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Poly(lactic acid) fibers obtained by solution blow spinning: Effect of a greener solvent on the fiber diameter

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ABSTRACT: Poly(lactic acid) (PLA) fibers has been obtained by solution blow spinning (SBS) using different solvents, however most of them are toxic and can be dangerous to human health or cause harm to the environment. Therefore, this work aimed to evaluate the use of dimethyl carbonate (DMC), a greener solvent, on the production of PLA fibers by SBS using surface response analysis to evaluate and compare the influence of three solvents (chloroform, DMC, and 1,1,1,3,3,3-hexafluoro-2-propanol, HFP) in the average fiber diameter. Scanning electron microscopy (SEM) was used to analyze the fiber morphology and different ranges of fiber diameter was observed when varying the solvents (chloroform: 260–970 nm; DMC: 240–650 nm; and HFP: 220–470 nm). Regression analysis showed the polymer concentration was significant for all solvents and the air pressure was significant when using chloroform and HFP. Regardless of the air pressure, increasing the PLA concentration increased the average fiber diameters for all solvents. Chloroform and HFP indicated a tendency of reduction on the average fiber diameter when the air pressure was decreased, however this behavior was not observed for DMC. It was also observed that the standard deviation indicated to be more affected by the polymer concentration than by the air pressure. The results also indicated that lower surface tension and viscosity can reduce fiber thickness. All solvents showed to be feasible to produce PLA fibers by SBS and DMC can be used to produce PLA fibers with an affordable price using a greener process. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43379.

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INTRODUCTION

Poly(lactic acid) (PLA) is a bio-based thermoplastic polyester biodegradable, biocompatible, and compostable.[1,2] PLA belongs to the family of aliphatic polyesters made from α-hydroxyacids and the lactic acid (2-hydroxypropanoic acid) can be produced by bacterial fermentation of sugars obtained from renewable sources or by chemical process, however most part of commercial lactic acid is produced by fermentation of *Lactobacillus* strain.[2,3] PLA is one of the most studied biodegradable polymers and has generated great interest because of its wide range of applications,[3,4] such as medical,[5,6] packaging,[7] delivery systems,[8–10] textile,[11,12] and nanocomposites.[13–15]

The production of polymer nanofiber has increased interest because when the diameter of fibers is decreased to the nanoscale, the surface area to volume ratio significantly increases and properties are improved.[16] These unique properties lead these nanostructured polymer materials to a wider range of applications such as water filtration and adsorption processes.[17,18] PLA fibers have been produced by several process such as melt spinning,[11,19,20] electrospinning,[21–23] and more recently solution blow spinning (SBS).[16,24]

SBS is a technique developed to produce micro- and nano-scale fibers from polymer solutions using pressurized air in a specialized nozzle, combining principles of melt blowing, and

electrospinning.[16,24] The specialized nozzle consists in a nozzle through which a polymer solution is pumped and the pressurized air is supplied by a concentric outer nozzle. The pressurized air generates a driving force and when it overcomes the solution surface tension, the polymer solution is released towards a collector. During the flight, the solvent is evaporated and creates a non-woven structure.[24] Alternative to conventional SBS apparatus, commercial airbrushes have been successfully used to produce polymer fibers, which is based on the same principles.[25–28] Highly viscous liquid jets moving with a high speed relative to the surrounding gas experience lateral distributed force, which tends to increase bending perturbations. Recently, Sinha-Hay *et al.*[29] suggested a model using equations of the mechanics of free liquid jets to predict three-dimensional configurations of the jets as they are deposited onto a collector and to predict fiber-size distributions obtained under different conditions. The model considered polymer solution viscoelasticity, jet interaction with the surrounding high-speed air flow, solvent evaporation, and jet solidification and the results of predicted fiber-size distributions were consistent with the experimental data obtained.

Many studies have been made to evaluate the influence of the process parameters on the fiber morphology, such as polymer solution concentration, air pressure, feed rate, work distance, and distance between nozzles. Among these, polymer solution concentration and air pressure have been shown to be the most important parameters affecting fiber diameter. Besides, the polymer-solvent system is also very important, since the solution viscosity and surface tension greatly influences the SBS process.[17,30,31] PLA fibers obtained by SBS have been studied using different solvents such as chloroform and acetone mixtures,[17,31] 1,1,1,3,3,3-hexafluoro-2-propanol (HFP),[16,32] and 2,2,2-trifluoroethanol (TFE).[33] Many of these solvents have high toxicity level and are also included in the volatile organic compounds (VOCs) list. In this way, the aim of this work was to evaluate the use of dimethyl carbonate (DMC) as a solvent to produce PLA fibers by solution blow spinning and compare with other solvents (chloroform and HFP). DMC is a VOC exception with a very low Maximum Incremental Reactivity (MIR) value, which measures the reactivity of a chemical in the atmosphere to form ground-level ozone and smog. Low MIR values means to be a more environmentally-friendly chemical. The mathematical and statistical approach of response surface methodology (RSM) has been used to optimize formulation and process parameters for obtain nanofibers of several polymers such as poly(lactic acid),[17,34,35] poly(ethylene oxide),[36] poly(methylmethacrylate),[37] polyvinyl alcohol,[38] and starch.[39] There is however no published study using RSM to optimize the SBS process parameters to produce poly(lactic acid) nanofibers using greener solvent. Therefore, PLA fibers were obtained using three different solvents and varying two process conditions to evaluate the influence of these parameters on the average fiber diameter.

Table I. Experimental Design 3^2 to Analyze the Influence of Using Three Different Solvents (Chloroform, DMC, and HFP) in the Average Diameter of PLA Fibers Obtained by SBS

Experiment	PLA concentration (% w/v)	Air pressure (MPa)
1	8	0.2
2	8	0.4
3	8	0.6
4	10	0.2
5	10	0.4
6	10	0.6
7	12	0.2
8	12	0.4
9	12	0.6

EXPERIMENTAL

Materials

Solution blow spinning fibers were produced using poly(lactic acid) (PLA, $M_n = 125{,}000$ g mol^{-1}) obtained from Biomater (São Carlos, Brazil). Polymer solutions were prepared with three different solvents: chloroform from Synth (6806), dimethyl carbonate (DMC) from Sigma-Aldrich (D152927), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) from Sigma-Aldrich (105228). All solvents were used as received.

Table II. Average Diameters (nm) of PLA Fibers Obtained by SBS Using Different Solvents and Process Conditions

		Solvent		
PLA concentration (% w/v)	Air pressure (MPa)	Chloroform	DMC	HPF
8	0.2	345 ± 164	255 ± 67	320 ± 131
	0.4	326 ± 161	308 ± 105	311 ± 138
	0.6	263 ± 116	214 ± 81	219 ± 95
10	0.2	396 ± 207	531 ± 170	348 ± 108
	0.4	462 ± 215	240 ± 93	341 ± 148
	0.6	278 ± 165	470 ± 193	335 ± 156
12	0.2	967 ± 507	366 ± 170	474 ± 181
	0.4	490 ± 225	574 ± 203	439 ± 168
	0.6	545 ± 265	647 ± 288	373 ± 94

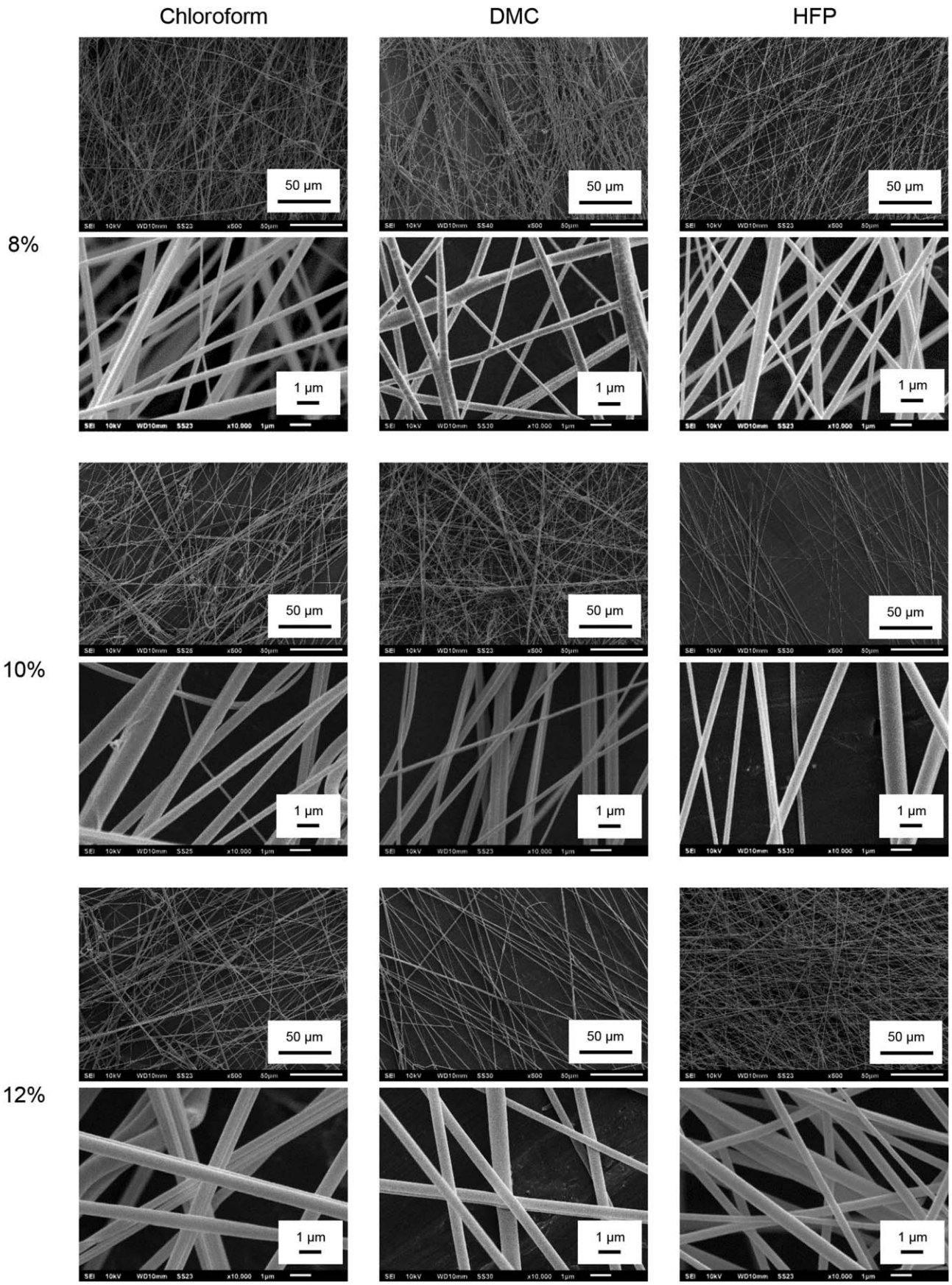

Figure 1. SEM micrographs of PLA fibers obtained by SBS using different solvents and polymer solution concentrations. All micrographs showed were using 0.4 MPa of air pressure.

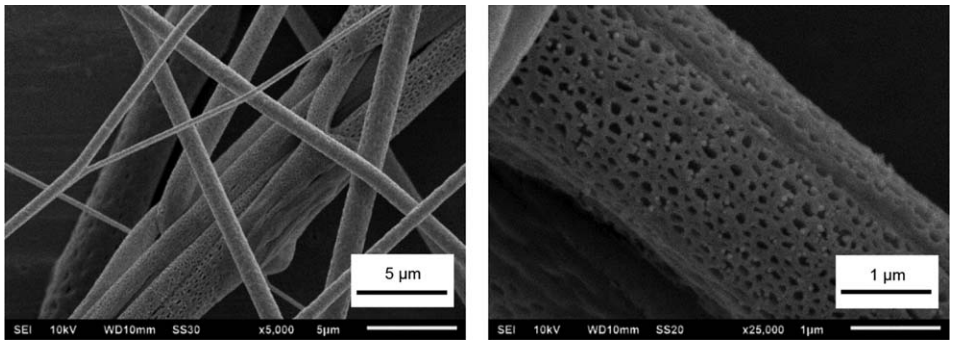

Figure 2. SEM micrographs of PLA fibers porous surface obtained by SBS using chloroform as solvent. Polymer concentration of 12% w/v and air pressure of 0.2 MPa.

Preparation of Polymer Solutions

Polymer solutions were prepared into a Falcon flask tube where the PLA and the solvent were disposed according to the proportions to make solutions according with the experimental designs (Table I) and maintained under vigorous stirring for several hours until complete polymer dissolution. After dissolution, the solution was transferred into a 10 mL glass syringe and connected to a SBS apparatus.

Characterization of the Solutions

The surface tension of the solutions was measured using a Krüss K100 Force Tensiometer with a platinum plate under ambient conditions. A roughened platinum plate was lowered into the polymer solution, the immersion depth of the plate was set at 2 mm, and the measurements were done with a detection speed of 10 mm min^{-1} and sensitivity of 0.005 g. The viscosity of the solutions was measured using a rheometer (TA Instruments, model AR2000) with concentric cylinder geometry at 25 °C and shear rate of 1 to 100 s^{-1}.

Experimental Design

Three 3^2 experimental designs was delineated to analyze the influence of three different solvents (chloroform, DMC, and HFP) on the average fiber diameter (response variable) of PLA fibers obtained by SBS. For each design, a different solvent was used varying two factors in three levels (X_1 = polymer solution concentration: 8, 10, and 12% w/v; X_2 = air pressure: 0.2, 0.4, and 0.6 MPa), totalizing 9 runs for each solvent. The 3^2 experimental designs are described in Table I.

Solution Blow Spinning (SBS)

SBS apparatus consisted in a specialized nozzle through which a PLA solution (8, 10, and 12% w/v) was pumped and the pressurized air was supplied by a concentric outer nozzle. The inner nozzle was positioned so it protruded 2 mm beyond the concentric outer nozzle. The distance between the concentric nozzles was 0.5 mm. The feed rate of PLA solution was controlled with a syringe pump (KD Scientific, model 781100, Holliston) which was fixed in 1.8 μL h^{-1}. The pressurized air was controlled with a pressure regulator, which varied according to the experiment (0.2, 0.4, and 0.6 MPa). The pressurized air generates a driving force and when it overcomes the polymer solution surface tension, it carried the polymer solution through a rotating collector with a controlled speed of 180 rpm. The collector was positioned at a fixed working distance from the nozzle of 10 cm. During the flight, the solvent was evaporated producing the polymer fibers.

Morphological Characterization

Scanning electron microscopy (SEM) was used to analyze PLA fiber morphology. For that, a Carl Zeiss DSM 940-A scanning electron microscope was used after gold coating. Fiber diameters were measured with the aid of ImageJ software (National Institutes of Health). For each experiment, average fiber diameter, standard deviation, and normal distribution were determined from at least 100 random measurements.

RESULTS AND DISCUSSION

PLA fibers were obtained by SBS using three different solvents (chloroform, DMC, and HFP). For each solvent a 3^2 experimental design was delineated varying two factors in three levels (X_1 = polymer solution concentration: 8, 10, and 12% w/v; X_2 = air pressure: 0.2, 0.4, and 0.6 MPa) to evaluate the influence of these parameters on the average fiber diameter (response variable) (Table I). Samples of these fibers were produced and characterized by scanning electron microscopy (SEM) and the average diameter was obtained (Table II). For the experimental designs, a significance level (α) of 0.05 was chosen. Regression models with linear and quadratic terms and interaction between factors were tested. The assumptions about the errors in regressions were checked and a transformation in diameter data was necessary to stabilize the variance for chloroform. Thus, for all solvents the polymer solution concentration was significant for the average fiber diameter and when HFP and chloroform were used the air pressure showed to be significant. The models of chloroform, DMC, and HFP are described in reduced eqs. (1–3), respectively, considering only the significant factors, where [P] and [A] means polymer solution concentration and air pressure, respectively. The model adjustment was expressed by the determination coefficient (R^2), which shows the percentage of response variability that can be explained by the model. The models of chloroform, DMC and HFP showed R^2 of 78%, 53%, and 90%, respectively. Therefore, the HFP indicates to be the best model that fits the data.

$$\text{Average diameter (Chloroform)} = (0.005379 - 0.000379*[P] + 0.002316*[A])^{-1} \quad (1)$$

$$\text{Average diameter (DMC)} = -273.841 + 67.450*[P] \quad (2)$$

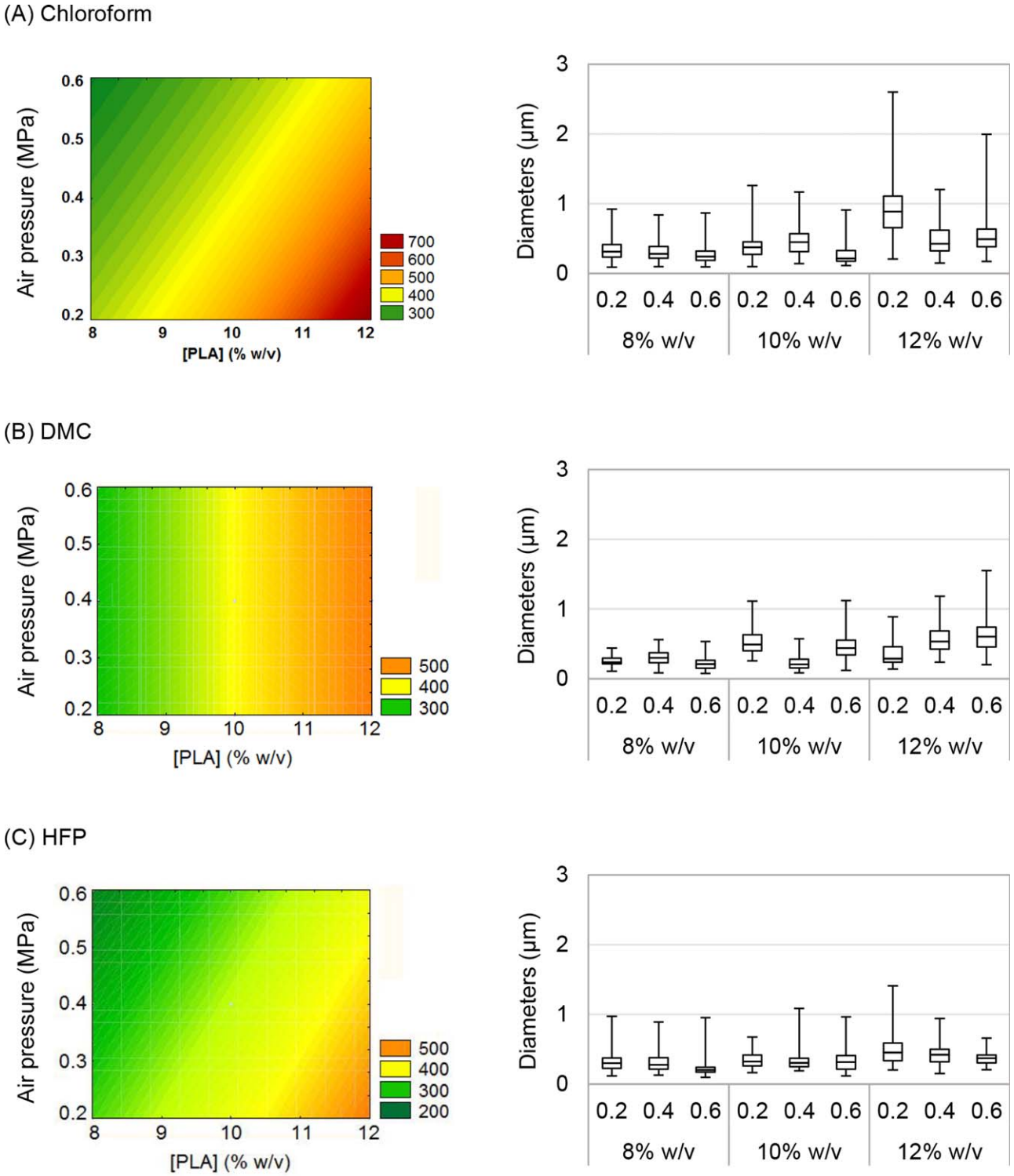

Figure 3. Response surfaces of average diameter (nm) of PLA fibers obtained by SBS using different process conditions and solvents: (A) chloroform, (B) DMC, and (C) HFP (left side). Boxplot of PLA fiber diameter: the horizontal line in the middle of each boxplot shows the median values. Margins of the box give 25% and 75% quartiles and bars outside box correspond to the maximum and minimum data points (right side). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

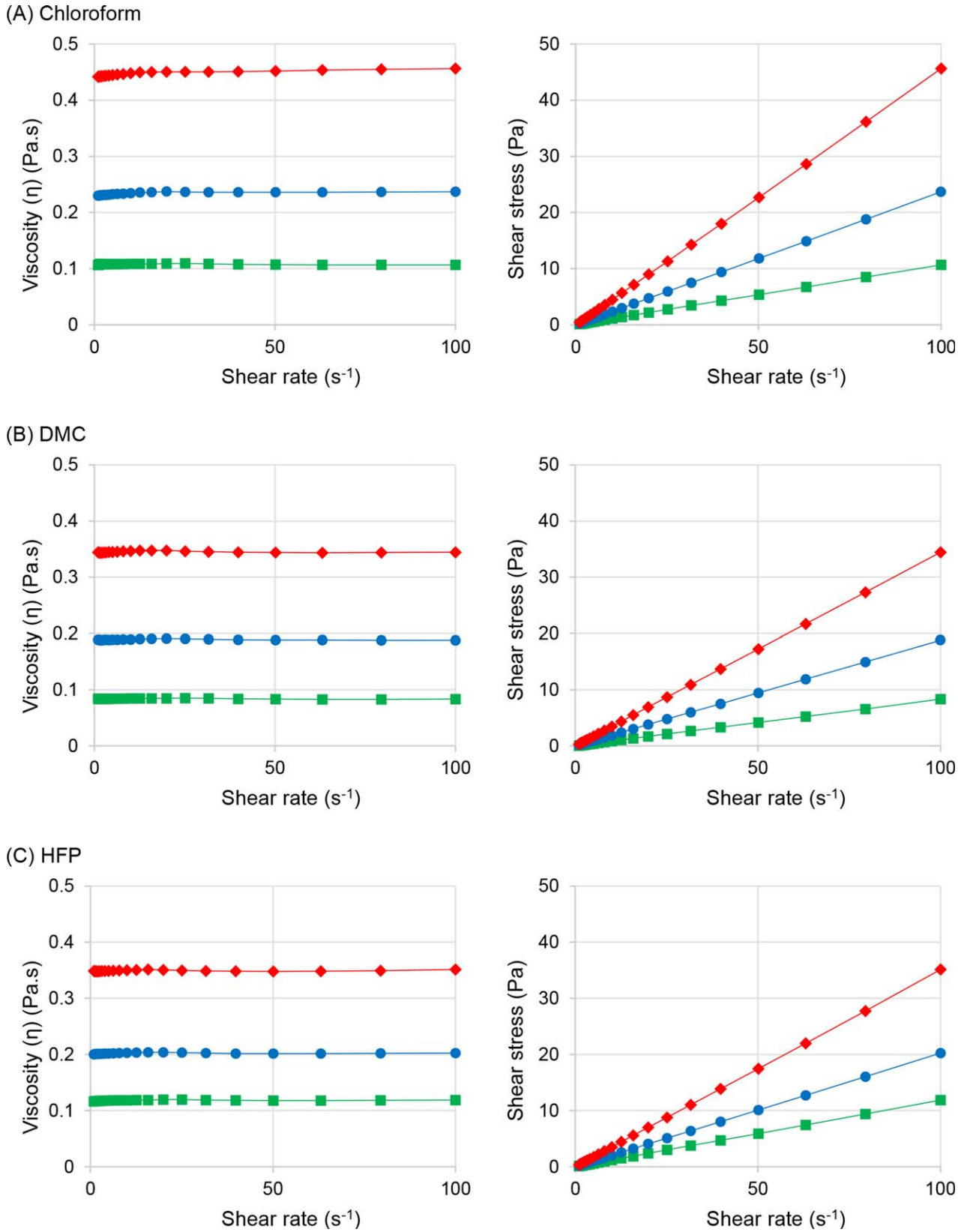

Figure 4. Viscosity and shear stress of PLA solutions of 8% w/v (■), 10% w/v (●), and 12% w/v (◆) in different shear rates (1 to 100 s^{-1}) at 25 °C using different solvents: (A) chloroform, (B) DMC, and (C) HFP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Surface Tension of the Solvents and Polymer Solutions

Solvent	PLA concentration (% w/v)	Surface tension (mN m^{-1})
Chloroform	0	26.4
	8	26.8
	10	27.2
	12	27.5
DMC	0	28.4
	8	28.6
	10	28.9
	12	29.1
HFP	0	16.0
	8	17.4
	10	17.6
	12	17.8

$$\text{Average diameter (HFP)} = 57.190 + 36.55*[P] - 179.050*[A] \quad (3)$$

Besides regression analysis, some variations and tendencies was observed on the range of average fiber diameter using different solvents (chloroform: 260–970 nm; DMC: 240–650 nm; and HFP: 220–470 nm). SEM micrographs (Figure 1) showed for most of experiments homogeneous fibers without porous or beads and virtually constant diameter along the fiber length, except the combination using chloroform, PLA concentration of 12% w/v and air pressure of 0.2 MPa (Figure 2), which will be explained hereafter. Homogeneous morphologies was reported elsewhere.[17,31] Low magnification images showed some packed bundles of aligned fibers, which is often observed in solution blow spun fibers.[28,35,40] Tutak *et al.*[28] found similar packed bundles for airbrushed fibers, however a different morphology was found when using electrospinning, in which single fibers were tightly packed and highly entangled. Bolbasov *et al.*[40] also observed similar morphology for SBS fibers and described it as a complex multi-level structure formed by three dimensional levels: macro, micro, and nano fiber scales.

Figure 3 shows the contour plots showing the response surfaces of average diameter of PLA fibers obtained by SBS using different solvents and process conditions. The contour plots showed that regardless of the air pressure used, increasing the PLA solution concentration for all solvents (chloroform, DMC, and HFP) increased the average fiber diameters. Same behavior was observed in other study.[17] Figure 3 also shows the boxplots of each experiment and it is observed that some combinations presented large variability in the diameter, which can be related with higher standard deviation. Brennan *et al.*[41] also observed a large range in the diameters of solution blow spun fibers in a comparative study to the electrospinning. The fibers obtained with the combination of chloroform solution of 12% w/v of PLA and air pressure of 0.2 MPa resulted in the highest average diameter and standard deviation [Figure 3(a)]. It also produced PLA fibers with porous surface (Figure 2), probably due the drag force generated by the air flow not to be enough to overcome the surface tension and the higher viscosity of the solution (Figure 4), forming non-continuos jets. Thus, the inconsistent jets produce thicker fibers, reducing the rate of solvent evaporation during the flight and forming porous fibers. Previous studies using electrospinning observed that other parameters, such as the relative humidity of the surrounding environment, can also affect the porosity of the fiber.[42] The use of chloroform [Figure 3(a)] and HFP [Figure 3(c)] indicated a tendency of decreasing the diameter of PLA fibers when the air pressure was increased, however, this behavior was not observed when DMC was used [Figure 3(b)]. The average diameter of PLA fibers showed not to be significantly affected by the pressurized air when using DMC [Figure 3(b)]. Medeiros *et al.*[16] also reported a decrease in the poly(methyl methacrylate) (PMMA) fiber diameter when increasing the air pressure and the fibers with the smallest diameters were produced at the highest pressure tested (0.5 MPa). Air pressures below 0.2 MPa (approximately) often do not generate the drag force needed to the fiber reach the target. Using DMC as solvent, only the polymer concentration indicated to contribute on the average fiber diameters and the air pressure showed almost none influence. It was also observed the DMC polymer solution with 8% w/v of PLA had the smallest standard deviation in all air pressure used, comparing with the others solvents and process conditions.

Solution viscosity and surface tension tend to increase with the increase of polymer concentration, demanding higher drag forces to carry the polymer solution to the collector, tending to produce thicker fibers. The behavior of the solutions using different polymer concentrations and solvents under different shear rates (1 to 100 s^{-1}) showed that all solutions exhibited Newtonian fluid behavior, which means that the viscosity of the solutions was independent of the shear stress rate (Figure 4). There was a linear and constant increase in shear stress with the increase of shear rate, which was also observed for all solutions. A higher curve slope was observed when the solution concentration was increased. However, higher viscosities were observed when polymer concentration was increased. The surface tension of the solvents and polymer solutions were measured and the results are shown in Table III. HFP showed lower surface tension compared to chloroform and DMC, indicating that lower surface tension can reduce the fiber thickness. For all solvents, the increase of polymer concentration increased the surface tension of the solutions, although the difference between the surface tension of the pure solvent and the solutions were not expressive. Previous studies showed that lower surface tension can reduce the formation of beads and avoid the production of interconnected fibers and continuous film.[17]

The histograms show the normal distributions of fiber diameters (Figure 5). Narrower curves with higher frequency peaks indicate smaller standard deviations. Therefore, it is clear to observe the experiments using chloroform, the polymer solution of 8% w/v of PLA and 0.6 MPa of air pressure results in the smaller standard deviation. However, the polymer solution of 12% w/v of PLA and 0.2 MPa of air pressure results in the highest standard deviation. Thus, it was observed that the

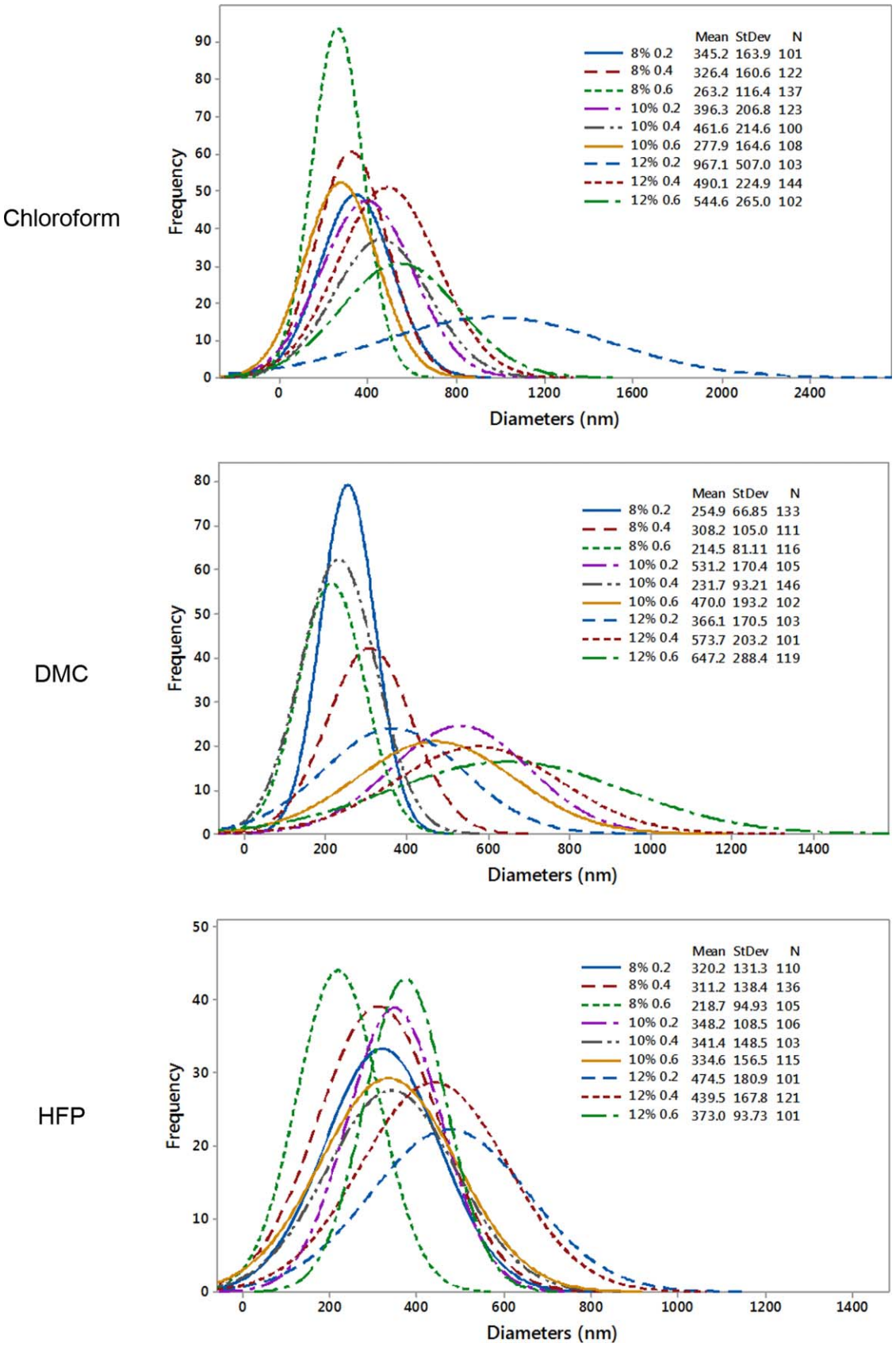

Figure 5. Normal distribution of PLA fiber diameter obtained by SBS using different solvents (chloroform, DMC, and HFP) and process conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

standard deviation indicated to be more affected by the polymer concentration than by the air pressure, since the higher values were found in the experiments using polymer solution concentrations of 12% w/v of PLA for all solvents. Oliveira *et al.*[17] also concluded that lower polymer solution concentrations gives lower standard deviation of fiber diameter regardless of air pressure or feed rate over the range of process conditions used. The control of the standard deviation is one of the most challenging topics in the solution blow spinning process and a lot of efforts have been done to enhance this issue. For all solvent used, the fiber diameter seems more responsive to polymer concentration than to air pressure.

CONCLUSIONS

The results showed that different solvents, solution concentration, and air pressure can affect the average diameter of PLA fibers and standard deviation. Surface tension and viscosity also showed to play an important role in fiber formation. Once more, it was presented that to reach an ideal average fiber diameter it is important to analyze all the process conditions together, not isolated. HFP showed to be a good solvent with the smaller average fiber diameters, however its high price and high toxicity can limit its use. Chloroform is widely used as solvent in several studies, including fiber production because of the lower price and capability to solubilize a large range of polymers, however it is also toxic and included in the VOC list. On the other hand, DMC is a VOC exception solvent and presented promising results on the fiber production by SBS, indicating to be a good choice to produce PLA fibers with an affordable price using a greener process.

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