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

Antonio Osamu Katagiri Tanaka, Héctor Alán Aguirre Soto

Abstract

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

Contents

1. Introduction

Diverse polymer patterning techniques have been developed for the fabrication of nanofibers, such as arc discharge [31], chemical vapor deposition, laser ablation [21], and vapor growth [18]. Nonetheless, those processes are expensive due to either the low product yield or the expensive equipment required. The electrospinning method (invented by Formhals

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Anton in 1934)can produce fibers with a range of diameters between 10 nm and 10 mm [12,2] from a polymer solution under the influence of an electrostatic force. The applied electric field and solution conductivity and viscosity is an important parameter the affects the fiber diameter during the spinning along with other parameters such as jet length, solution viscosity surrounding gas, flow rate and the collector geometry [1, 14, 4, 26].

Even though electrospinning is an old invention [2], it is currently a trending topic among researchers [11, 22, 23]. 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 [15]. As Reneker and Yarin state: "Electrospinning has rapidly changed fiber making from a capital intensive, large scale process to a low cost, broadly applicable method that manufactures fibers on a laboratory bench, to serve diverse needs ranging from materials science and technology to life sciences and clinical medicine.“ [22]

The main components of the electrospinning technique are the fluid control unit (e.g. syringe pump) and a DC power supply. The process also requires a target electrode or combination of electrodes on which the fibers can be collected. Figure 6.2 describes a typical electrospinning set-up. [15] 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 electrospinning. [7] Moreover, if the distance between the collector and the dispensing needle is greater, the configuration is known as FFES or far-field electrospinning. [19] The difference between NFES and mechano-electrospinning is the presence of a mechanical collector that allows higher precision when patterning. Figure 6.3 shows a typical near field mechano-electrospinning apparatus.

2. NFES

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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)	Deionized water	Low-Voltage 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*	[1]
Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) with Poly(ethylene oxide) (PEO)	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 $100\mu m$	[2]

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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 $709\pm131nm$	[3]
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*	[4]

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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	[5]
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	[6]

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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:** $5.13 \pm 6.67\mu m$	[7]
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*	[8]

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Table 1 continued

Poly(9-Vinyl Carbazole) (PVK)	Styrene	Typical NFES process	**Solution Concentration:** 3.96$wt\%$ 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	[9]
Polystyrene (PS)	1,2,4-Trichloro benzene	Electrohydro-dynamic (EHD) jet printing	**Solution Concentration:** 1 to 5$wt\%$ 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*	[10]
Poly(ethylene oxide) (PEO)	*Not determined*	Typical NFES process	**Solution Concentration:** 3$wt\%$ 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	[11]

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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	[12]
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-$326\mu m$	[13]

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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	[14]
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	[15]

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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-$3\mu m$ **Distance between adjacent fibers:** $40\mu m$	[16]
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*	[17]

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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:** $70\mu m$	[18]
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 $214\pm27nm$ **Distance between adjacent fibers:** *Not determined*	[19]

Continued on next page

Table 1 continued

Poly(co-Glycolic) acid (PLGA)	Dimethyl Carbonate (DMC)	Tethered Pyro-Electrohydrodynamic 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 $5.5x10^7$ V/m **x-y stage velocity:** *Not determined* **Fiber Diameter:** $304.7nm$ **Distance between adjacent fibers:** *Not determined*	[20]
Poly(ethylene oxide) (PEO) with Tetrabutylammonium tetrafluoroborate (TBF) and SU-8 2002	N,N Dimethylformamide (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*	[21]

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Table 1 continued

Poly(ethylene oxide) (PEO)	Water:Ethanol (3:2)	Suspension NFES	**Solution Concentration:** $14 wt\%$ PEO **Nozzle:** stainless steel needle (25 G) with inner diameter of $0.25 mm$ **Solution deposition rate:** $3 nL/s$ **Nozzle-to-substrate distance:** between 0.5 and $10 mm$ with $0.5 mm$ increments **Substrate composition:** Planar silicon electrodes **Applied voltage:** $1.6 kV$ **x-y stage velocity:** 50, 150, and $250 mm/s$ **Fiber Diameter:** $300 nm$ **Distance between adjacent fibers:** 0.1 and $0.5 mm$	[22]
Poly(ethylene oxide) (PEO)	Deionized water		**Solution Concentration:** $10 wt\%$ PEO **Nozzle:** 32G metal needle **Solution deposition rate:** (Jet impact speed of $5 mm/s$) **Nozzle-to-substrate distance:** $0.5 mm$ **Substrate composition:** p-type silicon wafer **Applied voltage:** $400 V$ **x-y stage velocity:** $5 mm/s$ **Fiber Diameter:** **Distance between adjacent fibers:** $50 \mu m$	[23]

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3. Polymer Solution and Process Parameters

4. Applications

5. Fiber Characterization

6. Conclusion

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