Solution Blow Spinning: A New Method to Produce Micro- and Nanofibers from Polymer Solutions

Eliton S. Medeiros,^{1,2} Gregory M. Glenn,¹ Artur P. Klamczynski,¹ William J. Orts,¹ Luiz H. C. Mattoso²

¹Bioproduct Chemistry and Engineering, Western Regional Research Center, United States Department of Agriculture, Agricultural Research Service, Albany, California 94710 ²Laboratório Nacional de Nanotecnologia para o Agronegócio, Embrapa Instrumentação Agropecuária,

R. XV de Novembro, 1452, São Carlos, SP 13560-970, Brazil

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ABSTRACT: A solution blow spinning technique was developed using elements of both electrospinning and melt blowing technologies as an alternative method for making non-woven webs of micro- and nanofibers with diameters comparable with those made by the electrospinning process with the advantage of having a fiber production rate (measured by the polymer injection rate) several times higher. The diameters of fibers produced ranged from 40 nm for poly(lactic acid) to several micrometers for poly(methyl methacrylate). This solution blow spinning method uses a syringe pump to deliver a polymer solution to an apparatus consisting of concentric nozzles whereby the polymer solution is pumped through the inner nozzle while a constant, high velocity gas flow is sustained through the outer nozzle. Analysis of the process showed that pressure difference and shearing at the gas/solution interface jettisoned multiple strands of polymer solution towards a collector. During

INTRODUCTION

Nanofiber production technology has gained wide interest because of the unique properties the fibers possess compared to larger diameter fibers made of the same material.^{1–3} Decreasing the diameter of fibers to the nanoscale markedly increases the surface area to volume ratio, improves sound and temperature insulation, increases liquid holding capacity, and changes texture and appearance.^{4–7} Nanofibers hold promise for medical uses such as for tissue scaffolds,^{8–10} the controlled release of drugs and medications,^{4,8,11} and as wound dressing for skin regeneration.^{9,12} Important applications for micro- and nanofibers have also been identified in non-medical products including air filters, protective clothing, sensors, optical electronics, and as a matrix for immobilization of catalysts.^{4,6,13–18} flight, the solvent component of the strands rapidly evaporates forming a web of micro and nanofibers. The effect of injection rate, gas flow pressure, polymer concentration, working distance, and protrusion distance of the inner nozzle was investigated. Polymer type and concentration had a greater effect on fiber diameter than the other parameters tested. Injection rate, gas flow pressure, and working distance affected fiber production rate and/or fiber morphology. Fibers were easily formed into yarns of micro- and nanofibers or non-woven films that could be applied directly onto biological tissue or collected in sheets on a rotating drum. Indeed, virtually any type of target could be used for fiber collection. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2322–2330, 2009

Key words: solution blow spinning; electrospinning; melt spinning; nanofibers; microfibers; polymers

The expanded use of micro- and nanofibers in non-woven fiber sheets or webs is projected to further increase the \$14 billion market for nonwovens.¹⁶ The contribution of nanofibers to the growth of the nonwovens market will depend heavily on the development of new, affordable technologies, especially those that can scale-up to handle large commercial volumes. Currently, most non-woven micro- or nanofiber webs are produced by melt spinning, electrospinning, or by melt blowing. The melt spinning process involves drawing down extruded strands of melted polymer to reduce the fiber diameter and induce orientation of the polymer chains.¹⁶ One of the limitations of melt spun fiber technology is that it is restricted to viscoelastic materials that can withstand the stresses developed during the drawing process.⁴ The diameter of fibers made by this process is typically greater than 2 μ m.^{16,18} A variation of melt spinning that produces nanofibers is the islands-in-the-sea process where several individual strands of one polymer component are produced within a larger single strand of a second polymer component.⁷ The bicomponent strands are extruded

Correspondence to: L. H. C. Mattoso (mattoso@cnpdia. embrapa.br).

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Figure 1 Solution blow spinning setup.

at the same time using specialized equipment. A novel variation of this process that requires only conventional twin-screw extrusion equipment utilizes two immiscible polymers.¹⁹ The process relies on self-assembled polymer strands that form during extrusion and can be drawn down to form bundles of nanofibers.¹⁹ The main limitation with these techniques is the need for solvents to remove the sea component and the limited number of polymeric materials that can be processed in this manner.^{7,19}

Electrospinning of polymers was first reported several decades ago²⁰ with increasing intense research activity in recent years because of its adaptability to a wide range of polymeric materials and its consistency in producing very fine fibers.³ Although several techniques have been developed to make nanofibers, electrospinning seems to be the only method currently available with the potential to scale-up up to commercial nanofibers production.^{11,21} Electrospinning produces fiber diameters usually in the range of 40 nm to 2 µm.^{16,18} In the electrospinning process, an electrical charge is applied to a polymeric solution. At a point where the charged solution overcomes the forces of surface tension, a fluid jet erupts and travels to a grounded collector.^{1,3} The high surface to volume ratio of the jet facilitates rapid evaporation of the solvent component and results in fine fibers that are randomly formed and can be collected to form a non-woven web.^{1–3} Electrospinning has also been demonstrated with thermoplastic melts, negating the need to use solvents.^{3,22} However, the fiber thickness is typically greater than with polymer solutions and is affected by the melt viscosity.²² Even though electrospinning is considered the technique with the most potential for scaling to commercial production,²¹ low fiber

production efficiency is still considered its greatest limitation.¹⁹ Furthermore, the solvents that are compatible with the electrospinning process may be limited by their dielectric constant.¹

Solution spinning, which has been used industrially since the end of the 19th century, is one of the oldest methods of synthetic fiber production. This process includes wet spinning and dry spinning. In both methods, a viscous solution of polymer passes through fine holes of a spinneret forming a fiber. During the process, the solvent is removed and the fibers are subsequently drawn mostly to reduce fiber diameter and improve mechanical strength. In dry spinning, the polymer solution is pushed through a spinneret into a heated column called the spinning tower where the polymer solidifies through evaporation of the solvent. In wet spinning the spinneret is placed in a chemical bath in which the polymer is precipitated by dilution or chemical reaction to form fibers.²³

Melt blowing is another method for making nonwoven webs that has proven to be scalable for commercial production.^{20,24,25} It involves extruding molten polymer through a narrow orifice and into a stream of high velocity hot air.^{24–26} The drag of the hot air on the surface of the polymer melt causes the polymer, under optimal conditions, to elongate into a fiber. The process can be controlled to produce fibers ranging in diameters from 1 to 50 μ m.²⁰ Although traditional melt blowing is an efficient and economical process for commercial production of non-woven fiber products, it cannot produce fibers with diameters in the same size range as electrospun fibers and it is limited to thermoplastic polymers.⁷

In order to further expand the non-woven market, there is a need for alternative methods to fabricate



Figure 2 The nozzle design used in solution blow spinning consisted of an inner nozzle through which a polymer solution is pumped and an outer nozzle through which a high pressure (P_1) stream of gas passes. The nozzle geometry creates a region of low pressure around the inner nozzle (P_2) which helps draw the polymer solution into a cone.

non-woven webs of fibers with diameters in the same size scale as those produced during electrospinning. The objective of the present study was to describe a novel solution blow spinning process that uses elements of both the electrospinning and melt blowing technologies to make non-woven webs of micro- and nanofibers with fiber diameters similar to those produced by electrospinning. A further objective was to demonstrate the effect of various processing parameters on fiber diameter and morphology, all of which imply the relative ease of process scale-up.

EXPERIMENTAL

Materials

In order to validate this technique, some of the most common polymers used in electrospinning were tested. Poly(methyl methacrylate) (PMMA) (M_w = 1.2×10^5 g/mol), and polystyrene (PS) ($M_w = 1.9 \times$ 10^5 g/mol) were purchased from Sigma-Aldrich (St. Louis, MO). Poly(lactic acid), PLA, (Polylactide Resin 4042D, $M_w = 6.6 \times 10^4$ g/mol) was acquired from NatureWorks LLC (Minnetonka, MN). Polyaniline (PAni) was chemically synthesized according to the methodology described in the literature.^{27,28}

The solvents used included 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) and toluene which were purchased from Sigma-Aldrich (St. Louis, MO) and 2,2,2-trifluoroethanol (TFE) which was purchased from Alfa Aesar (Ward Hill, MA).

Methods

Solution blow spinning apparatus

The spinning apparatus used in this study consisted of a nozzle through which a polymer solution was injected into a stream of accelerated gas. The setup consisted of a source of compressed gas, such as nitrogen, argon and air, equipped with a pressure regulator, a 5-mL hypodermic syringe, a syringe pump (KD Scientific, USA) to control the injection rate (β) of the polymer solutions, a spraying apparatus that consisted of concentric nozzles, and a collector with a controllable rotation speed (Fig. 1). The collector was positioned at a fixed working distance from the nozzle. The spraying apparatus consisted of an inner and a concentric outer nozzle (Fig. 2). The polymer solution was pumped through the

Effect of Processing Variables on the Diameter of PMMA Fibers Made by the Solution Blow Spinning Technique								
β (μ L/min)	5	10	20	40	60	80	100	
Fiber Dia. (µm) (std)	1.22 (0.58)	1.77 (1.46)	2.26 (1.24)	1.39 (0.66)	1.41 (0.96)	1.52 (0.94)	1.01 (0.46)	
p (kPa)	69.0	138	276	414	517	. ,	. ,	
Fiber Dia. (µm) (std)	1.32 (0.72)	2.01 (1.13)	2.26 (1.24)	1.59 (0.83)	0.84 (0.43)			
WD (cm)	7.2	12.5	17	25				
Fiber Dia. (µm) (std)	1.57 (0.73)	2.57 (0.87)	2.76 (1.64)	2.48 (1.48)				
D (mm)	0	1	2	2.6	3	3.5		
Fiber Dia. (µm) (std)	3.46 (1.53)	2.43 (1.26)	3.85 (2.40)	2.98 (1.33)	3.04 (1.42)	3.37 (1.52)		
c (%)	5	10	15					
Fiber Dia. (µm) (std)	0.87 (0.39)	3.05 (1.71)	5.19 (2.54)					

TABLE I

Process variables include injection rate (β), gas pressure supplied to outer nozzle (p), working distance (WD, See Fig. 1), inner nozzle protruding distance (D), and polymer concentration (c).

	Elect	rospinning	Solution blow spinning	
Polymer/solvent	V (kV)	β (μ L/min)	p (kPa)	β (μL/min)
PS/Toluene	20	6.0	276	20
PLA/TFE	11	5.0	276	20
PLA : PAni (96 : 4 wt %)/HFP	20	6.0	276	20
PMMA/Chloroform	11	5.0	276	20

 TABLE II

 Experimental Conditions Used to Produce Electrospun and Solution Spun Fibers

inner nozzle and high velocity gas (pressurized) passed through the concentric outer nozzle (Fig. 2).

Experimental design

A series of experiments was performed by varying processing parameters using a polymer solution consisting of 10% PMMA in chloroform. Processing variables were tested to determine their effect on fiber thickness and morphology. Standard process conditions included an injection rate (β) of 20 μ L/min, gas (nitrogen) pressure (p) of 276 kPa, working distance of 20 cm, a distance (d) of 2 mm that the inner nozzle protruded beyond the outer nozzle, and a polymer concentration (c) of 10%. The effect of individual processing variables was studied using the standard conditions and changing only a single variable at a time. Processing variables are indicated in Table I. Fiber diameters were measured for a minimum of fifty fibers for each variable tested. Fiber morphology was determined by scanning electron microscope (SEM). Solutions (10%, w/v) of PLA and PS in TFE and toluene, respectively, were also prepared to demonstrate the solution blow spinning technique with a variety of polymer solutions.

Electrospinning

An electrospinning apparatus was set-up and conditions were optimized as previously described.^{29–31} Electrospinning and solution blow spinning techniques were compared by producing fibers from both techniques using the same polymer solutions. The experimental conditions used for electrospinning each polymer/solvent system are listed in Table II. In each experiment, polymer concentration (10%, w/v), working distance (20 cm), and rotation speed of the collector (800 rpm) were kept constant.

Solution blow spinning imaging

Strands of polymer solution that jettisoned from the inner nozzle were photographed with a rolling shutter camera (Model SI1280M-CL, Silicon Imaging, Inc., Costa Mesa, CA) at 450 frames per second. The camera was mounted on a stereomicroscope (Model MZ 16 F, Leica Microsystems Ltd, Heerbrugg, Switzerland) and focused on the inner nozzle tip. A white background and a fiber optic light source (Model MC500, Schott Instruments GmbH, Mainz, Germany) provided high contrast imaging. Polyaniline (PAni) was blended with PLA (4:96 wt %)



Figure 3 Microphotographs of solution spun fibers taken by a high speed camera. The low pressure region at the end of the inner nozzle formed the polymer solution into a cone (A). The region enclose by dashed lines was magnified and shown in (B–D). Jets of polymer solution formed near the cone tip can be seen streaming toward the collector (B–D).

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Figure 4 Solution spun polymer fibers collected on rotating drum also used for collecting electrospun fibers. (A) Photograph of a non-woven fiber mat deposited on the drum, and SEM pictures of (B) PMMA, (C) PS, and (D) PLA fibers. Note the partial alignment of the fibers as a consequence of the target rotation during spinning. Scale bar = $50 \mu m$ for (B) and $5 \mu m$ for (C) and (D).

in HFP to further enhance image contrast by making it darker and more opaque.

SEM characterization

Samples were spun onto a rotating collector and collected for SEM analysis. SEM samples were coated by gold sputtering for 45 s and analyzed for fiber morphology using a Hitachi Scanning Electron Microscope (Model S4700, Hitachi High-Technologies, Japan) operated at a voltage of 2 kV. Fiber thickness was measured on SEM images using specialized software (MeasureIT, version 5.0, Olympus Soft Imaging Solutions, GmbH).

RESULTS AND DISCUSSION

The melt spinning process proved to be a simple method of producing non-woven webs of microand nanofibers. This process makes use of Bernoulli's principle in which changes in pressure is converted into kinetic energy, i.e., as the high pressure gas stream (Fig. 2, P_1) exits the outer nozzle, the pressure quickly drops (Fig. 2, P_{atm}) increasing the kinetic energy of the stream and resulting in an

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increase in the velocity of the gas.^{32,33} This increase in velocity promotes a drop in pressure at the center of the jet (P_2), creating a driving force that is responsible for acceleration of the polymer solution. The high velocity gas also induces shearing at the gas/ solution interface that is responsible for deforming the polymer solution exiting the inner nozzle into a conical shape. When the surface tension is overcome by these forces, fine streams of polymer solution are jettisoned towards the collector. While in flight, solvent rapidly evaporates from these streams forming polymer fibers which accumulate on the collector.

When there was no gas flowing through the outer nozzle, a convex droplet of polymer solution typically was formed at the inner nozzle as illustrated in Figure 2 (dashed line). As gas flow to the outer nozzle was initiated, a region of low pressure was developed near the orifice of the inner nozzle (Fig. 2, P_2). The low pressure zone could be further verified by disengaging the injection pump and observing that polymer solution could be drawn through the inner nozzle by simply providing gas flow to the outer nozzle. The convex droplet of polymer solution was drawn into a cone shape as gas flow increased through the outer nozzle [Figs. 2 and 3(A)]. Photomicrographs revealed that strands of



Figure 5 Photographs showing the feasibility of spraying fibers directly on living tissues. (A) Non-woven PLA fiber mat coating a hand and (B) partial removal of mat showing that a coating had been formed over the skin.[Color figures can be viewed in the online issue, which is available at www.interscience.wiley.com]

polymer solution were jettisoned from the apical region of the cone towards the collector. The strands were consistently shot to the collector due to the combination of the low pressure zone and shearing at the solution/gas interface [Fig. 3(B–D)]. As with the electrospinning process,^{2,3} the high surface to volume ratio of the strands coupled with the high gas turbulence caused the solvent component to evaporate by the time the strand reached the collector.

Fibers made from polymer solutions of PMMA, PS, PLA, and PLA/PAni using the standard processing conditions mentioned earlier were readily formed into non-woven sheets (Fig. 4) by using a rotating collector as shown in Figure 1. Non-woven

webs were also easily and safely collected on a variety of targets including living tissue (Fig. 5). The solution blow spinning technique could prove extremely useful in medical applications where nonwoven webs can be applied directly to tissue cultures or to living tissue for a variety of medical procedures without applying, for example, high electric voltage, as in electrospinning. Moreover, by controlling the relative humidity of the surrounding environment³⁰ where the fibers are being formed and polymer concentration, it is possible to produce porous fibers with potential application in controlled drug release, for example (Fig. 6).

As with electrospinning, the solution blow spinning technique generated multiple fiber strands



Figure 6 Porous fibers produced by solution blow spinning. Scale bar = $5 \mu m$.



Figure 7 A: PMMA yarn several centimeters in length. B: SEM image of the yarn shows it is made up of long fibers with diameters ranging from 700 nm up to 2 μ m. Scale bar = 1 cm for A and 200 μ m for B (Inset 20 μ m).

which made it difficult to measure the continuous length of a given fiber. Nevertheless, some fibers isolated from the collector appeared to be several centimeters in length, and it is possible that some fibers could be much longer, depending on how they are collected. For example, continuous yarns several centimeters in length were made by positioning a barrier (e.g., a wire) in front of the nozzle apparatus to capture fibers as they flowed from the nozzle towards the collector (Fig. 7).

A direct comparison was made between polymersolution pairs that could be both electrospun and solution blow spun (which has fewer relative limitations). The diameters of solution blow spun and electrospun fibers made from 10% PMMA, PLA, PS and PLA/PAni blends were similar (Table III). The diameter of fibers produced by solution blow spinning of polymer solutions containing PMMA were also comparable to fiber diameters of electrospun PMMA fibers reported elsewhere.31 Solution spun PMMA fibers had diameters in the range of 1 to 7.8 µm using the standard processing conditions. However, fibers with diameters as small as 160 nm were produced for the same polymer concentration when spun at 517 kPa. Although the standard injection rate used for solution blow spinning was 20 μ L/min, an injection rate of up to 200 μ L/min was successfully tested. By comparison, the injection rate typically used for electrospinning is only 4-10 μ L/min, roughly more than an order of magnitude lower than that obtained for the solution blow spinning technique. Indeed, higher polymer

injection rates can be successfully used if a certain ratio between injection rate and gas pressure is maintained.

Variations in processing parameters affected fiber diameter, morphology, and ease of processing, although, interestingly, the injection rate did not have a pronounced effect on the mean fiber diameter (Table I). However, injection rates of 60 μ L/min and above resulted in fibers that were more consistent in thickness at much higher fiber production rates. Injection rates below 20 μ L/min did not adequately supply polymer solution to the nozzle and caused only intermittent flow at the nozzle.

The gas flow pressure (*p*) had a relatively small but significant effect on the fiber diameter. When gas pressure settings were too low, the fiber strands lost velocity and often did not have the force needed to reach the target. The fiber diameter increased as gas pressure increased from 69 to 276 kPa but then decreased with higher pressures. The fibers with the smallest diameters were produced at the highest pressure tested (Table I). As with electrospinning,³¹ there is a balance between gas pressure and polymer injection rate required for successful solution blow spinning. Elevating the gas pressure may lead to the formation of beaded fibers. However, by maintaining the pressure constant and adjusting the injection rate higher, the gas flow and injection rate once again become balanced and uniform, smooth fibers without beads can be obtained.

The working distance (WD) did not have a significant effect on fiber diameter (Table I). However, this

 TABLE III

 Comparison of Fiber Diameters for Solution and Electro Spun Micro and Nanofibers

	Range of fiber dia	meter (nm)	
Polymer/solvent	Solution blow spinning	Electrospinning	
PLA/TFE	80–260	90-220	
PLA:PAni/HFP	140-590	130-800	
PS/Toluene	220-4400	200-1800	
PMMA/Chloroform	1000-7800	1000-5000	



Figure 8 SEM of PLA nanofibers. Scale bar = 500 nm.

parameter was important in fiber morphology. When the WD was too short, the fibers did not have adequate opportunity to fully dry before reaching the collector and simply adhered to other fibers or, in extreme cases, they coalesced immediately with other fibers into a film.

The distance (d) the inner nozzle protruded beyond the plane of the outer nozzle had little effect on fiber diameter. However, processing was affected by d; when d was zero or greater than 3 mm, residue from the polymer solution formed around the nozzle opening or on the inner nozzle itself. The residue build-up required that the process be interrupted momentarily to remove the residue before resuming fiber spinning.

The concentration of polymer in solution had a significant and relatively large effect on fiber diameter. Increasing the polymer concentration increased the fiber diameter and conversely, fiber diameters were smallest when using lower polymer concentrations. For example, when a 5% PLA solution in TFE was spun (Fig. 8) using the standard conditions, fibers with diameters as small as 40 nm were produced. Because the driving forces for fiber formation in this technique are mostly physical ones, polymer type and concentration are key factors to determine rheological behavior and surface tension of the solutions and, therefore, fiber morphology.

CONCLUSIONS

The solution blow spinning technique is useful for making a range of micro- and nanofibers from polymer solutions. This technique produces fibers in the same size range as fibers made by electrospinning with greater potential for commercial scale-up. Relative to the electrospinning process, solution blow spinning can be performed at much higher injection rates (an order of magnitude higher). Furthermore, the solution blow spinning process does not require high voltage equipment or any electrically conductive collector, but it can be used to coat any type of material with a broader array of polymer solutions. It is not limited to solvents with a high dielectric constant, nor does it adversely affect heat or voltage sensitive polymers, such as proteins, etc. The solution blow spinning process may be extremely instrumental in efforts to further expand commercial production of non-woven polymer webs.

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