

Effect of Solvent on The Physical and Morphological Properties of Poly(Lactic Acid) Nanofibers Obtained by Solution Blow Spinning

Juliano Oliveira, Gláucia Silveira Brichi, José Manoel Marconcini, PhD,
Luiz Henrique Capparelli Mattoso, PhD, Gregory Melvin Glenn, PhD, Eliton Souto Medeiros, PhD

Universidade Federal da Paraíba, João Pessoa, Paraíba BRAZIL

Correspondence to:

Juliano Oliveira email: juliano.materiais@gmail.com

ABSTRACT

Solution blow spinning (SBS) is a simple, safe, and inexpensive alternative to electrospinning for making nanofibers from polymer solutions. However, since SBS is a relatively new technique, there is a general lack of information on polymer solutions and properties that affect fiber morphology and intrinsic properties. The present study reports the solution properties of poly (lactic acid) (PLA) dissolved in chloroform, dichloromethane, and dichloroethane at 4%, 6%, or 8% (w/v) and the properties of fibers made by SBS. In contrast to 4% polymer solutions, fibers made from 6% polymer solutions had few beads and diameters in the range of 120-320 nm. Diameters were greater (311-570 nm) for fibers made from 8% polymer solutions. Solvent evaporation rate affected the fiber porosity and formation. Hansen solubility parameters indicate that dichloromethane was the solvent most miscible with PLA. Fibers made with PLA in dichloromethane had the broader range in fiber diameter. Hansen parameters could be a valuable predictive tool for identifying highly miscible polymer/solvent systems for the SBS process. Polymer solutions with high viscoelasticity and viscosity were well suited for the SBS process. Fibers made from polymer solutions containing dichloromethane had lower crystallinity compared to fibers made from the other solvents.

Keywords: rheology, viscosity, biofibers, biocompatibility, crystallization

INTRODUCTION

Interest in nanofiber technology has grown steadily in recent years because of the unique properties of nanofibers and their potential application in tissue engineering, tissue scaffolds, wound dressing, and their use in control-release devices as well as various other industrial uses [1]. Nanofibers have surface areas 103 times greater than that of microfibers and typically demonstrate properties superior to larger

fibers or other forms of the parent material [2]. Micro- and nanofibers have been made using various techniques including drawing, [3] template synthesis, [4] phase separation, [5] self-assembly, and electrospinning [6]. Electrospinning is perhaps the most intensively studied technique for making nanofibers due to its simplicity and because it is considered to be one of the most promising technologies for scaling up to commercial production [7].

In electrospinning, although some systems use a polymer melt, [8] nanofibers of polymers are typically made by first dissolving the polymer in an appropriate solvent. The polymer solvent is slowly metered through a capillary tip where an electric field is applied causing a stream of polymer solution to jet towards a grounded collector. A polymer solution with sufficient chain overlap and entanglements is stretched and drawn due to mechanical stress induced by bending instability during flight. The diameter of the jet may be reduced several orders of magnitude before the solvent evaporates and the fiber reaches the collector [9, 10]. Over time, the collector becomes coated with a porous, nonwoven mat of fibers with extremely high surface area [10]. The nonwoven mats can be used for an array of products as described earlier.

Electrospinning has been used to create nanofibers from a wide array of polymers. The fiber diameters may range from several nanometers to greater than 1 μm [4]. Fundamental studies on various aspects of the electrospinning process have identified important parameters that affect the fiber size and morphology. These parameters may be divided into three groups including ambient conditions, processing conditions, and the intrinsic properties of the polymer solution (viscosity, polymer concentration, molecular weight of the polymer, elasticity, surface tension, solvent

volatility and electrical conductivity) [11-14]. The list of polymers and biopolymers used for making fibers by electrospinning has expanded in large part due to the growing knowledge of solvent/polymer properties. Of the many solvent and polymer solution properties studied, dipole moment and viscosity are of the most relative importance in determining fiber size and morphology of electrospun fiber [15-18].

The choice of solvent used to dissolve a polymer is important since solvents interact differently with polymers [19]. Some solvents may completely dissolve a polymer while others may only partially dissolve or swell a polymer [20]. The concept of a solubility parameter (δ) was introduced by Hildebrand and Scott [21]. They predicted that materials with similar δ values would be miscible [21]. However, while the δ parameter was valuable, there were solvents identified with very similar δ values that varied considerably in polymer miscibility [20]. Hansen parameters were later developed that have proven very useful in understanding and predicting miscibility of polymers and solvents. Hansen parameters essentially divide the total cohesive energy into three components including polar interactions (δ_p), hydrogen bonding (δ_h), and dispersive or van der Waals interactions (δ_d) [22]. Hansen parameters are based on the notion that "like dissolves like" and materials with similar δ_d , δ_p , and δ_h values are more miscible.

The solvent/polymer interaction can impact fiber processing by its effect on the viscosity and surface tension of a polymer solution [13, 23]. Eda and Shivkumar [24] observed the formation of solution jets during electrospinning and reported differences in the jet stability with different solvents. Solvent/polymer interaction can also affect the intrinsic properties of the finished fiber [13]. Giller et al [25] reported they were able to vary the crystal structure of Nylon 6 by varying the rate of solvent evaporation during electrospinning.

Recently, an alternative method referred to as solution blow spinning or SBS has been used to produce nanofibers similar to those produced by electrospinning [26]. The SBS method uses a specialized nozzle in which a polymer solution is forced through the inner nozzle at an appropriate rate. The formed droplet at the tip is stretched by a high speed stream of compressed gas to form a structure similar to the Taylor's cone [27]. When a critical gas pressure is exceeded, surface tension of the liquid is overcome and solution jets from the apex of the cone towards its target. Nanofibers are produced by the drag of a high speed gas stream across the surface of

the cone rather than by electric potential as with electrospinning. As these jets travel across the working distance, they are stretched by the pressure drop, while the solvent evaporates, obtaining submicrometric and nanometric polymer fibers. The SBS process is simple, scalable and provides an attractive alternative to electrospinning for making nanofibers of several important polymers including poly (lactic acid). Some polymer solution properties important in electrospinning such as viscosity may also be important in the SBS process while other properties such as conductivity are likely irrelevant.

There is a need to investigate the effect of fundamental properties of polymer solutions on SBS processing of nanofibers. The objective of the present study was to investigate the polymer solution properties using three common PLA solvents (chloroform, dichloromethane, dichloroethane) and determine their effect on the morphology, size, and intrinsic properties of nanofibers produced using SBS.

EXPERIMENTAL

Materials

Poly(lactic acid) (PLA, $M_n=75,000$ g/mol) was obtained from Biomater (São Carlos, Brazil). Chloroform ($CHCl_3$, CAS 67-66-3), dichloromethane (CH_2Cl_2 , CAS 75-09-02) and dichloroethane (CH_3CHCl_2 , CAS 75-34-03) were purchased from Synth Chemical (São Paulo, Brazil).

Polymer Solutions

Polymer solutions were made by carefully weighing dry PLA (80°C, 24 hrs) into 25 ml testtubes. Solvent was added to achieve final polymer concentrations of (4%, 6%, and 8%, w/v). Solvents used in making polymer solutions included chloroform, dichloromethane, and dichloroethane. The samples were stirred vigorously for several hours to ensure complete dissolution of the PLA.

Solution Blow Spinning (SBS)

Polymer solutions were spun into nanofibers by SBS as per earlier reports [26]. Briefly, a syringe pump (KD scientific, model 781100) was used to feed polymer solution ($120 \mu L \cdot min^{-1}$) through a central nozzle. Pressurized air was delivered through the concentric outer nozzle at a constant pressure (0.4MPa). The inner nozzle was positioned so it protruded 2 mm beyond the concentric outer nozzle. The distance between concentric nozzles was 0.5 mm and de working distance of 12 cm. The SBS parameters were kept constant for all experiments. Nanofibers produced by SBS were collected on a

rotating drum (200 rpm) to produce nonwoven fiber mats. Fiber mats were collected and stored in a desiccator until needed for further analysis.

Fiber Morphology

Microscopy

Morphology of solution blow spinning fibers was analyzed using scanning electron microscopy (SEM, Zeiss, model DSM960, Germany). Samples were prepared by cutting fiber mats with a razor blade and mounting on aluminum stubs using double-sided adhesive tape. Samples were then gold sputter coated (Balzers model SCD 050, Balzer Union AG, Balzers, Lichtenstein). Fiber diameters were measured with the aid of imaging software (Image J, National Institutes of Health, USA). Average fiber diameter and size distribution were determined from approximately 100 random measurements using micrographs representative of fiber morphology.

Solution Characterization

Rheology Experiments

Viscoelastic properties of the polymer solutions were measured at 20°C with a rheometer (MCR 301, Paar Physica, Messtechnik, Stuttgart, Germany). Concentric cylinder geometry (24 and 28 mm diameters) was used. First, the viscosity of the polymeric solutions was measured at 10-100 s⁻¹ shear rate. Subsequently, oscillatory single frequency time sweep curves were performed at a constant angular frequency and strain deformation of 10 rad·s⁻¹ and 1%. All measurements were done in triplicate, and their means were reported.

Evaporation Rate Experiments

The rate of evaporation of pure solvent and polymer solutions containing PLA (6%, w/v) was measured according to published methods with minor modifications [28]. In brief, polymer solutions were pipetted into 10 ml beakers. The beakers were kept in an enclosed chamber. Weight measurements were

recorded every 10 min. All tests were performed in triplicate at 23°C and 60% relative humidity. Evaporation rate for each polymer solution was determined from the slope of the weight loss curves for each solvent.

Fiber Analysis

X-ray Diffraction (XRD)

Nonwoven fibrous mats produced by SBS were collected on aluminum foil and deposited on a circular glass slides for analyses. The XRD patterns were recorded using a Shimadzu XRD-6000 X-ray diffractometer. Scans were carried out from 5 to 35° (2θ) at a scan rate of 2°/min using Ni filtered CuKα radiation (wavelength at 1.54 Å) at 50 kV and 20 mA.

Thermal Analysis

Differential scanning calorimetry (DSC, TA Instruments calorimetric analyzer, model Q100) was performed under nitrogen atmosphere, at a flow rate of 20 mL/min. The samples were heated from 0 to 180°C for all PLA fibers at a scanning rate of 10°C/min using aluminum pans.

RESULTS AND DISCUSSION

Fiber Morphology

Microscopy

The SBS process was successful in producing PLA fibers in the micro- and nanometer range (*Figures 1-3*). The fibers generally appeared to be more porous in fibers made from PLA/dichloromethane and PLA/chloroform than made from PLA/dichloroethane, probably due differences in the solvent evaporation rate (*Figures 1-3*). Fiber diameter measurements from SEM micrographs (*Table I*) indicate that fiber diameters ranged from approximately 100-550 nm. As with electrospinning, the polymer concentration was positively correlated with fiber diameter (*Table I*).

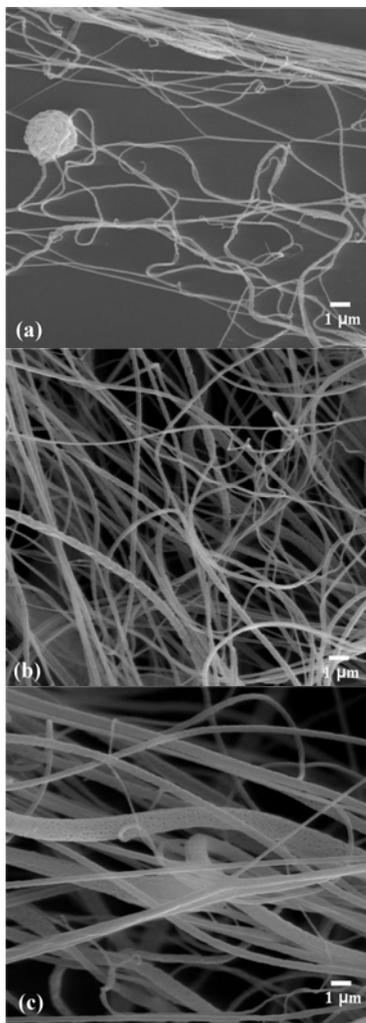


FIGURE 1. SEM of structures obtained by SBS of PLA solutions in chloroform at different concentrations: (a) 4%; (b) 6% and (c) 8% by weight.

Polymer solutions with only 4% PLA generally had poor fiber quality and contained polymer beads (Figure 1a, 2a, 3a). Fibers made from polymer solutions containing 4% PLA/dichloroethane also contained films probably due to the excess of dichloroethane (Figure 2a) that did not evaporate completely as fibers traveled from the nozzle to the collector, therefore forming a film. Polymer solutions with 6 and 8% PLA generally resulted in useful fibers with no polymer beads (Figure 1b, 1c, Figure 2b, 2c, Figure 3b, 3c). The one exception was the polymer solution containing 6% PLA in dichloroethane (Figure 3b). The correlation between fiber thickness and polymer concentration was nearly linear for the sample set containing dichloromethane (Table I). This linear behavior was also found in other polymer/solvent systems in our previous work [26]. Statistical analysis (ANOVA, 0.05 level) indicated a

significant relationship between fiber diameter and the choice of solvent as well as polymer concentration of the polymer solution.

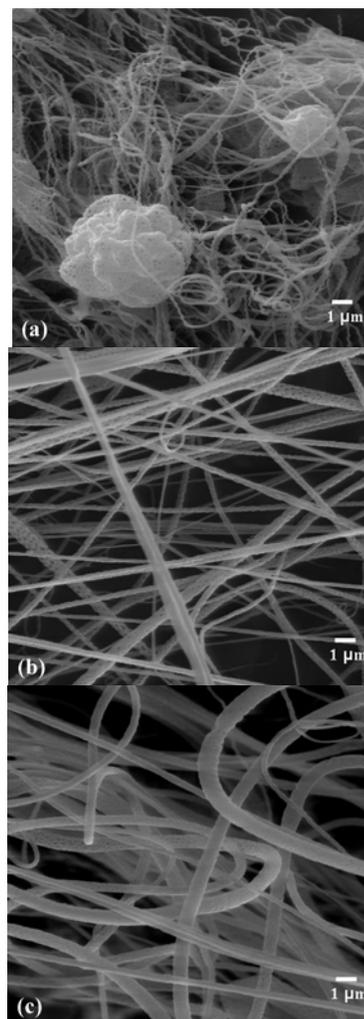


FIGURE 2. SEM of structures obtained by SBS of PLA solutions in dichloromethane at different concentrations: (a) 4%; (b) 6% and (c) 8% by weight.

TABLE I. Mean values for diameter measurements of fibers from solution blow spun polymer solutions of PLA (4%, 6%, 8%) in chloroform, dichloromethane, and dichloroethane. Values in parenthesis represent standard deviations.

Solvent	Concentration (%)	Mean diameter (nm)
Chloroform	4	150±54
	6	126± 98
	8	362±248
Dichloromethane	4	103±84
	6	316 ± 154
	8	567 ± 274
Dichloroethane	4	151 ± 46
	6	152 ± 52
	8	311 ± 132

Solution Characterization

A comparative plot of solvent evaporation rates for polymer solutions containing chloroform, dichloromethane, and dichloroethane revealed broad differences among the polymer solutions (Figure 4). Similar results were obtained for pure solvents (data not shown). The evaporation rates calculated from the slope of evaporation curves were -0.7, -0.9 and -0.2 %/min for the PLA solutions containing chloroform, dichloromethane, and dichloroethane, respectively. Evaporation rates are undoubtedly much higher in the SBS fibers due to the high surface area and the exposure to accelerated streams of air. Nevertheless, the relative evaporation rates of each solvent should be similar under SBS processing conditions.

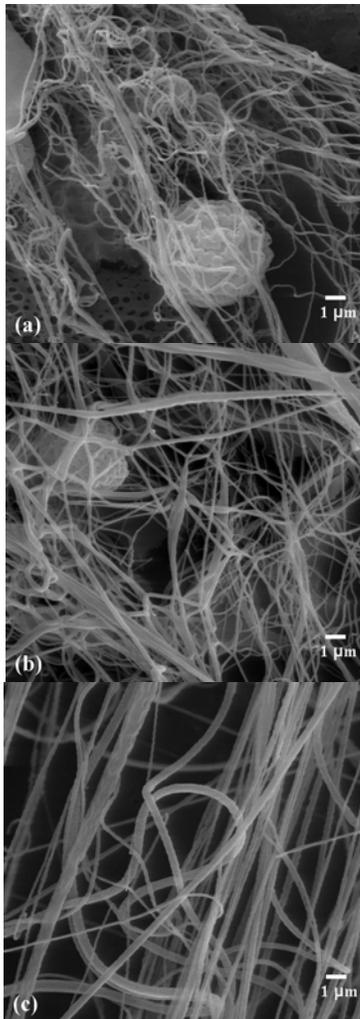


FIGURE 3. SEM of structures obtained by SBS of PLA solutions in dichloroethane at different concentrations: (a) 4%; (b) 6% and (c) 8% by weight.

Nearly all of the dichloromethane evaporated within 90 min and approximately 70% of the chloroform evaporated within 100 min (Figure 4). The higher rate of evaporation of dichloromethane solutions could account for the porous morphology observed in fibers made with 6 and 8% PLA solutions (Figure 2b, 2c).

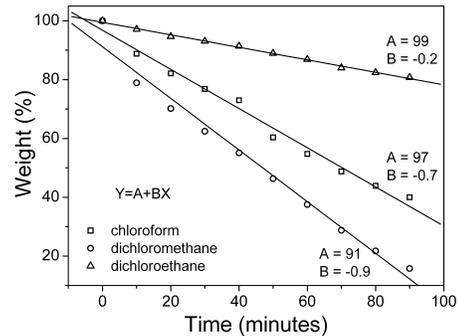


FIGURE 4. Evaporation rate of 6% wt poly(lactic acid) solutions in different solvents.

Previous work [26] has shown that a clad/core structure is formed during fiber formation due to rapid solvent evaporation at the surface of the jettisoned stream. During this time, the diameter of the nascent fiber is still decreasing. Further evaporation of solvent trapped in the core region creates internal vapor pressure that is relieved by the formation of small pores that form directly through the clad structure. This process is sensitive to relative humidity higher than 30%. It is likely that solvents with lower vapor pressures create lower internal pressure beneath the clad during the process of fiber formation. In the case of solvents with lower vapor pressure, the solvent may simply diffuse through the clad structure leaving no discernable pores.

TABLE II. Hansen parameters for PLA and solvents [20, 22].

System	δ_p	δ_h	δ_d
Poly(lactic acid)	9.9	6	18.6
chloroform	3.1	5.7	17.8
dichloromethane	6.3	6.1	18.2
dichloroethane	7.8	3.0	16.5

The dichloroethane had a much slower evaporation rate compared to the other two solvents. Even though some fibers and beads were formed with the 4% polymer solution, a film also formed due to the coalescence of wet fibers (Figure 3a). Polymer solutions made using solvents with slow evaporation rates would need a longer working distance to ensure that the fibers sufficiently dry before they reach the collector.

The viscometry data for each of the polymer solutions revealed differences in their solution properties (Figure 5). Plots of viscosity at different shear rates for PLA solutions indicate both a polymer concentration effect and a solvent effect (Figure 5). Viscosity curves for polymer solutions of PLA in chloroform and dichloroethane revealed a Newtonian behavior for each concentration of PLA tested (Figure 5a, 5c).

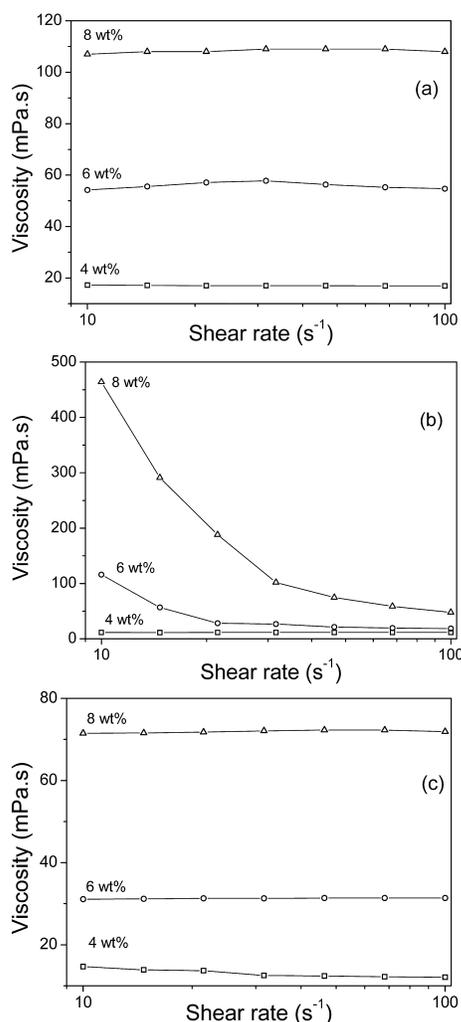


FIGURE 5. Viscosity of poly(lactic acid) solutions in (a) chloroform, (b) dichloromethane and (c) dichloroethane.

The viscosity of the PLA solutions increased with higher concentrations of PLA. However, viscosity was higher in chloroform PLA solutions compared to dichloroethane solutions of similar PLA concentration (Figure 5a, 5c).

Some possible reasons to explain differences in solution viscosity for polymer solutions containing different solvents can be found by studying Hansen

solubility parameters. The Hansen parameters for PLA, chloroform, dichloroethane, and dichloromethane are available from various published sources (Table II) [20, 22]. While the sum of all three Hansen parameters for chloroform and dichloroethane were similar, as mentioned earlier, the polymer solutions differed in viscosity (Figure 5a, 5c). The higher viscosity of PLA solvent solutions in chloroform (Figure 5) may be explained by the differences in the individual Hansen parameters. Chloroform had higher δd and δh indicating greater degree of hydrogen bonding and dispersive or van der Waals interactions with PLA compared to dichloroethane.

Dichloromethane had Hansen parameters most similar to PLA of the three solvents studied (Table II). The high viscosity of the PLA/dichloromethane polymer solutions at low shear rates could be due to a greater degree of polymer solubility and dispersion of PLA polymer chains in dichloromethane. The dichloromethane polymer solutions showed Newtonian behavior at 4% PLA (w/w) and pseudoplastic behavior at 6 and 8% polymer concentration (Figure 5b). Although the PLA/dichloromethane polymer solutions had relatively high viscosities at low shear rates, the viscosity dropped sharply as shear rates were increased demonstrating a shear-thinning behavior (Figure 5b). The shear thinning behavior of the dichloromethane solvent solutions could be due to the degree of chain entanglement in the polymer solution and the physicochemical interaction between the solvent and the PLA chains. The results support the notion that while a number of different solvents may solubilize PLA, they may each interact with PLA differently and create polymer solutions with unique properties that could impact SBS processing and thus fiber morphology.

Rheology

Rheological measurements were performed to determine whether the solvent choice affected the elastic (storage modulus) and viscous (loss modulus) behavior of the polymer solutions (Figure 6). The elastic modulus of the polymer solutions increased the most as polymer concentration increased from 6 to 8%, especially in the dichloroethane sample (Figure 6c). However, by analyzing the ratio of loss modulus and elastic modulus ($\tan\delta$) we notice a change only in solutions of dichloroethane.

The viscoelastic properties of a polymer solution are important in the electrospinning process [29]. Viscoelasticity of polymer solutions was identified as a key parameter in producing electrospun nanofibers

from polyethylene oxide [29]. High viscoelasticity enables a polymer solution to be stretched and drawn down in diameter as it travels to the collector [9]. The elastic component of the polymer solution containing dichloromethane was greater than that of the other polymer solutions (*Figure 6a-c*). This may be due to its greater miscibility in PLA and its interaction with the polymer chains as indicated by the Hansen parameters (*Table II*). Polymer solutions with low elasticity or very high $\tan\delta$ values resulted in fibers with a wide range in fiber diameters (compare *Figure 6 and Table II*). Polymer solutions with higher viscoelasticity yielded fibers with a more narrow size range in diameter and had no beads. While higher viscoelasticity can improve the SBS processing of polymer solutions, extremely high elastic solutions may produce fibers with a wide range in diameter due, in part, to the formation of ropes where two adjacent fibers come together to form a chord-type structure.

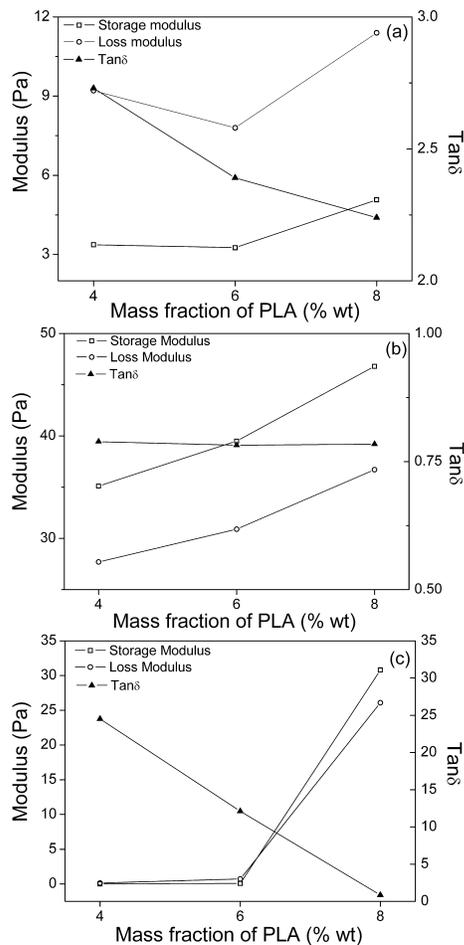


FIGURE 6. Rheological properties (10% of strain) of poly(lactic acid) solutions in (a) chloroform, (b) dichloromethane and (c) dichloroethane.

When a highly elastic polymer solution is spun, molecules are forced to align in the direction of gas flow to form fibers. However, aligned chains tend to relax in order to assume their original entangled and unaligned conformation. This recovery effect is more pronounced when highly elastic polymer solutions are spun. If the timescale is favorable, the elastic recovery may counteract fiber forming tendencies giving rise to fibers with a broad range of diameters.

Fiber Analysis

X-ray Diffraction (XRD)

Diffractograms from XRD scans on SBS fibers indicate very similar patterns for polymer solutions (6% PLA, w/v) in chloroform, dichloroethane, and dichloromethane. In all cases, the presence of crystalline phases α ($2\theta=13$ and 16°) and β ($2\theta=25^\circ$) poly(lactic acid) were identified. The R^2 values for the crystallization parameters based on the Lorentzian model were significant (*Table III*). The crystallization parameters for PLA fiber produced by SBS using the three solvents indicated little difference in the interplanar spacing. However, fibers made with polymer solutions containing dichloromethane had lower crystallinity (X) compared to SBS fibers made from chloroform or dichloroethane (*Table III*).

TABLE III. Crystallization parameters for fibers obtained by solution blow spinning polymer solutions of PLA (6% w/v) in chloroform, dichloromethane, and dichloroethane.

Solvent	Crystal size (nm)	Interplanar spacing (Å)	R^2
Chloroform	2.2	5.3	0.9
Dichloromethane	2.3	5.2	0.9
Dichloroethane	2.1	5.3	0.9

The smaller crystals (*Table III*) and lower crystallinity (*Table IV*) may be due to the slow evaporation rate of the dichloroethane (*Figure 4*) and the low elasticity of the solution (high value of $\tan\delta$) (*Figure 6*). The persistence of the dichloroethane in the fiber combined with the low solution elasticity could hinder crystal formation. Trace amounts of solvents in other polymer/solvent fiber systems may be affected by solvent persistence long after fiber formation [30].

Thermal Analysis

Differential calorimetry curves for the PLA fibers obtained by solution blow spinning polymer solutions made with three different solvents show characteristic temperatures and enthalpies for each sample (*Table IV*). The greatest differences in the thermal properties of the samples were the absence of

cold crystallization for the fibers made from polymer solutions containing dichloroethane and its highest crystallinity. We can observe the similar values of heat of fusion for all samples, then this difference in crystallinity can be associate chain orientation during SBS process for solutions of PLA/dichloromethane and PLA/chloroform. These facts indicate that the choice of solvent can affect chain orientation and in the crystallization process during fiber formation in SBS.

TABLE IV. Glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), heat of crystallization (ΔH_c), and heat of fusion (ΔH_m) for solution blow spun fibers made from polymer solutions of PLA (6%) in chloroform, dichloromethane, or dichloroethane.

Solvent	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)	X(%)
Chloroform	59	114	147	15.8	26.2	11
Dichloromethane	59	115	148	15.8	20.1	5
Dichloroethane	59	-	149	-	25.6	27

CONCLUSION

Solution blow spinning is an alternative technique to electrospinning for making fibers in the nanometer range. The selection of fiber/solvent systems is important since it not only affects fiber processing and fiber morphology, but it also can affect the intrinsic properties of the fiber such as crystallinity. PLA and dichloroethane had the less similar Hansen solubility parameters and lower solvent evaporation rate, and did not produced consistent fibers. Hansen solubility parameters and solvent evaporation rate could prove useful in predicting other solvent/polymer systems or solvent blends that could produce high quality nanoscale fibers.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from FINEP/MCT, CNPq (Process N° 474121/2011-9), CAPES, Embrapa/LNNA, and FAPESP funding agencies.

REFERENCES

[1] Loh, X.J., et al., *Controlled drug release from biodegradable thermoresponsive physical hydrogel nanofibers*. Journal of Controlled Release, 2010. 143(2): p. 175-182.

[2] Huang, Z.-M., et al., *A review on polymer nanofibers by electrospinning and their applications in nanocomposites*. Composites Science and Technology, 2003. 63(15): p. 2223-2253.

[3] Nakata, K., et al., *Poly(ethylene terephthalate) Nanofibers Made by Sea-Island-Type Conjugated Melt Spinning and Laser-Heated Flow Drawing*. Macromolecular Rapid Communications, 2007. 28(6): p. 792-795.

[4] Tao, S.L. and T.A. Desai, *Aligned Arrays of Biodegradable Poly(μ -caprolactone) Nanowires and Nanofibers by Template Synthesis*. Nano Letters, 2007. 7(6): p. 1463-1468.

[5] Zhao, J., et al., *Preparation, structure and crystallinity of chitosan nano-fibers by a solid-liquid phase separation technique*. Carbohydrate Polymers, 2011. 83(4): p. 1541-1546.

[6] Dong, H., S.E. Paramonov, and J.D. Hartgerink, *Self-Assembly of \pm -Helical Coiled Coil Nanofibers*. Journal of the American Chemical Society, 2008. 130(41): p. 13691-13695.

[7] Zhang, Y., et al., *Recent development of polymer nanofibers for biomedical and biotechnological applications*. Journal of Materials Science: Materials in Medicine, 2005. 16(10): p. 933-946.

[8] Dalton, P.D., et al., *Direct in Vitro Electrospinning with Polymer Melts*. Biomacromolecules, 2006. 7(3): p. 686-690.

[9] McKee, M.G., C.L. Elkins, and T.E. Long, *Influence of self-complementary hydrogen bonding on solution rheology/electrospinning relationships*. Polymer, 2004. 45(26): p. 8705-8715.

[10] Lee, K.H., et al., *Characterization of nano-structured poly([epsilon]-caprolactone) nonwoven mats via electrospinning*. Polymer, 2003. 44(4): p. 1287-1294.

[11] Wannatong, L., A. Sirivat, and P. Supaphol, *Effects of solvents on electrospun polymeric fibers: preliminary study on polystyrene*. Polymer International, 2004. 53(11): p. 1851-1859.

[12] Son, W.K., et al., *The effects of solution properties and polyelectrolyte on electrospinning of ultrafine poly(ethylene oxide) fibers*. Polymer, 2004. 45(9): p. 2959-2966.

[13] Veleirinho, B., M.F. Rei, and J.A. Lopes-da-Silva, *Solvent and concentration effects on the properties of electrospun poly(ethylene terephthalate) nanofiber mats*. Journal of Polymer Science Part B-Polymer Physics, 2008. 46(5): p. 460-471.

- [14] Shin, D.S., S.G. Lee, and W.S. Lyoo, Effect of solvents on the morphology of electrospun atactic polystyrene. *Polymers & Polymer Composites*, 2006. 14(8): p. 755-765.
- [15] Pattamaprom, C., et al., The influence of solvent properties and functionality on the electrospinnability of polystyrene nanofibers. *Macromolecular Materials and Engineering*, 2006. 291(7): p. 840-847.
- [16] Nirmala, R., et al., Effect of Solvents on High Aspect Ratio Polyamide-6 Nanofibers via Electrospinning. *Macromolecular Research*, 2010. 18(8): p. 759-765.
- [17] Kim, H.S., et al., Effect of Solvent on the Morphology of High Molecular Weight Poly(N-vinyl carbazole) Web Prepared by Electrospinning. *Polymers & Polymer Composites*, 2010. 18(8): p. 461-467.
- [18] Chuangchote, S., T. Sagawa, and S. Yoshikawa, Electrospinning of Poly(vinyl pyrrolidone): Effects of Solvents on Electrospinnability for the Fabrication of Poly(p-phenylene vinylene) and TiO(2) Nanofibers. *Journal of Applied Polymer Science*, 2009. 114(5): p. 2777-2791.
- [19] Qian, Y.F., et al., Electrospinning of Polymethyl Methacrylate Nanofibres in Different Solvents. *Iranian Polymer Journal*, 2010. 19(2): p. 123-129.
- [20] Abbott, S., Chemical compatibility of poly(lactic acid): A practical framework using Hansen solubility parameters, in *Poly(lactic acid) Synthesis, Structure, Properties, Processing, and Application*, R. Auras, et al., Editors. 2010, John Wiley and Sons, Inc.: Hoboken, New Jersey. p. 83-89.
- [21] Hildebrand, J.H., R. Scott, and D. (3rd ed.), *New York (1964). The Solubility of Nonelectrolytes 3rd ed.* 1964, Dover, New York.
- [22] Vay, K., S. Scheler, and W. Frieb, Application of Hansen solubility parameters for understanding and prediction of drug distribution in microspheres. *International Journal of Pharmaceutics*, 2011. 416(1): p. 202-209.
- [23] Wu, X.H., et al., Effect of solvent on morphology of electrospinning ethyl cellulose fibers. *Journal of Applied Polymer Science*, 2005. 97(3): p. 1292-1297.
- [24] Eda, G., J. Liu, and S. Shivkumar, Solvent effects on jet evolution during electrospinning of semi-dilute polystyrene solutions. *European Polymer Journal*, 2007. 43(4): p. 1154-1167.
- [25] Giller, C.B., et al., Effect of solvent evaporation rate on the crystalline state of electrospun Nylon 6. *Polymer*, 2010. 51(18): p. 4225-4230.
- [26] Medeiros, E.S., et al., Solution blow spinning: A new method to produce micro- and nanofibers from polymer solutions. *Journal of Applied Polymer Science*, 2009. 113(4): p. 2322-2330.
- [27] Oliveira, J.E., et al., Structural and Morphological Characterization of Micro and Nanofibers Produced by Electrospinning and Solution Blow Spinning: A Comparative Study. *Advances in Materials Science and Engineering*, 2013. 2013: p. 14.
- [28] Beverley, K.J., J.H. Clint, and P.D.I. Fletcher, Evaporation rates of structured and non-structured liquid mixtures. *Physical Chemistry Chemical Physics*, 2000. 2(18): p. 4173-4177.
- [29] Talwar, S., et al., Electrospun Nanofibers with Associative Polymer-Surfactant Systems. *Macromolecules*, 2010. 43(18): p. 7650-7656.
- [30] Nam, J., et al., Materials selection and residual solvent retention in biodegradable electrospun fibers. *Journal of Applied Polymer Science*, 2008. 107(3): p. 1547-1554.

AUTHORS' ADDRESSES

Juliano Oliveira
Glaúcia Silveira Brichi
José Manoel Marconcini, PhD
Luiz Henrique Capparelli Mattoso, PhD
Gregory Melvin Glenn, PhD
Eliton Souto Medeiros, PhD
 Universidade Federal da Paraíba
 Centro de Tecnologia
 João Pessoa, Paraíba 58051900
 BRAZIL