites, Composites Science and Technology 63 (15) (2003) 2223–2253. doi:10.1016/S0266-3538(03)00178-7.

[3] D. H. Reneker, A. L. Yarin, Electrospinning jets and polymer nanofibers, Polymer 49 (10) (2008) 2387–2425. doi:10.1016/J.POLYMER.2008.02.002.

[4] J. D. Schiffman, C. L. Schauer, A Review: Electrospinning of Biopolymer Nanofibers and their Applications, Polymer Reviews 48 (2) (2008) 317–352. doi:10.1080/15583720802022182.

[5] Q. Li, Chapter 7: Liquid Crystal-Functionalized Nano- and Microfibers Produced by Electrospinning - Liquid Crystals Beyond Displays: Chemistry, Physics, and Applications, John Wiley & Sons, 2012. doi:9781118078617.

[6] A. Cisquella-Serra, M. Magnani, Álvaro Gual-Mosegui, S. Holmberg, M. Madou, M. Gamero-Castaño, Study of the electrostatic jet initiation in near-field electrospinning, Journal of Colloid and Interface Science 543 (2019) 106–113. doi:10.1016/J.JCIS.2019.02.041.

[7] S. K. Nataraj, K. S. Yang, T. M. Aminabhavi, Polyacrylonitrile-based nanofibers—A state-of-the-art review, Progress in Polymer Science 37 (3) (2012) 487–513. doi:10.1016/J.PROGPOLYMSCI.2011.07.001.

[8] G. S. Bisht, G. Canton, A. Mirsepassi, L. Kulinsky, S. Oh, D. Dunn-Rankin, M. J. Madou, Controlled Continuous Patterning of Polymeric Nanofibers on Three-Dimensional Substrates Using Low-Voltage Near-Field Electrospinning, Nano Letters 11 (4) (2011) 1831–1837. doi:10.1021/nl2006164.

[9] D. D. Camillo, V. Fasano, F. Ruggieri, S. Santucci, L. Lozzi, A. Camposeo, D. Pisignano, Near-field electrospinning of conjugated polymer light-emitting nanofibers, Nanoscale 5 (2013) 11637–11642. doi:10.1039/C3NR03094F.

[10] C. Chang, K. Limkrailassiri, L. Lin, Continuous near-field electrospinning for large area deposition of orderly nanofiber patterns, Appl Phys Lett (2008) 3doi:10.1063/1.2975834.

[11] Y. Duan, Y. Ding, Z. Xu, Y. Huang, Z. Yin, Helix Electrohydrodynamic Printing of Highly Aligned Serpentine Micro/Nanofibers., Polymers 9 (9) (sep 2017). doi:10.3390/polym9090434.

[12] A. Gupta, A. M. Seifalian, Z. Ahmad, M. J. Edirisinghe, M. C. Winslet, Novel Electrohydrodynamic Printing of Nanocomposite Biopolymer Scaffolds, Journal of BIOACTIVE AND COMPATIBLE POLYMERS 22 (2007). doi:10.1177/0883911507078268.

[13] Y. Huang, Y. Duan, Y. Ding, N. Bu, Y. Pan, N. Lu, Z. Yin, Versatile, kinetically controlled, high precision electrohydrodynamic writing of micro/nanofibers, Scientific Reports 4 (1) (2015) 5949. doi:10.1038/srep05949.

[14] J. Jiang, X. Wang, W. Li, J. Liu, Y. Liu, G. Zheng, J. Jiang, X. Wang, W. Li, J. Liu, Y. Liu, G. Zheng, Electrohydrodynamic Direct-Writing Micropatterns with Assisted Airflow, Micromachines 9 (9) (2018) 456. doi:10.3390/mi9090456.

[15] J. Kim, B. Maeng, J. Park, Characterization of 3D electrospinning on inkjet printed conductive pattern on paper, Micro and Nano Systems Letters 6 (1) (2018) 12. doi:10.1186/s40486-018-0074-1.

[16] S.-Y. Min, T.-S. Kim, B. J. Kim, H. Cho, Y.-Y. Noh, H. Yang, J. H. Cho, T.-W. Lee, Large-scale organic nanowire lithography and electronics, Nature Communications 4 (1) (2013) 1773. doi:10.1038/ncomms2785.

[17] C. Song, J. A. Rogers, J.-M. Kim, H. Ahn, Patterned polydiacetylene-embedded polystyrene nanofibers based on electrohydrodynamic jet printing, Macromolecular Research 23 (1) (2015) 118–123. doi:10.1007/s13233-015-3024-2.

[18] D. Sun, C. Chang, S. Li, L. Lin, Near-Field Electrospinning (2006). doi:10.1021/nl0602701.

[19] H. Wang, S. Huang, F. Liang, P. Wu, M. Li, S. Lin, X. Chen, Research on Multinozzle Near-Field Electrospinning Patterned Deposition, Journal of Nanomaterials 2015 (2015) 1–8. doi:10.1155/2015/529138.

[20] Z. Wang, X. Chen, J. Zeng, F. Liang, P. Wu, H. Wang, Controllable deposition distance of aligned pattern via dual-nozzle near-field electrospinning, AIP Advances 7 (3) (2017) 035310. doi:10.1063/1.4974936.

[21] Z. Wang, X. Chen, J. Zhang, Y.-J. Lin, K. Li, J. Zeng, P. Wu, Y. He, Y. Li, H. Wang, Fabrication and evaluation of controllable deposition distance for aligned pattern by multi-nozzle near-field electrospinning, AIP Advances 8 (7) (2018) 075111. doi:10.1063/1.5032082.

[22] J. Xu, M. Abecassis, Z. Zhang, P. Guo, J. Huang, K. Ehmann, J. Cao, Accuracy Improvement of Nano-fiber Deposition by Near-Field Electrospinning, International Workshop on Microfactories IWMF2014 (9th) (2014).

[23] N. Xue, X. Li, C. Bertulli, Z. Li, A. Patharagulpong, A. Sadok, Y. Y. S. Huang, Rapid Patterning of 1-D Collagenous Topography as an ECM Protein Fibril Platform for Image Cytometry, PLoS ONE 9 (4) (2014) e93590. doi:10.1371/journal.pone.0093590.

[24] G. Zheng, W. Li, X. Wang, D. Wu, D. Sun, L. Lin, Precision deposition of a nanofibre by near-field electrospinning, Journal of Physics D: Applied Physics 43 (41) (2010) 415501. doi:10.1088/0022-3727/43/41/415501.

[25] J.-Y. Zheng, H.-Y. Liu, X. Wang, Y. Zhao, W.-W. Huang, G.-F. Zheng, D.-H. Sun, Electrohydrodynamic Direct-Write Orderly Micro/Nanofibrous Structure on Flexible Insulating Substrate, Journal of Nanomaterials 2014 (2014) 1–7. doi:10.1155/2014/708186.

[26] N. Bu, Y. Huang, X. Wang, Z. Yin, Materials and Manufacturing Processes Continuously Tunable and Oriented Nanofiber Direct-Written by Mechano-Electrospinning Continuously Tunable and Oriented Nanofiber Direct-Written by Mechano-Electrospinning (2012). doi:10.1080/10426914.2012.700145.

[27] S. Coppola, V. Vespini, G. Nasti, O. Gennari, S. Grilli, M. Ventre, M. Iannone, P. A. Netti, P. Ferraro, Tethered Pyro-Electrohydrodynamic Spinning for Patterning Well-Ordered Structures at Micro-and Nanoscale, Chem. Mater 26 (2014) 3360. doi:10.1021/cm501265j.

[28] A. R. Nagle, C. D. Fay, Z. Xie, G. G. Wallace, X. Wang, M. J. Higgins, A direct 3D suspension near-field electrospinning technique for the fabrication of polymer nanoarrays, Nanotechnology 30 (19) (2019) 195301. doi:10.1088/1361-6528/ab011b.

[29] D. Shin, J. Kim, J. Chang, Experimental study on jet impact speed in near-field electrospinning for precise patterning of nanofiber, Journal of Manufacturing Processes 36 (2018) 231–237. doi:10.1016/J.JMAPRO.2018.10.011.