

Solution Blow Spinning Poly(vinyl alcohol) Sub-microfibers Produced from Different Solvents

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Abstract:

Poly (vinyl alcohol) (PVA) presents a good chemical stability at room temperature, and interesting physical and mechanical properties that enable a wide range of applications of this material. The relationship between the type of polymer-solvent interaction and the physical properties of the gel can be considered, as a key factor to produce PVA micro- and nanofibers by solution blow spinning (SBS) technique. In this work, the influence of changes in the polymer-solvent interaction as a function of the solvent composition on SBS fiber formation are presented. The low molecular weight PVA solutions were obtained by dissolving the PVA in deionized water, and then adding a more volatile solvent to adjust the final concentration at 0.08 g/mL. The addition of different solvents was performed to modify the chemical nature of the solvent and consequently the polymer-solvent interaction. The viscosity measurements were performed as a function of temperature and shear rate. The rheological characterization of the solutions revealed significant changes in the viscosity value as a function of the solvent nature, although the solution's rheological behavior showed no significative changes. Finally, the solutions showed potential to produce homogeneous PVA sub-microfibers by solution blow spinning technique.

Keywords: nanofibers; poly(vinyl alcohol); rheology; viscosity; solution blow spinning

1. Introduction

Poly(vinyl alcohol), PVA (C_2H_4O)_x, is a water soluble polymer extensively studied in the literature due its potential for many applications [1-5]. The PVA rheological properties depends of the mol % of hydroxyl groups, which is termed the degree of hydrolysis (DH). Usually, the DH can vary from 87% to 99.9%, which improves their crystallinity, mechanical and water resistance. Due its great chemical compatibility, PVA became a very interesting polymer to produce nanofibers, acting as a template, improving the solution rheology of a variety of systems [6-8].

The production of micro and nanofibers has shown a recently new development with the Solution Blow-Spinning technique (SBS) [9,10], which exhibits low cost and easy implementation, among other advantages [11,12]. In the SBS

fiber production the solution rheology, concentration, molecular mass and solvent volatility are decisive parameters to successfully produce nanofibers [13,14]. Among those, the solution rheology behavior can be considered as the most important parameter in the SBS fiber production. The solution viscosity strongly depends on polymer nature (intrachain interaction), solvent, concentration and temperature.

In general, the most common and less expensive PVA present low molecular weight, with DH between 87% - 89%. Therefore, is very important to determine the rheological properties of PVA solutions into different solvent and analyze its potential to produce nanofibers by SBS. The most suitable solvent is distilled water, but its low volatility delays the drying of fibers in the collector, which cause significant changes in the fiber morphology [15]. In this paper, we

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demonstrate the effect of mixing more volatile solvents in water solution, such as Isopropyl alcohol (C_3H_8O) (IA), Ethyl alcohol (C_2H_6O) (EA) and Acetone (C_3H_6O) (AC), to accelerate the evaporation process and its impact on fiber formation as an alternative to the usual procedures at high temperatures [15]. The rheological characterization of PVA solution, and the analysis of the polymeric solution properties as function of solvent, concentration and temperature are presented. Finally, PVA polymeric fibers were produced by SBS and its properties analyzed.

2. Results and Discussion

The Figure 1 shows the rheological characterization of PVA solutions as function of temperature and shear rate. The rheological properties of PVA solutions are mainly determined by the equilibrium configuration between different polymer chains and polymer chain-water interactions by hydrogen bonding [16].

The typical exponential decay of viscosity solution's as the temperature increase, Figure 1(a), could be observed for all systems studied. This behavior is important to infer about the continuous flow of the fluid, under external shear stress, in addition to the degree of polymer chains folding in solution [16-18], an important parameter for continuous fiber formation at SBS. At low temperature, a great difference of solution's viscosity can be observed to each solution; it can be associated with the increase of intra and inter polymeric chain interaction, promoted by the poor solvent nature due to the introduction of organic solvent into the water, so a decrease in the interaction between polymer-water by hydrogen bonding are expected. Nevertheless, as the temperature increase there is enough thermal energy to overcome the hydrogen bonding interactions and disrupt intra and inter chain interactions, and we observe almost the same value of solution viscosity at 60°C.

The Figure 1(b) shows the relationship between viscosity and shear rate for PVA solution in different solvent media. It is seen from the figure that the viscosity increases significantly when organic solvents are adding

into the solution at room temperature. The viscosity value is almost constant for all interval investigated, with values around 0.136 Pa.s to IA, 0.111 Pa.s to EA, 0.070 Pa.s to AC and finally 0.029 Pa.s to water.

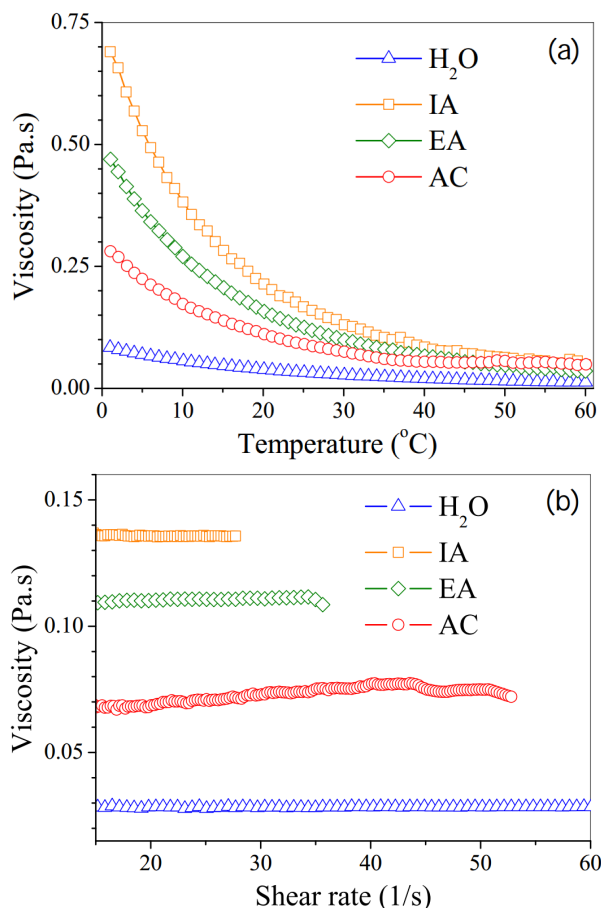


Figure 1. Rheological characterization of PVA solutions (0.04 g/mL) at different solvent media, Isopropyl alcohol (IA), Ethyl alcohol (EA) and Acetone (AC), as function of (a) temperature and (b) shear rate at 26 °C.

The viscosity values vary from a maximum value of 4.00 Pa.s at 0.10 g/mL in IA solution to a common minimum of around 0.02 Pa.s at 0.02 g/mL, Figure 2. In general, the viscosity (η) and concentration (c) of the polymer solution are related by expression to the fourth power. This dependence is valid for a wide concentration range, which can be divided in a diluted, semi-diluted and concentrated regime, for the same concentration regime, the behavior of η vs c can be approximately linear [19]. The Figure 2 shows a polynomial dependence type and not a linear behavior to the viscosity solution in function of concentrations. This viscosity increasing for

higher concentrations, can be assigned to the gradual increase of inter and intra chain hydrogen bonding between PVA molecules. The same behavior has been reported in the literature [17,18], and probably not associated with different dilute regime.

The Figure 3 shows the sample morphology obtained by SBS from the different solutions studied. The formation of a rough and continuous film, Figure 3(a), resulting from deposition of entire PVA drops, was observed when acetone was introduced into the solvent. Besides of the high volatility of acetone, the higher solution viscosity prevents fiber formation, since the drag forces at gas pressure employed is not enough to pull fibers from the tip. Although, after an entire drop be formed in the tip, the competing forces could eject the solution drop from the tip to the collector, as can be observed at Figure 3(a) by the round patterns identified. At this condition, PVA micro particles can be more

easily formed than fibers, and obtained by only small experimental adjust of the collecting conditions.

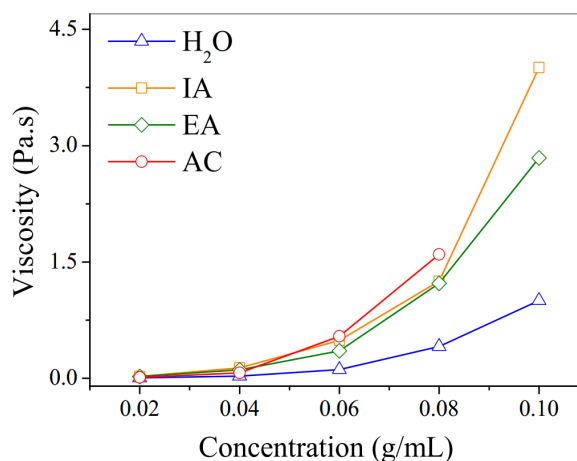


Figure 2. Viscosity of the solution at different solvents as function of concentrations (26 °C).

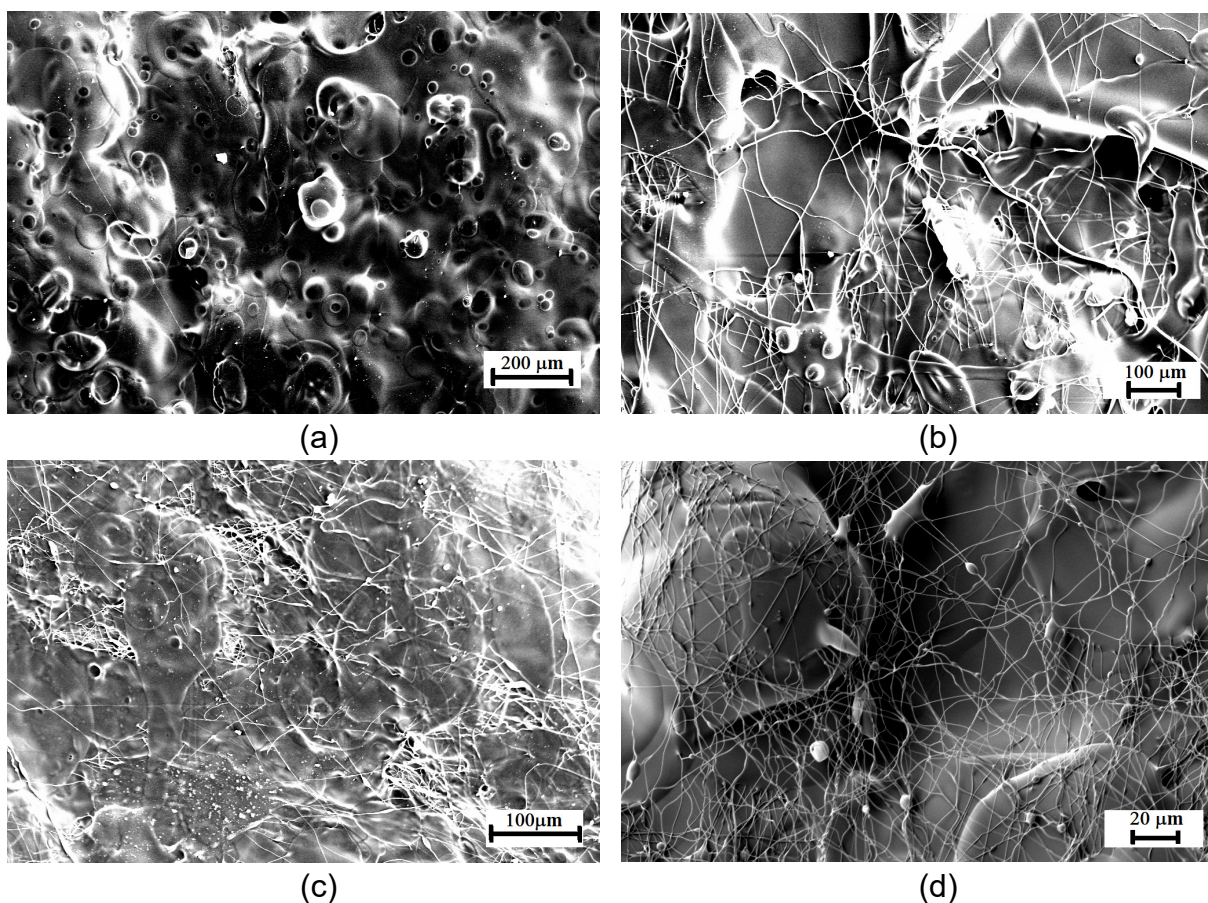


Figure 3. SEM images of PVA samples produced by SBS, with concentration of at 0.08 g/mL. Different solvent media tested: (a) Acetone, (b) Ethyl alcohol, (c) Isopropyl alcohol and (d) Distilled water.

Few fibers were obtained by using EA and IA into the solution, besides the few fiber formation, many defects caused by entire drop ejection from the needle tip was also observed in the samples, Figure 3(b) and Figure (c), respectively. This behavior can be associated with the high volatile character of the solvent, as soon as, the solution reaches the needle tip it's volatilizes, and a high concentrated drop takes place in the process. Then, an entire drop is ejected from the tip and deposited on the collector.

The best condition for fiber formation was obtained by using only distilled water as solvent, spinning a higher amount of fibers compared to the other samples by more efficient dissolution of PVA due to low water volatility,

Figure 3(d). In this case, small defects could be identified in the SEM images, which can be seen in detail in Figure 4.

The Figure 4(a) shows a detailed morphology of the SBS PVA sub-microfibers produced by using pure distilled water as solvent. The mean diameter of these fibers, Figure 4(b), was centered around 433 nm. Beads formation could be evidenced along the PVA fibers (red circle), the beads formation is related to the surface tension from the water content in the fiber after the pulling process [20]. The weak evaporation properties of water molecules promote some solvent remain after the fiber formation by SBS, causing the shrinkage of parts of the fibers, thus forming the beads [15].

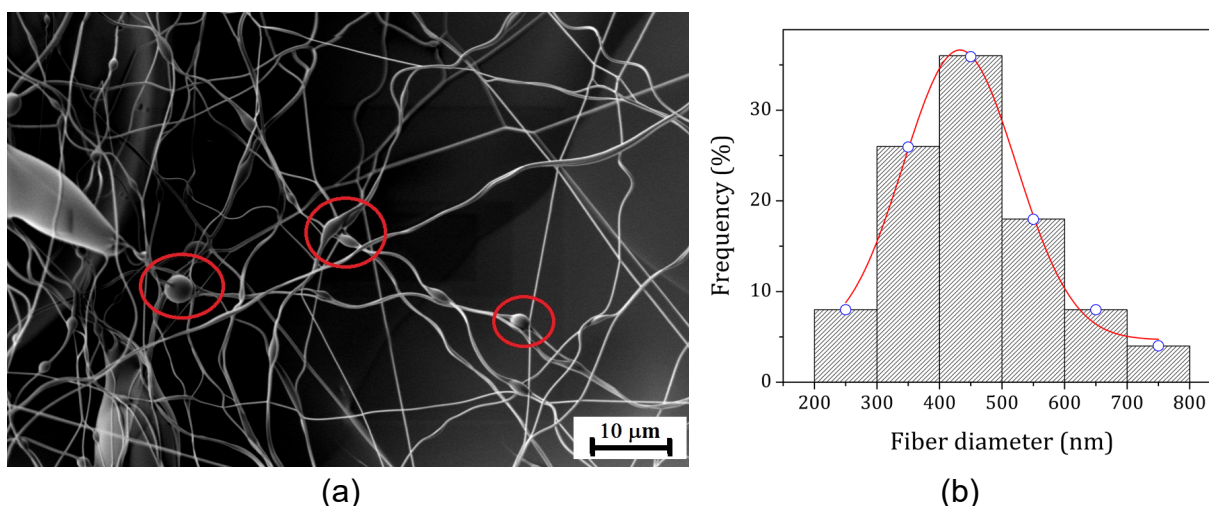


Figure 4. (a) PVA nanofibers produced by SBS using distilled water as solvent. The beads formation along the fiber length are evidenced (red circle). (b) respective histogram.

PVA sub-microfibers FTIR spectra, Figure 5, showed the main bands associated with poly(vinyl alcohol). The bands at 1254 cm^{-1} and at 851 cm^{-1} are assigned to the stretching mode of C–O and C–C groups, respectively. The band centered around 1098 cm^{-1} is assigned to contributions associated with C–H bending and C–OH stretching. Two strong bands are observed at 1571 and 913 cm^{-1} and attributed respectively to the bending and stretching modes of CH_2 group. The band around 1732 cm^{-1} is assigned to C=O stretching. The band around 2920 cm^{-1} is assigned to the stretching vibration of C–H from alkyl groups. Finally, the large band in the range $3000\text{--}3577\text{ cm}^{-1}$ is assigned to the stretching of O–H from the intramolecular and intermolecular hydrogen bonds [21,22].

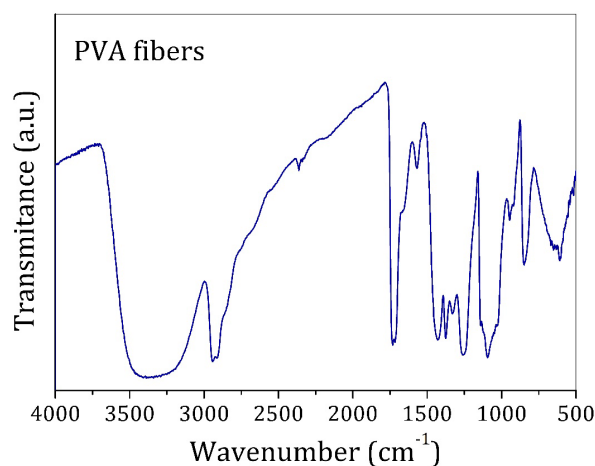


Figure 5. FTIR spectra of PVA nanofibers, produced by SBS using distilled water as solvent.

3. Material and Methods

Solution and fiber preparation

Poly (vinyl alcohol) (PVA), $(C_2H_4O)_x$ was supplied from Dinâmica Chemical Company, Brazil, in powder form. The PVA solution was prepared by slow dissolution of PVA powder in hot water (70° C) under constant stirring for 5 hours. Then blend solutions were prepared by adding 20 volume % of (i) Isopropyl alcohol (C_3H_8O) (IA), (ii) Ethyl alcohol (C_2H_6O) (EA) and (iii) Acetone (C_3H_6O) (AC) into the solution at 26 ° C under constant stirring for 1 hour. The fiber formation tests was performed in the SBS by using the following conditions: polymer concentration of 0.08 g/mL, injection rate of 0,11 mL/min, gas pressure of 120 kPa, collector rotation of 350 rpm, needle (22 G) and work distance of 30 cm between the collector and the needle.

Sample characterization

The solution rheology was evaluated in a Brookfield rheometer, (DV-II + Pro) with concentric geometry, equipped with a thermostath with circulating water, from 0 to 60° C. SEM (Scanning Electron Microscopy) images were obtained in a Carl Zeiss, model EVO-LS15, 8 – 10 kV with SE detector. The aspect ratio (the ratio between length and width) and morphology of the fibers were analyzed. The FTIR spectra of the fibers was collected by using Nicolet Nexus 670 model spectrometer.

4. Conclusions

The PVA viscosity showed to be influenced by the solvent media, adding organic solvents at PVA/water solutions considerable increase of solution viscosity. An unexpected behavior of solution viscosity as function of solution concentration could be observed, a non-linear dependence was evidenced. The PVA viscosity behavior showed to be driven by intra and inter chain interactions, according with the solvent nature. The PVA sub-microfibers produced by solution blow spinning technique, by using PVA of low DH (87%), showed to be possible at concentration of 0.08 g/mL. Besides the low production rate the improvement of solution volatility does not contribute to fiber formation,

but also poor solution volatility drives to beads formation.

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References and Notes

- [1] Lee, S. J.; Lee, S. G.; Kim, H.; Lyoo, W. S. *J. Appl. Polym. Sci.* **2007**, *106*, 3430. [\[Crossref\]](#)
- [2] Zhang, C.; Yuan, X.; Wu, L.; Han, Y.; Sheng, J. *Eur. Polym. J.* **2005**, *41*, 423. [\[Crossref\]](#)
- [3] Hong, P. D.; Chou, C. M.; Chuang, W. T. *J. Appl. Polym. Sci.* **2001**, *79*, 1113. [\[Crossref\]](#)
- [4] Guerrini, L. M.; Brancifort, M. C.; Bretas, R. E. S.; Oliveira, M. P. *Polimeros* **2006**, *16*, 285. [\[Crossref\]](#)
- [5] Son, W. K.; Youk, J. H.; Lee, T. S.; Park, W. H. *Mater. Lett.* **2005**, *59*, 1571. [\[Crossref\]](#)
- [6] Lee, J. S.; Choi, K. H.; Ghim, H. D.; Kim, S. S.; Chun, D. H.; Kim, H. Y.; Lyoo, W. S. *J. Appl. Polym. Sci.* **2004**, *93*, 1638. [\[Crossref\]](#)
- [7] Jun, Z.; Hou, H.; Wendorff, J. H.; Greiner, A. *e-Polym.* **2005**, *38*, 01.
- [8] Ji, H. M.; Lee, H. W.; Karim, M. R.; Cheong, I. W.; Bae, E. A.; Kim, T. H.; Islam, M. S.; Ji, B. C.; Yeum, J. H. *Colloid Polym. Sci.* **2009**, *287*, 751. [\[Crossref\]](#)
- [9] Cena, C. R.; Larios, G. S.; Bica, M. R. R.; Canassa, T. A.; Freitas, G. Q.; Torsoni, G. B. *Rev. Bras. Fisica Tecnol. Aplic.* **2015**, *2*, 32. [\[Crossref\]](#)
- [10] Cena, C. R.; Behera, A. K.; Behera, B. *J. Adv. Ceram.* **2016**, *5*, 84. [\[Crossref\]](#)
- [11] Cena, C. R.; Torsoni, G. B.; Zadorosny, L.; Malmonge, L. F.; Carvalho, C. L.; Malmonge, J. A. *Ceram. Int.* **2017**, *43*, 7663. [\[Crossref\]](#)
- [12] Larios, G. S.; Nogueira, F. S.; Viana, J. L.; Oliveira, R. H.; Ferreira, D. C. O.; Ilha, V. N.; Canassa, T. A.; Praça, L.F. *J. Exp. Tech. Instrum.* **2018**, *1*, 1. [\[Crossref\]](#)
- [13] Cena, C. R.; Silva, M. J.; Malmonge, L. F.; Malmonge, J. A. *J. Polym. Res.* **2018**, *25*, 238. [\[Crossref\]](#)
- [14] Silva, T. H.; Oliveira, J.E.; Medeiros, E. S. *Polimeros* **2005**, *25*, 229. [\[Crossref\]](#)
- [15] Santos, A. M.; Medeiros, E. L.; Blaker, J. J.; Medeiros, E. S. *Mater. Lett.* **2016**, *176*, 122. [\[Crossref\]](#)
- [16] Briscoe, B.; Luckham, P.; Zhu, S. *Polymer* **2000**, *41*, 3851. [\[Crossref\]](#)

- [17] Saxena, R.; Bhatt, S. C. *J. Chem.* **2017**, *10*, 1340.
- [18] Hong, P.; Chou, C. M.; Chuang, W. T. *J. Appl. Polym. Sci.* **2001**, *79*, 1113. [\[Crossref\]](#)
- [19] Mckee, M. G.; Wilkes, G. L.; Colby, R. H.; Long, T. E. *Macromolecules* **2004**, *37*, 1760. [\[Crossref\]](#)
- [20] Fong, H.; Chun, I.; Reneker, D. H. *Polymer* **1999**, *40*, 4585. [\[Crossref\]](#)
- [21] Hdidar, M.; Chouikhi, S.; Fattoum, A.; Arous, M. *Ionics* **2017**, *23*, 3125. [\[Crossref\]](#)
- [22] Mansur, H. S.; Orefice, R. L.; Mansur, A. A. P. *Polymer* **2004**, *45*, 7193. [\[Crossref\]](#)