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APPLICATION OF THE SOLUTION BLOW SPINNING TECHNIQUE FOR NON-WOVEN FIBER PRODUCTION USING PVA

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Abstract. *When the skin is damaged, bacteria and fungi can infiltrate, leading to infections that may evolve quickly. Cases in which the extent of the injury is large, such as burns and amputations, require more efficient treatments, as these infections can lead to death. Recently, new technologies for bioactive dressings based on nanofibers have been developed to create non-woven fiber that replace conventional textile fibers, such as cotton or gauze, which passively protect injuries. These new dressings can be made from hydrofibers and bactericides can be added to them, which can also be gradually released. The most used method to produce nanofibers is Electrospinning, a technique that has as its main disadvantage the low production efficiency, in addition to the need for a high voltage source. A process that allows the production of fabrics more efficiently, with low cost and speed, without the need for high electrical fields, is the Solution Blow Spinning (SBS). This work, then, is intended for production of bioactive non-woven fiber by SBS. These non-woven fibers will be produced based on poly(vinyl alcohol) (PVA), a biocompatible water-soluble. Due to the current difficulty in accessing the laboratories, for an analysis of the production viability, an experimental set was created to manufacture PVA fabrics by SBS. This set was built using a 3D printer (Creality Ender 3 Pro), compressor (SCHULZ), a nozzle, a 3 mL syringe with a needle, a collector and a stepper motor. To prepare the solution, PVA (Neon) was used, which was dissolved in water. With this assembly, biopolymeric PVA films were produced varying some parameters such as composition of the solution and distance between nozzle and collector. The characteristics of the films produced varied considerably according to the parameters used, however it was observed that to produce fibers from this polymer, it is necessary to reduce the drying time of the fabric. This was done by coupling a dryer as a source of hot air to the experimental apparatus and adding a solvent, with a lower boiling point, to the solution. Based on these results and verifying that the control of these parameters is essential, an experimental apparatus is being developed that will allow the control of the injection speed, rotation of the collector, and heating.*

Keywords: *Nanofibers, Solution Blow Spinning, Poly (vinyl alcohol).*

1. INTRODUCTION

Due to illness or accident, thousands of people suffer each year from loss or injury to organs or tissues. According to *Lee et al. (2001*) each year, more than 32 million surgeries have been performed in the USA, resulting in a cost of, approximately, 17% of the Gross Domestic Product (GDP) *(Portal da enfermagem, 2019)*.

The most common treatment for those who have had any type of injury is organ or skin transplantation. The major problem with this method is that the body does not always accept the transplant and few donors are causing long waiting lines for an organ or tissue *(Lee et al. 2001)*.

In 1988, the term tissue engineering was defined as the replacement or improvement of organs or tissues in the human body using synthetic materials using engineering and biological principles and methods *(Caló et al. 2015).* One application of tissue engineering is the use of hydrogels as a delivery agent for bioactive substances (carrying drugs), filling agents *(Caló et al. 2015; Wang et al. 2014).*

Hydrogels are composed of a three-dimensional network similar to human body tissue. These polymeric materials are porous, have a smooth consistency, and are capable of absorbing water or biological fluids in large amounts *(Caló et al. 2015; Wang et al. 2014).* Due to these properties, they simulate body tissue more than any other synthetic biomaterial *(Caló et al. 2015).*

Poly(vinyl alcohol) (PVA), one of the most produced synthetic resins in the world, is a semicrystalline polymer with important characteristics like nontoxicity and biocompatibility. This resin is used in various industrial applications in the production of adhesives, fiber, artificial membranes, and drug carriers *(Garg et al. 2012; Costa Jr. et al. 2008).* Other important characteristics of this material worth to mention are its excellent resistance to oxygen permeability and good resistance to solvents; it is considered an excellent adhesive and is one of the few water-soluble polymers *(Garg et al.*

2012; Costa Jr. et al. 2008). PVA is available within a range of hydrolysis degree and its high hydrophilic character is strongly dependent on that. A PVA of low degree of hydrolysis results in a much hydrophilic polymer *(Park et al. 2010).*

Preparation of biodegradable mats and fibers from PVA solution, mainly using the electrospinning technique, has been reported, showing that the resulting structure can vary largely from beads to fibers depending on the rheological characteristics of the solution *(Shenoyet et al. 2005; McKee et al. 2004)*. Besides that, other important solution parameters that may influence the morphology and diameter of the fibers, such as concentration, molecular weight *(Koski et al. 2004)*, pH *(Son et al. 2005)*, surfactant molecules *(Yao et al. 2003)* and degree of hydrolysis *(Park et al. 2010)*, have also been investigated.

The electrospinning method, although already stablished for fibrous mats production, has as its main drawback the need for high uniform electric fields in large areas. As a simpler and cheaper method, however, stands the Solution Blow Spinning (SBS), a technique developed by Medeiros (2009), that uses concepts of Electrospinning and Conventional Wiring.

The basic experimental arrangement for applying the blow spinning technique is shown in Figure 1.

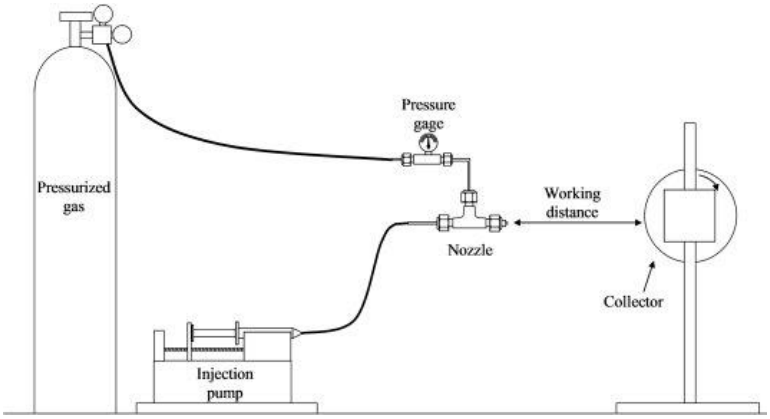

Figure 1 – Basic SBS scheme. The solution is pumped into a pressurized gas stream, directing the polymer to the collector *(Medeiros et al. 2009).*

The elements used are simple: an injection pump, a gas source (cylinder or compressor), a pressure regulator, a manifold, and a concentric nozzle *(Medeiros et al. 2009)*. The main SBS difference from the electrospinning is the use of a pressurized gas (nitrogen, argon, or air), instead the electric field, as the driving force. Among the advantages are the low cost, fast tissue production (which may be faster than electrospinning), and no need for electric fields *(Medeiros et al. 2009; Zadorosnv et al. 2013)*.

The successful use of this technique for fibrous mats production from polymer solution is gaining *visibility (Kumar and Sinha-Ray, 2018)*. Cena (2015) reports the use of the SBS technique with the intent of PVA fiber production, however, smooth, uniform diameter fibers without beads could not be prepared. The reason would be the low molecular weight PVA used. The difficulty in preparing PVA fibers from aqueous solution is reported by Santos (2016), that added a heat flux in order to enhance the solvent evaporation and successfully prepare PVA fibers. In their experiment, it was necessary to use a hot air source to force the evaporation of the solvent, since water evaporation does not occur at room temperature during the flight between nozzles and collector.

The aim of this work is to produce an equipment, and determine process parameters, that allow the reliable production of PVA fibers intended for use as drug carrier in human tissue injuries treatments.

2. EXPERIMENTAL METHOD

The experiments performed in this work were divided in Preparation of the SBS method without control, Preparation of the SBS method with injection control, and Tissue production with PVA. Each of these steps will be described below.

2.1 Preparation of the Solution

For the PVA-H_2O solution preparation, PVA powder (NEON) with hydrolysis degree of 88% was added to water at 60 °C, until a concentration of 100 g/L. For total mixing, the composition was kept for 2 h in agitation in a Britânia blender and another 24h at rest, to allow the bubbles formed during the mixing to vanish. That step is accompanied of a color change, from whitish to transparent, and an increase in viscosity.

A second solution was prepared by adding 20% of 70% ethyl alcohol to water, that is, 800 mL of water and 200 mL of alcohol were used to achieve a PVA concentration in solution of 100g/L.

2.2 Solution Blow Spinning experimental setup

For this article, two experimental apparatuses of the SBS method were assembled, the equipment was found based on existing apparatuses from published works. Both are presented below.

2.2.1 First experimental setup - Rohs stepper motor

The setup is a PLA printed model, modeled using the cad software Catia V5. In Figure 2 the CAD modelled parts are numbered from 1 to 7. The idea for this prototype was to develop pieces that were easy to fit together (like a Lego). All parts (except the stepper motor) are fitted together without the use of screws.

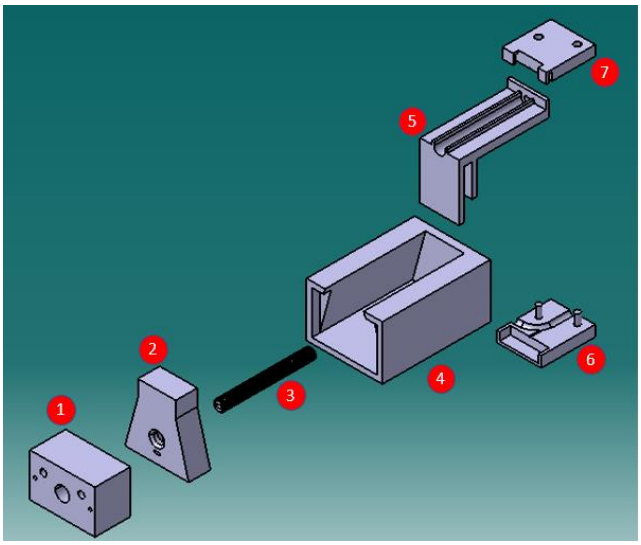

Figure 2 - 3D CAD model of the injection pump: Part 1 – Stepper motor support; Part 2 – Plunger; Part 3 – M10 threaded spindle; Part 4 - Base; Part 5 - Syringe Support; Part 6 – Lower nozzle; Part 7 - Top nozzle.

Part 2 displaces axially in part 3 thanks to the dovetail type of fitting, that allows the use of a smaller number of parts. This format is usually time-consuming and complicated to perform in conventional machining, but through additive manufacturing, the setup assembly is very fast and precise.

The experimental setup, printed with a Creality Ender 3 Pro 3D Printer, is shown in Figure 3.

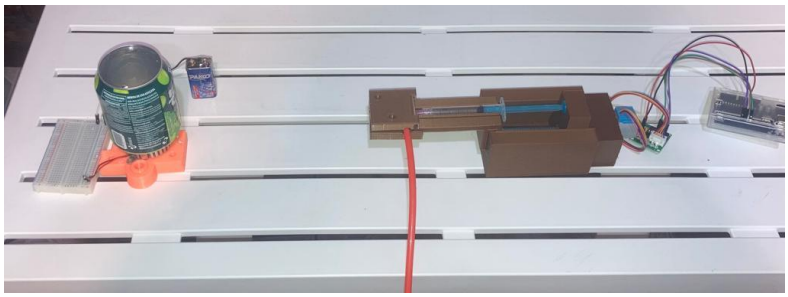

Figure 3 - Injection control apparatus (right) and collector (left).

In Figure 3, at the left end of the prototype, there is a fixed support for the 3 mL syringe. A 5V Rohs stepper motor is embedded at the right end of the prototype and is controlled via Arduino Uno. The inner piece is free to move within the box in a straight line and, when the stepper motor is turned on it pushes the inner piece which in turn compresses the syringe plunger. The rotation used was 75 rpm. As collector, an aluminum can, coupled to a DC 5V motor (used as a cooler in computers), was used.

The syringe needle is inserted directly in the compressed air tube, red tube in Figure 4. To avoid possible air recirculation, the nozzle was remodeled to facilitate the passage of air and, consequently, the flight of the solution to the collector.

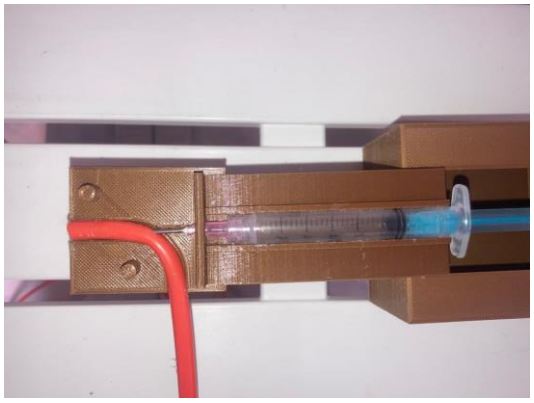

Figure 4 - Nozzle prototype

2.2.2 Second experimental setup – Nema 17 stepper motor

After analysis of the PVA films produced with the previous setup, a new experimental apparatus was built. For fiber production with the new apparatus the stepper motor to control the injection rate was changed to the Nema 17 (higher torque) and the compressor was also changed to a model with a higher pressure than the previous one. The nozzle outlet has been kept the same.

2.3 Film production

Samples were produced using both equipment described above. Additionally, solutions with addition of ethanol in a 1:4 ratio to water were prepared aiming at increasing the rate of solvent evaporation. For that also, a hot air flow was stablished using a GAMMA thermal dryer at two nominal temperatures of 300 and 550 ºC. The samples were named for comparison depending on the solution used, with (WA) or without alcohol (WOA) addition, and the dryer temperature, 300 and 550. They are designated by 300WA, 300WOA, 550WA and 550WOA.

The samples were analyzed using an optical microscope to analyze their morphology, crystalline characteristics analysis via X-Ray diffraction, and surface analysis using SEM. All analyzes were performed at PUCPR facilities.

3. RESULTS

3.1 First experimental setup

In the Figure 5, the optical microscopy images of the samples produced using the first experimental setup are shown. Although not yet ideal, compared to the samples described previously, the samples produced with the 3D printed setup are more fibrous with a lesser plastic film character.

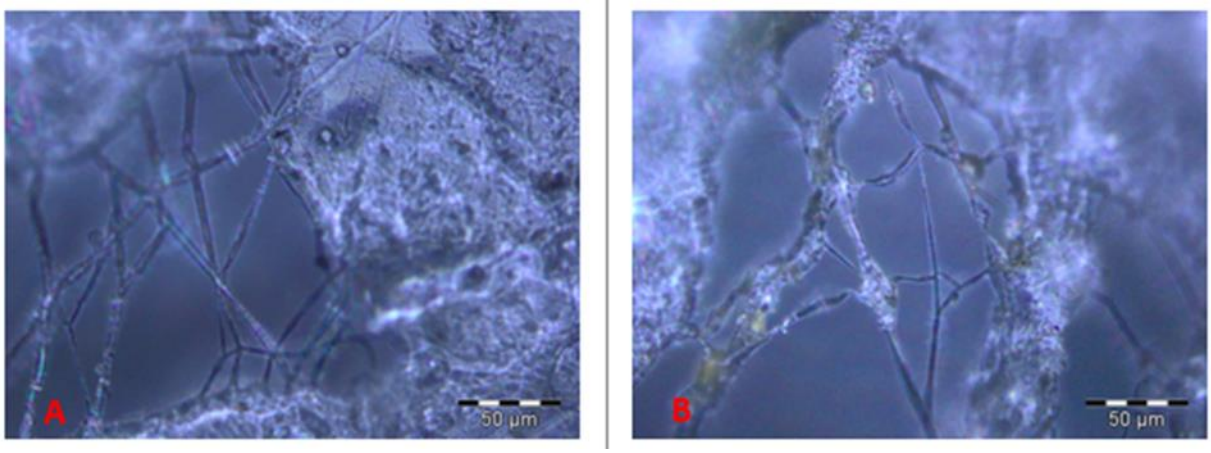

Figure 5 – Optical microscopy images of PVA samples prepared from the (A) polymeric water solution and (B) polymeric alcohol miexd solution, both with air blower at a temperature of 300 °C.

In Figure 5A, the optical microscopy image shows the morphology of the samples prepared from the PVA aqueous solution. The samples have an apparent irregularity on their fiber surface when compared to the fibers of the samples in Figure 5B, which were prepared from the PVA alcohol mixed solution and are more uniform. The non-uniformity on the

surface may have been induced by the drying of the fiber, since the alcohol evaporates more easily and thus dries the sample in a shorter time.

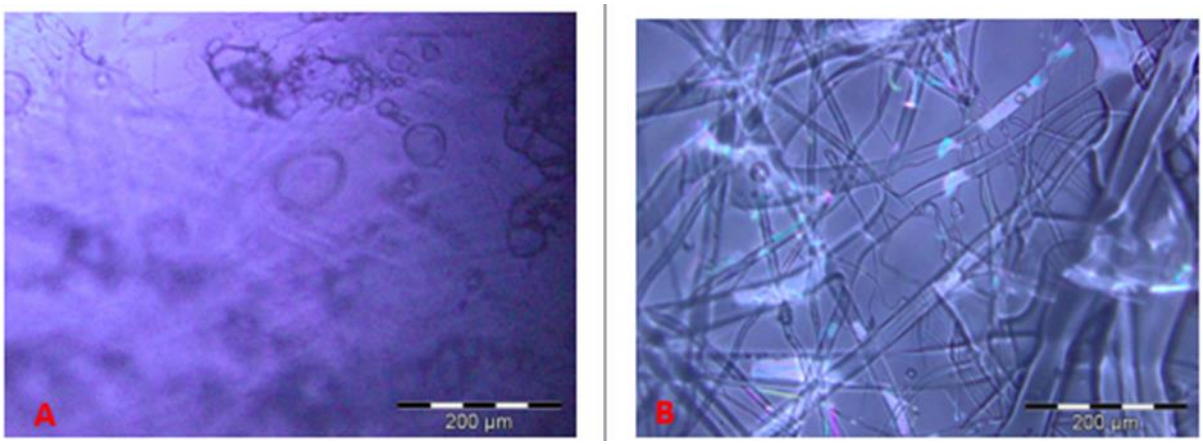

Figure 6 – Optical microscopy images of PVA samples prepared from the (A) polymeric water solution and (B) polymeric alcohol mixed solution, both with air blower at a temperature of 550 °C.

In samples prepared with air flux temperature of 550 ºC (Fig. 6), the fibers were more transparent comparatively the to samples prepared with air flux temperature of 300 ºC. Due to this characteristic, it was not possible to see very clearly the fibers quality of the samples shown in figure 6A. In the samples prepared with the solution to which alcohol was added (Figure 6B), it was possible to see fibers superimposed forming a web.

In figures 7 and 8 are the images made using SEM. It is possible to observe few fibers on the agglutinated surfaces. This confirms the assumption that these accumulations are the fibers gathered during the deposition process. Also, it is possible to verify that there is a greater presence of fibers for the samples in which alcohol was used.

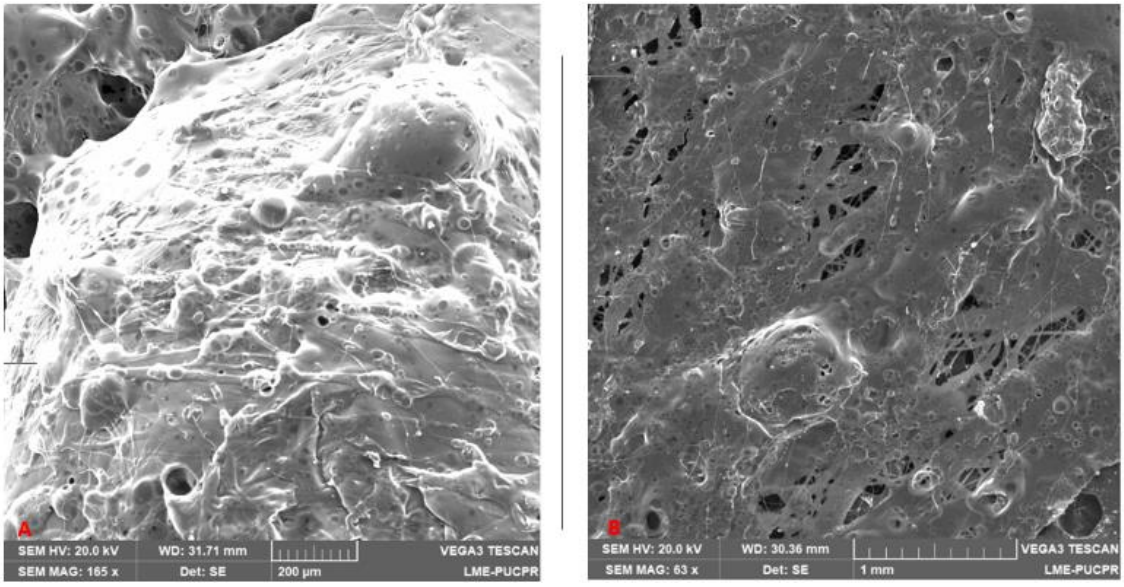

Figure 7 – SEM images of PVA samples prepared with air flux temperature of 300 ºC from (A) water solution (sample 300WOA), and (B) alcohol mixed water solution (sample 300WA).

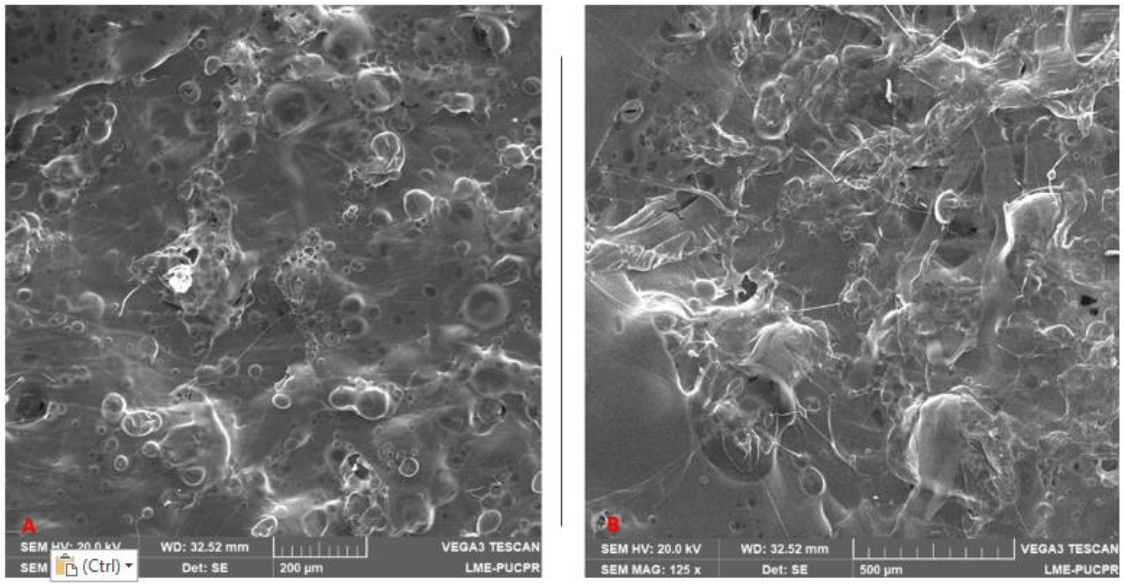

Figure 8 – SEM images of PVA samples prepared with air flux temperature of 550 ºC from (A) water solution (sample 550WOA), and (B) alcohol mixed water solution (sample 550WA).

In order to evaluate the crystallinity of the samples produced, they were submitted to X-ray diffractometry. The results are shown in figure 9.

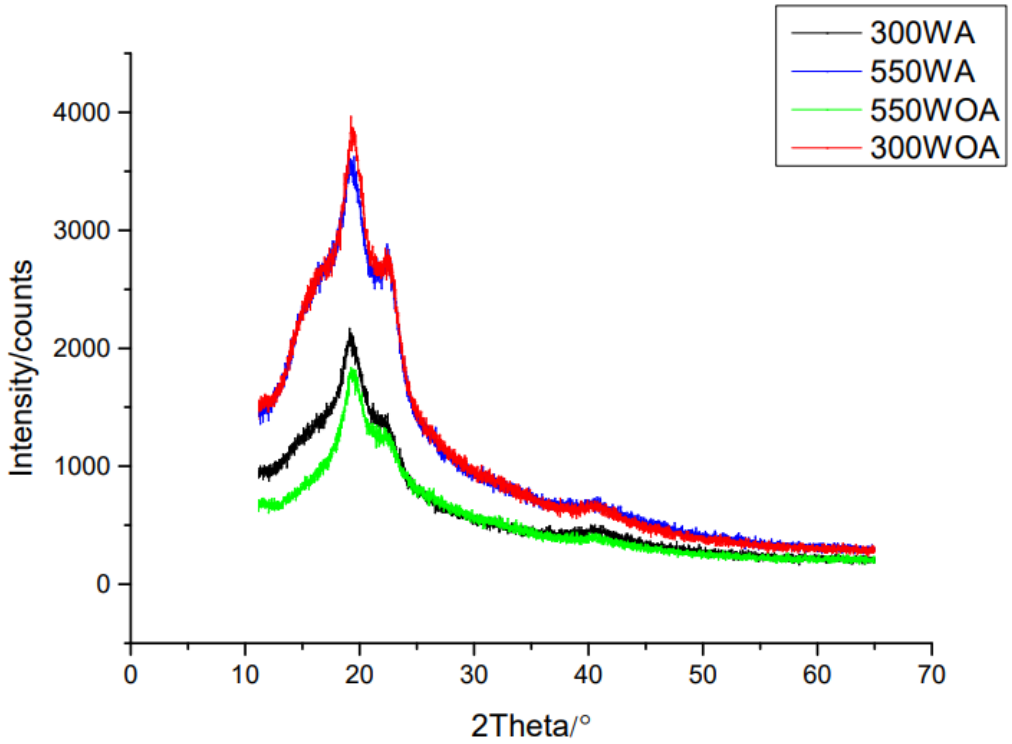

Figure 9 – X-Ray Diffraction spectra from samples prepared from alcohol added solutions at 300 ºC (300WA) and 550 ºC (550WA), and from aqueous solutions at 300 ºC (300WOA) and 550 ºC (550WOA).

From figure 9, one observes that the diffractograms for all samples are very similar, departing from each other only in intensities. In all diffractograms the PVA characteristic peaks, at about 20º and 23º, (100) and (101) diffraction planes, are present diffused in the amorphous region. Since there is no other peak but those of the PVA, it is possible to infer that the samples did not degrade during the production process, nor did they suffer any kind of alteration with the addition of alcohol in the solution or use of high temperature.

3.2 Second experimental setup

During the tests of the previous apparatus, it was observed that the stepper motor used did not have enough torque to keep a constant injection rate. Because of this, the stepper motor was replaced with a Nema 17 with a torque of 4.8 kgf.cm (motor used in 3D printers).

The result of the new injection pump is shown in figure 10.

Figure 10 – injection pump with stepper motor Nema 17.

Another point observed in previous experiments was the compressor pressure. Based on analyzes and tests carried out, the compressor used does not have enough pressure to make the jet carry the fiber to the collector. The new compressor chosen was the Hammer brand with a power of 650 W.

In all tests, the solution contained concentrations of alcohol and the only difference to the previous tests was that for some tests with this method the solution was heated before application to see if there are visible differences in fiber formation.

In figures 11 and 12 are the results of the formation of fibers verified by optical microscopy.

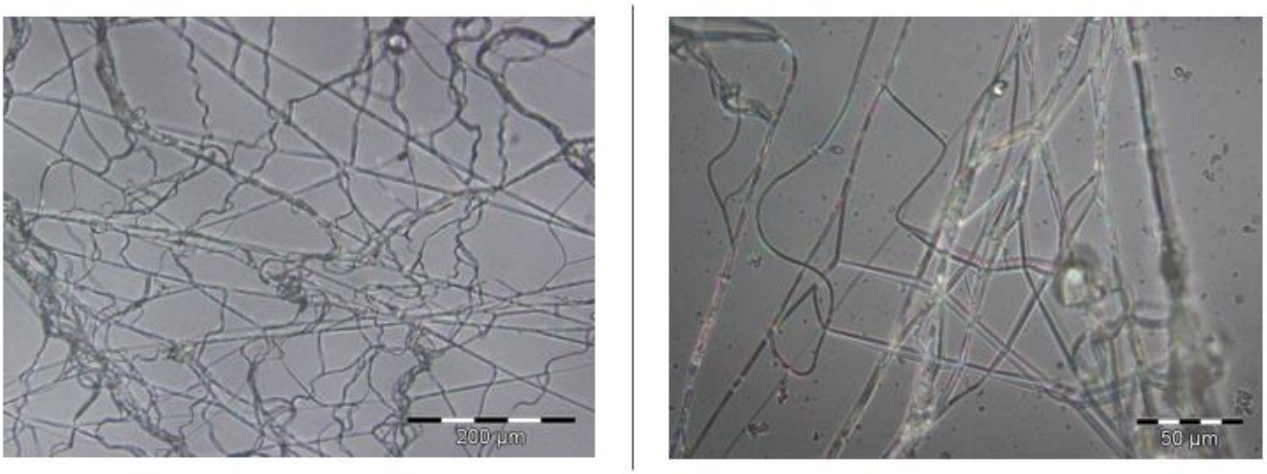

Figure 11 – Optical microscopy images of PVA samples prepared from the heated polymeric alcohol mixed solution, with air blower at a temperature of 550 °C

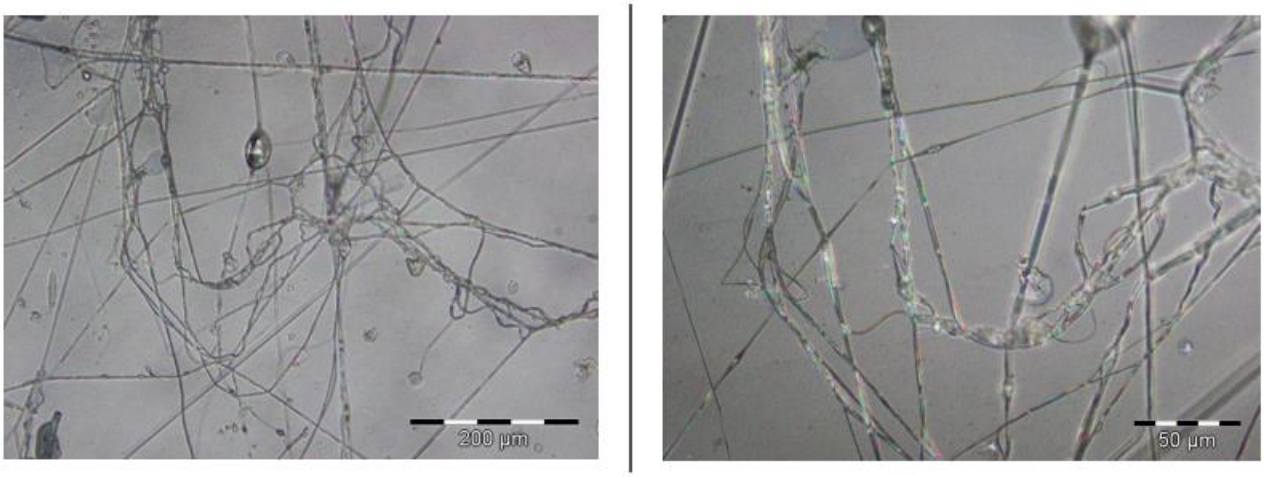

Figure 12 – Optical microscopy images of PVA samples prepared from the polymeric alcohol mixed solution, with air blower at a temperature of 550 °C.

Analyzing the images in figures 11 and 12, it was possible to observe that there are several differences between the methods. The first to be observed are the agglutinate formations in the samples, in the images in figures 5 and 6 it is possible to verify that there are large agglutination points, while in the samples in images 11 and 12 these details are not observed.

By changing the air pressure and temperature it was possible to produce longer fibers with more homogeneous diameters.

No differences in fiber formation were observed in figures 11 and 12 when the solution was heated before manufacturing. There are similar defects.

4. CONCLUSION

All samples showed some type of defect in the formation of fibers, however, using the second method where the injection control is done by the nema 17 stepper motor, there was an improvement in tissue uniformity. With this, it is possible to obtain fibers with better quality if the necessary optimal parameters as, for example, injection speed, are determined.

The use of alcohol in the solution improved the surface quality of the fibers, probably due to enhanced drying, and its use does not affect the crystallinity of the samples, as verified from the diffraction spectra.

As for the temperature, more tests are necessary to understand the transparency of the samples prepared at a temperature of 550 ºC.

Although the difficulty in obtaining PVA fabric using the SBS method in this first tests, by adjusting the parameters it may be possible to achieve conditions that may improve fiber formation and reduce the agglutination in the samples.

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