

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

Antonio Osamu Katagiri Tanaka, Héctor Alán Aguirre Soto

Abstract

Near-field electrospinning (NFES) have demonstrated to be one of the top techniques for the fabrication of nano and micro fibers with accurate spatial control. In the attempt to create NFES has suffered a number of variations

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One-dimensional (1-D) nanostructures have attracted enormous research interest due to their unique physicochemical properties and wide application potential. These 1-D nanofibers are being increasingly applied to biomedical fields owing to their high surface area-to-volume ratio, high porosity, and the ease of tuning their structures, functionalities, and properties. Many biomedical nanofiber reviews have focused on tissue engineering and drug delivery applications but have very rarely discussed their use as wound dressings. However, nanofibers have enormous potential as wound dressings and other clinical applications that could have wide impacts on the treatment of wounds. Herein, the authors review the main fabrication methods of nanofibers as well as requirements, strategies, and recent applications of nanofibers, and provide perspectives of the challenges and opportunities that face multifunctional nanofibers for active therapeutic applications.

Near field electrospinning is one of the leading techniques in accurate placement of nanofibers. This technique has evolved from using AFM tips to supply a limited volume of solution for electrospinning to nozzle-based system where a continuous stream of solution can be extruded.

The precision and accuracy of the fiber deposition has also vastly improved from simple formation of oriented fibers on a collector to precise deposition of the fiber at a specific point. Despite the progress, several intrinsic limitation or characteristic of near-field electrospinning still needs to be noted when employing this technique.

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

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1. Introduction

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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 <i>wt%</i> 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 <i>V</i> and dispensed at 200-400 <i>V</i> x-y stage velocity: $10\text{-}40mm/s$ Fiber Diameter: $50\text{-}425nm$ Distance between adjacent fibers: <i>Not determined</i>	[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 process	NFES 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: SiO ₂ /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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<i>Table 1 continued</i>				
	Poly(ethylene oxide) (PEO)	Water	Scanning Tip Electrospinning and NFES	<p>Solution Concentration: 7wt% PEO [3]</p> <p>Nozzle: Needle outer diameter of 200μm and inner diameter of 100μm</p> <p>Solution deposition rate: 0.1$\mu L/h$</p> <p>Nozzle-to-substrate distance: 500μm</p> <p>Substrate composition: <i>Not determined</i></p> <p>Applied voltage: polymer jet initiated at 1.5 kV and dispensed at 600V</p> <p>x-y stage velocity: 120mm/s</p> <p>Fiber Diameter: 709\pm131nm; 49-74nm when applied voltage is 800V</p> <p>Distance between adjacent fibers: <i>Not determined</i></p> <p>Notes: 108m yield in 15min with a fiber diameter of 709\pm131nm</p>
4	Poly(vinylidene fluorid) (PVDF)	N,N Dimethyl-formamide (DMF)	Helix Electrohydrodynamic Printing (HE-printing)	<p>Solution Concentration: 1.8g PVDF in 4.1g of DMF and 4.1g of acetone. The resulting concentration is 18% PVDF. [4]</p> <p>Nozzle: Needle outer diameter of 510μm and inner diameter of 260μm</p> <p>Solution deposition rate: 400nL/min</p> <p>Nozzle-to-substrate distance: 10-50mm</p> <p>Substrate composition: Poly(dimethylsiloxane) (PDMS) on Ecoflex</p> <p>Applied voltage: 1.5–3kV</p> <p>x-y stage velocity: 0-400mm/min</p> <p>Fiber Diameter: about 1.5-3μm</p> <p>Distance between adjacent fibers: <i>Not determined</i></p>

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<i>Table 1 continued</i>				
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 500 μm to 2mm Substrate composition: <i>Not determined</i> Applied voltage: 8.0-10.0kV x-y stage velocity: 10mm/s Fiber Diameter: 5-50 μm Distance between adjacent fibers: 250 μm	[5]
Poly(ethylene oxide) (PEO)	Distilled water	Electrohydrodynamic Writing or Mechano-electrospinning (MES)	Solution Concentration: 6wt% PEO Nozzle: <i>Not determined</i> Solution deposition rate: 1200nL/min Nozzle-to-substrate distance: 7.5mm Substrate composition: <i>Not determined</i> 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: 5 μm	[6]

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<i>Table 1 continued</i>				
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 μ 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 μ m Distance between adjacent fibers: 5.13 \pm 6.67 μ 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 μ m Solution deposition rate: 14 nL/min Nozzle-to-substrate distance: 750 μ 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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<i>Table 1 continued</i>				
Poly(9-Vinyl Carbazole) (PVK)	Styrene	Typical process	NFES	Solution Concentration: 3.96wt% PVK in styrene [9] Nozzle: Needle inner diameter of 100 μm Solution deposition rate: 500nL/min Nozzle-to-substrate distance: around 2.5mm Substrate composition: Si/SiO ₂ Applied voltage: 3-4kV x-y stage velocity: 13.3cm/s Fiber Diameter: 289.26 \pm 35.37nm Distance between adjacent fibers: 50 μm Notes: 15m yield in 2min
Polystyrene (PS)	1,2,4-Trichloro benzene	Electrohydrodynamic (EHD) jet printing		Solution Concentration: 1 to 5wt% PS [10] Nozzle: Glass nozzle inner diameter of 2 μm and outer diameter of 2.66 μm 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 60-170 μm Distance between adjacent fibers: <i>Not determined</i>
Poly(ethylene oxide) (PEO)	<i>Not determined</i>	Typical process	NFES	Solution Concentration: 3wt% PEO [11] Nozzle: <i>Not determined</i> Solution deposition rate: <i>Not determined</i> Nozzle-to-substrate distance: 500 μm Substrate composition: Si Applied voltage: 1000V x-y stage velocity: 20cm/s Fiber Diameter: 300nm Distance between adjacent fibers: 25 μm

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<i>Table 1 continued</i>				
Poly(ethylene oxide) (PEO)	Distilled water		Multinozzle NFES	Solution Concentration: 5wt% [12] Nozzle: four-nozzle and six-nozzle array with needle spacing changes from 1.5mm to 3.5mm Solution deposition rate: 1-3 μ 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 μ m Distance between adjacent fibers: 3-5 mm
Poly(ethylene oxide) (PEO)	Distilled water		Multinozzle NFES	Solution Concentration: 5wt% [13] 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 μ 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 μ m

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<i>Table 1 continued</i>				
Poly(ethylene oxide) (PEO)	Distilled water		Multinozzle NFES	<p>Solution Concentration: 5 wt% [14]</p> <p>Nozzle: Dual-28G-needle array with needle inner diameter of 180μm and outer diameter of 360μm; with needle spacing changes of 2.0mm</p> <p>Solution deposition rate: 0.2μL/min</p> <p>Nozzle-to-substrate distance: 4.0mm</p> <p>Substrate composition: chromium-plated glass</p> <p>Applied voltage: 2.5kV</p> <p>x-y stage velocity: 20mm/s</p> <p>Fiber Diameter: Not determined</p> <p>Distance between adjacent fibers: 2.3002-2.7224mm</p>
Poly(ethylene oxide) (PEO)	Not determined	determined	Typical process	<p>NFES</p> <p>Solution Concentration: 2wt% [15]</p> <p>Nozzle: G30 needle with inner diameter of 0.15mm</p> <p>Solution deposition rate: Not determined</p> <p>Nozzle-to-substrate distance: 1-3mm</p> <p>Substrate composition: Silicon</p> <p>Applied voltage: 1250V</p> <p>x-y stage velocity: Not determined</p> <p>Fiber Diameter: Not determined</p> <p>Distance between adjacent fibers: 20μm</p>

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<i>Table 1 continued</i>				
Gelatin (porcine skin)	Acetic and Acetate	Acid Ethyl	Typical process	NFES
Solution Concentration: 11wt% gelatin, 30wt% wa- ter, 35.4wt% acetic acid, 23.6wt% ethyl acetate Nozzle: 19G needle tip with outer diameter of 1.08mm Solution deposition rate: <i>Not determined</i> Nozzle-to-substrate distance: 1.25mm Substrate composition: Poly(Dimethylsiloxane) (PDMS) films Applied voltage: 1000V x-y stage velocity: <i>Not determined</i> Fiber Diameter: around 2-3 μ m Distance between adjacent fibers: 40 μ m				
Poly(ethylene ox- ide) (PEO)	Water/Ethanol (v/v = 60/40)		Typical process	NFES
Solution Concentration: PEO concentrations of 16% adn 18% Nozzle: 40 μ 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 μ m Distance between adjacent fibers: <i>Not determined</i>				

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<i>Table 1 continued</i>			
Poly(ethylene oxide) (PEO)	Water/Ethanol (v/v = 3/1)	Electrohydrodynamic Direct-Write (EDW)	Solution Concentration: 14wt% PEO [18] Nozzle: Stainless needle with inner diameter of 210 μm and outer diameter of 400 μm 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: 15-35 μm Distance between adjacent fibers: 70 μm
Poly(ethylene oxide) (PEO)	Deionized water	Mechano-Electrospinning	Solution Concentration: 3wt% PEO [19] Nozzle: Stainless steel nozzle with inner diameter of 160 μm and outer diameter of 310 μm 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 \pm 32 to 214 \pm 27nm Distance between adjacent fibers: Not determined

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<i>Table 1 continued</i>				
Poly(co-Glycolic acid (PLGA)	Dimethyl Carbonate (DMC)	Tethered Electrohydrodynamic Spinning (TPES)	Pyro-	<p>Solution Concentration: <i>Not determined</i> [20]</p> <p>Nozzle: nozzle-free</p> <p>Solution deposition rate: The drop reservoir is placed directly on a flat substrate</p> <p>Nozzle-to-substrate distance: Taylor's cone is focused and put in direct contact with the collector</p> <p>Substrate composition: Poly(tetrafluoroethylene) (PTFE) coated glass slide</p> <p>Applied voltage: pyro-electric field of between 2.7×10^7 V/m and 5.5×10^7 V/m</p> <p>x-y stage velocity: <i>Not determined</i></p> <p>Fiber Diameter: $304.7nm$</p> <p>Distance between adjacent fibers: <i>Not determined</i></p>
Poly(ethylene oxide) (PEO) with Tetrabutylammonium tetrafluoroborate (TBF) and SU-8 2002	N,N-Dimethylformamide (DMF)	Typical process	NFES	<p>Solution Concentration: SU-8/PEO/TBF blend with 0.75wt% PEO, 1wt% TBF; the blend is diluted with 30vol% DMF [21]</p> <p>Nozzle: needle inner diameter of $533\mu m$ and outer diameter of $710\mu m$</p> <p>Solution deposition rate: <i>Not determined</i></p> <p>Nozzle-to-substrate distance: <i>Not determined</i></p> <p>Substrate composition: Brass disk with a diameter of $38mm$</p> <p>Applied voltage: 980V</p> <p>x-y stage velocity: <i>Not determined</i></p> <p>Fiber Diameter: <i>Not determined</i></p> <p>Distance between adjacent fibers: <i>Not determined</i></p>

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<i>Table 1 continued</i>			
Poly(ethylene oxide) (PEO)	Water:Ethanol (3:2)	Suspension NFES	<p>Solution Concentration: 14wt% PEO [22]</p> <p>Nozzle: stainless steel needle (25 G) with inner diameter of 0.25mm</p> <p>Solution deposition rate: 3nL/s</p> <p>Nozzle-to-substrate distance: between 0.5 and 10mm with 0.5mm increments</p> <p>Substrate composition: Planar silicon electrodes</p> <p>Applied voltage: 1.6kV</p> <p>x-y stage velocity: 50, 150, and 250mm/s</p> <p>Fiber Diameter: 300nm</p> <p>Distance between adjacent fibers: 0.1 and 0.5mm</p>
Poly(ethylene oxide) (PEO)	Deionized water		<p>Solution Concentration: 10wt% PEO [23]</p> <p>Nozzle: 32G metal needle</p> <p>Solution deposition rate: (Jet impact speed of 5mm/s)</p> <p>Nozzle-to-substrate distance: 0.5mm</p> <p>Substrate composition: p-type silicon wafer</p> <p>Applied voltage: 400V</p> <p>x-y stage velocity: 5mm/s</p> <p>Fiber Diameter:</p> <p>Distance between adjacent fibers: 50μm</p>

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3. Polymer Solution and Process Parameters

4. Applications

5. Fiber Characterization

6. Conclusion

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