

Effect of organic solvents in morphology and mechanical properties of electrospun polyvinylpyrrolidone fibers

Christian Narváez-Muñoz, Nathaly Villacís, Diego Narváez, Karla Vizuete, Carlos Arroyo

Abstract: - In this work, the electrospinning technique was used to obtain fibers for mechanical characterization. polyvinylpyrrolidone (PVP) was combined with organic solvents (ethanol and dimethylformamide (DMF)) to generate solutions, looking for the appropriate parameters to obtain fibers with the best morphology and the best mechanical properties. Starting from previous investigations to find the adequate percentages of solvent and PVP, several solutions were made, varying the different parameters like voltage, flow, tip collector distance. Seeking to obtain acceptable samples, the diameter was measured in a scanning electron microscope (SEM). The elastic modulus was measured for the fibers with the best aspect. Mechanical properties were measured in an atomic force microscope (AFM) with the Hertz contact method and the data were approximated to its mathematical model. The solutions that resulted in the best morphological properties were: ethanol - 8% PVP, DMF - 14% PVP, 70% ethanol - 30% DMF - 8% PVP, with diameters in the micrometer range of 1.6, 1.22 and 1.35 respectively, and elastic modulus of 40.08 MPa, 8.8 MPa and 32.78 MPa correspondingly. An analysis of all the parameters influencing the process was performed and an analysis of the influence of the solvents, based on the data of the elastic moduli was carried out.

Key-Words: - electrospinning, electrospun, PVP, elastic modulus, Young's modulus

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I. INTRODUCTION

The electrospinning technique, in which an electric field is applied between a needle and a collector to obtain fibers, has been extensively applied in medicine and engineering to produce fibers with a variety of shapes and sizes from different polymeric solutions and replicate natural structures, such as spider nets [1,2]. In this process, a conductive polymeric solution is pumped at very low rates through the needle, and when repulsive electrostatic forces have overcome surface tension, a jet is created [2]. As the stream travels to the collector through the air, the solvent evaporates, leaving a path of charged fibers, which can be gathered in the collector. Fig. 1 shows a general setup for this technique. As presented, it has a capillary (needle, cone, etc.) from which the polymeric solution is expelled, a pump that controls the flow rate, a collector (conductive metal sheet, rotating drum, etc.), and a high voltage power supply with two electrodes. One of the electrodes is connected to the needle, while the other is attached to the collector.

Generally, electrospinning fibers are characterized by their shape and size; they have to be uniform, without beads and maintain a constant diameter along the path they follow for the process to be considered successful [2]. The majority of studies regarding electrospinning fibers have analyzed how the parameters of the machine, like feed rate, voltage, and distance to the collector, affect the morphology of the fibers, while leaving aside the solvent used in the polymeric solution, which could also influence fibers' configuration.

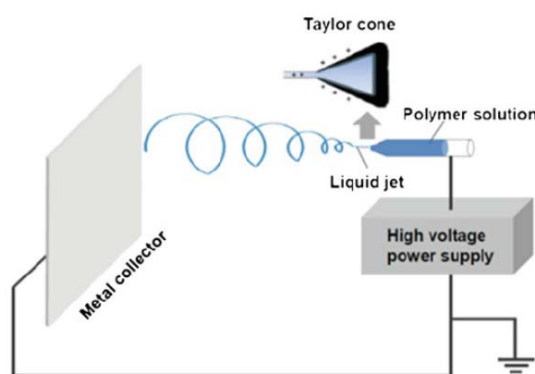


Fig. 1: Basic electrospinning setup [3].

From the studies that do have analyzed the effect of solvents, they focus on the fibers' structure and morphology. Megelski, S. et. al. [4] study how the surface morphology of fibers of polycarbonate (PC), polyethylene oxide (PEO), and polymethyl methacrylate (PMMA) changes when using different solvents, being carbon disulfide (CS_2), Toluene, and tetrahydrofuran / dimethylformamide (THF/DMF). Son, W. K. et. al. [5] carried out an analysis with PEO and different solvents, being chloroform, ethanol, DMF, and water. They found out that for higher values of the dielectric constant of the solvent, thinner fibers were obtained. Wannatong, L., Sirivat, A., & Supaphol, P. [6] used acetic acid, acetonitrile, m-cresol, toluene, THF, and DMF in combination with PS to produce electrospun fibers. They concluded that higher density and boiling point of the solvent resulted in greater diameters, and that DMF gave the highest productivity and optimal morphological characteristics. Similarly, in the work of Jarusuwannapoom, T. et. al. [7], eighteen solvents were tested with PS to produce electrospinning fibers. They arrived to the conclusion that dipole moment of the solvent and conductivity of both the solvent and the resulting solution must be high enough to achieve electrospinnable solutions. Wu, X. et. al. [8] tested ethyl cellulose (EC) with different concentrations of THF and dimethylacetamide (DMAc) and concluded that the composition of the solvent affects the diameter and distribution of fibers; particularly, adding DMAc decreases the diameter, and the morphology changes for different compositions. In the study conducted by Choktaweasap, N. et. al. [9], fibers of gelatin with different solvents were fabricated. They observed that dimethyl sulfoxide (DMSO) and ethylene glycol (EG) gave reduced diameters in comparison to glacial acetic acid (AA). Casasola, R. et. al. [10] showed that poly lactic acid (PLA), with a proportion 60/40 v/v of acetone (AC)/DMF produced thinner nanofibres than other

configurations; also, they found that by increasing the amount of acetone, the diameter of nanofibers decreased.

None of the studies mentioned have investigated how the mechanical properties of the fibers are modified when the solvent changes. Iwamoto, S. et. al. [11] used an atomic force microscope (AFM) to determine the elastic modulus of cellulose fibers, but a relation to the solvent was not established. Only Veleirinho, B., Rei, M. F., & Lopes-DA-Silva, J.A. [12], in their work with solutions with polyethylene terephthalate (PET) and trifluoroacetic acid (TFA)/dichloromethane (DCM) state that the characteristics of the solvent influence mechanical properties of the nanofibrous mats. The elastic modulus, tensile strength, and elongation of the bulk material were measured for the different configurations of TFA/DCM tested, concluding that the fibers with the largest modulus were the ones that used 70% TFA, while the ones with 40-50% TFA were the smallest. They also showed that for a higher amount of DCM, the mechanical performance decreases.

With all of the above mentioned, determining the best solvent for fibers becomes of crucial importance, as well as establishing a connection between mechanical properties and solvent in electrospinning fibers, which is the aim of this work.

II. EXPERIMENTAL SECTION

II.a MATERIALS

All the materials used for this research were of analytical grade. Polyvinylpyrrolidone, PVP K90, was purchased from XI'AN LUKEE BIO-TECH CO. LTD, a Chinese company. Ethanol and Dimethylformamide were bought in "La Casa del Químico", in Quito, Ecuador.

II.b ELECTROSPINNING

The electrospinning machine was assembled at the laboratory and has the following parts: a Genvolt voltage supply, model 73030, that can reach up to 30 kV, a Just Infusion syringe pump, model NE-300, an aluminum collector, a CCD camera, and a lamp. A NIPRO plastic syringe of 10 ml was used to store the PVP solution, and a 0.4 mm diameter needle was used as the charged capillary. Fig. 2 indicates the general setup to obtain electrospray particles; for electrospinning purposes, the configuration is horizontal.

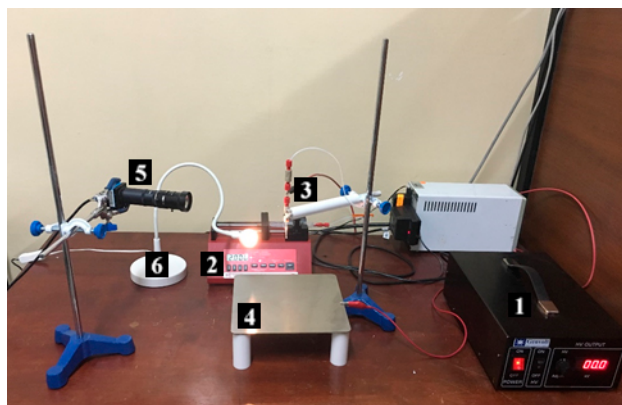


Fig. 2. Electrospay setup used in the laboratory. 1 High voltage source. 2 Syringe Pump. 3 Stainless steel needle. 4 Collector. 5 Camera. 6 Flashlight. [13]

All electrospinning processes were carried out under laboratory conditions (room temperature and humidity). Different weight percents were tested for the solutions in the electrospinning process. Using ethanol as the solvent, the weight percent of PVP was varied from 4% to 10%. For DMF, PVP was varied from 8% to 14%. A combination of both of the solvents was also used, with a ratio of 70/30 in weight for ethanol/DMF, and 8% of PVP. The feed rate, distance from needle's tip to collector, and voltage were modified for every solution tested until achieving a stable jet.

III.c MORPHOLOGY OF FIBERS

Morphology and size of electrospinning fibers were measured in a Mira Tescan 3XM field-emission gun scanning electron microscope (FEG-SEM). All samples taken to the FEG-SEM were covered with a conductive layer of gold, using a Quorum Q150 ES sputtering evaporator. Low ($\times 1000$), medium ($\times 5000$) and high ($\times 10000$) micrographs were taken to observe distribution, uniformity, and diameter of the fibers.

III.d ELASTIC MODULUS

The mechanical properties of the fibers were measured in a MFP-3D Infinity Asylum Research atomic force microscope (AFM) with a 20 nm silicon tip coated with Ti/Ir. The Sader method was used to determine the spring constant and the tip sensitivity, and calibrate the machine. The Hertz contact model was used to obtain the force plots, with a scanning area of $10 \mu\text{m} \times 10 \mu\text{m}$, and a resolution of 8×8 pixels. The AFM has its own software, AR 15.06.109, which analyzes the data

gathered and gives an approximate value of the Young's modulus.

III.RESULTS

III.a MORPHOLOGICAL ANALYSIS

Tables 1-3 show the parameters employed, mean diameter, and uniformity of fibers, obtained for the solutions of ethanol, DMF, and a combination of the two, respectively. The following nomenclature was used: Q = feed rate [ml/h], D = distance to collector [cm], V = voltage [V], d = mean diameter [μm], B = defect for beads, Bif = defect for bifurcated fibers, DD = defect for different diameters, C = defect for low concentration of fibers.

Table I: Parameters and results for the ethanol solutions

No.	PVP w/wt	Q	D	V	d	Defects
1	4	5	12	5	0.84	B, Bif, C
2	4	5	20	5.5	1.16	B, Bif, C
3	6	5	15	5	1.1	B, Bif
4	6	5	20	5.5	1.48	Bif
5	8	4	15	6	1.6	---
6	10	5	17	6	3.62	C

Table II: Parameters and results for the DMF solutions

No.	PVP w/wt	Q	D	V	d	Defects
7	8	6	10	5.7	0.22	B, Bif
8	10	0.5	15	5.5	0.57	B
9	12	0.5	15	5.6	0.66	DD, C
10	12	0.5	20	5.4	1	C
11	14	0.5	16	5.2	1.22	---
12	14	0.5	20	6	0.6	DD

Table III: Parameters and results for the ethanol with DMF solutions

No.	PVP w/wt	Q	D	V	d	Defects
13	8	5	20	6	0.73	B
14	8	5	17	6	1.35	---

As can be seen in the previous tables presented, for each solvent (or combination of solvents) used, there is one configuration in weight percent in which fibers have the best properties. In these cases, not only the weight percent was adequate, but also the machine parameters used, like feed rate, distance to collector and voltage. As far as the defects is concerned, when the feed rate is too high, beads can appear, as is the case of the first sample, shown in

Fig. 3, which corresponds to ethanol with 4% wt PVP. If the weight percent of the solution is too low, bifurcated fibers can show up, as in the case of the fourth sample, with ethanol and 6% PVP, shown in Fig. 4. When the distance from needle's tip to collector is too large, the number of fibers deposited in the collector decreases, as seen in the tenth sample, in Fig. 5, for DMF and 12% PVP.

In the case of the fibers without defects, their micrographs are shown in Fig. 6-8.

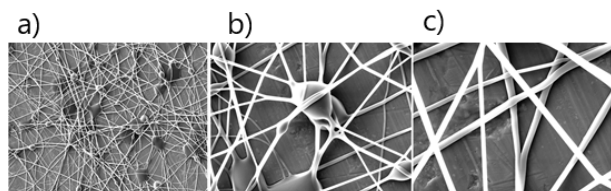


Fig. 3. Micrographs of sample No. 1, ethanol and 4% wt PVP. a) 1000x, b) 5000x, c) 10000x. Beads and bifurcated fibers are observed, as well as a low concentration of fibers.

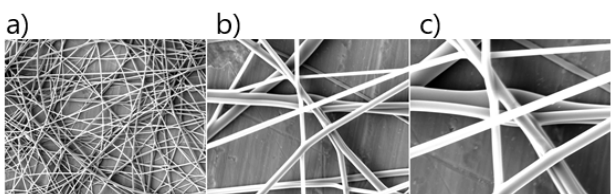


Fig. 4. Micrographs of sample No. 4, ethanol and 6% wt PVP. a) 1000x, b) 5000x, c) 10000x. Bifurcated fibers are observed, which is not acceptable.

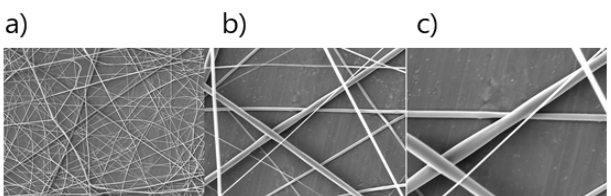


Fig. 5. Micrographs of sample No. 10, DMF and 12% wt PVP. a) 1000x, b) 5000x, c) 10000x. There is a low concentration of fibers.

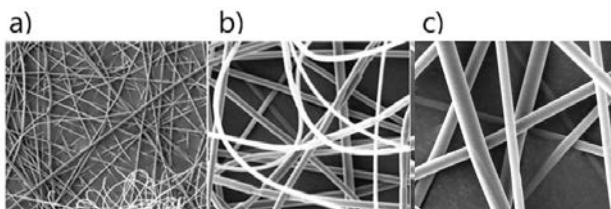


Fig. 6: Micrographs of sample No. 5, ethanol and 8% wt PVP. a) 1000x, b) 5000x y c) 10000x. Fibers are homogeneous, uniform, without beads or bifurcations, and the concentration is adequate.

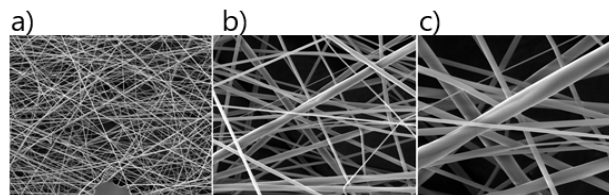


Fig. 7: Micrographs of sample No. 11, DMF and 14% wt PVP. a) 1000x, b) 5000x y c) 10000x. Fibers are uniform, without beads or bifurcations, the diameters are similar, and the concentration is adequate.

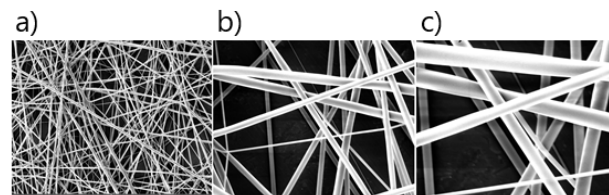


Fig. 8: Micrographs of sample No. 14, ethanol with DMF and 8% wt PVP. a) 1000x, b) 5000x y c) 10000x. Fibers are uniform, without beads or bifurcations, the diameters are similar, and the concentration is adequate.

What is also noticeable from Tables 1-3 is that as the weight percent increases, so does the diameter. For all the successful fibers, the Young's modulus was measured.

III.b MECHANICAL ANALYSIS

Samples 5, 11, and 14, with ethanol and 8% wt PVP, DMF and 14% wt PVP, and ethanol with DMF in 70/30 ratio and 8% wt PVP, respectively, were analyzed to find the elastic modulus of the fibers.

For sample No. 5, a mean of 40.08 MPa for the Young's modulus was obtained, with a standard deviation of 7.4 MPa. Sample No. 11 had a mean of 8.8 MPa for the Young's modulus, with a standard deviation of 2.1 MPa. With sample No. 14, a mean Young's modulus of 32.78 MPa was measured, with a standard deviation of 20.7 MPa.

Fig. 9, Fig. 11, and Fig. 13 show all the measured values for the elastic modulus with their corresponding mean, for samples 5, 11, and 14, correspondingly, while Fig. 10, Fig. 12, and Fig. 14 present the histogram of frequencies for their respective sample.

Making a comparison among the three solutions analyzed, the one that had the greater Young's modulus was sample No. 5, which used ethanol and 8% wt PVP. The one with the lowest standard deviation is sample No. 11, made of DMF and 14% wt PVP. The solution which used a combination of

the two solvents still had a greater mean Young's modulus than the one that used only DMF.

For the histograms of frequencies corresponding to samples 11 and 14, if a distribution were drawn, it would be biased to the left, with few values in the right tail. In contrast, sample 5 could be considered an almost symmetric distribution.

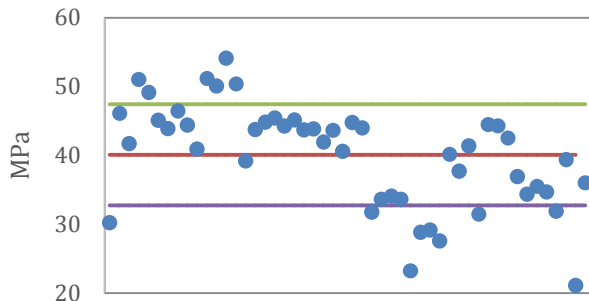


Fig. 9: Young's modulus mean value and standard deviation, corresponding to a solution of ethanol and 8% wt PVP.

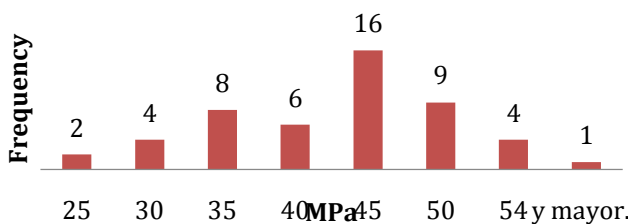


Fig. 10: Histogram of frequencies corresponding to a solution of ethanol and 8% wt PVP.

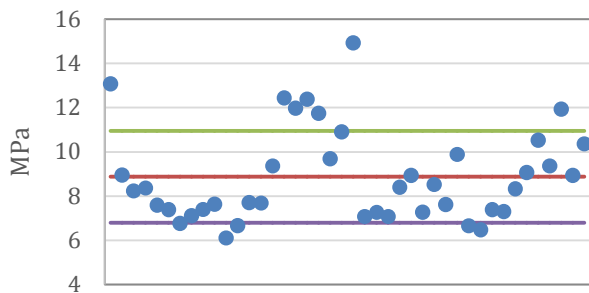


Fig. 11: Young's modulus mean value and standard deviation, corresponding to a solution of DMF and 14% wt PVP.

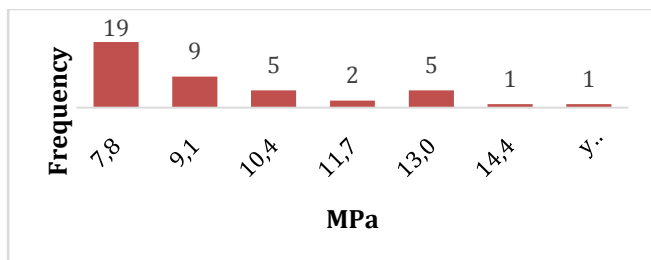


Fig. 12: Histogram of frequencies corresponding to a solution of DMF and 14% wt PVP.

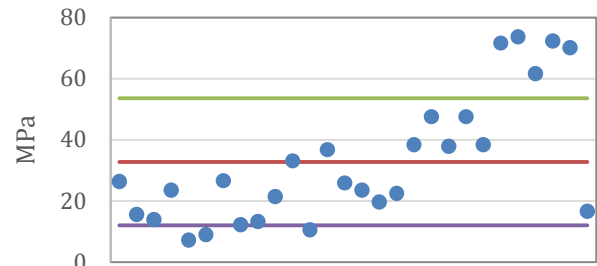


Fig. 13: Young's modulus mean value and standard deviation, corresponding to a solution of ethanol and DMF in a 70/30 ratio and 8% wt PVP.

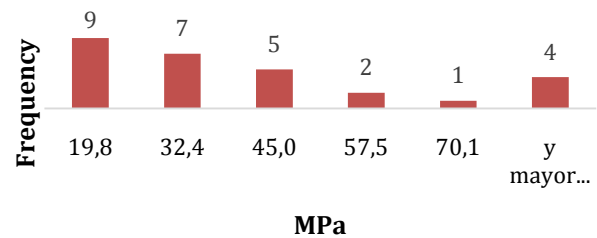


Fig. 14: Histogram of frequencies corresponding to a solution of ethanol and DMF in a 70/30 ratio and 8% wt PVP.

IV. CONCLUSIONS

The morphological characterization of fibers with solutions of PVP with two types of solvents was carried out in the present work, being the solvents ethanol and DMF, respectively. Different parameters were modified to obtain homogeneous fibers, such as weight percent, feed rate, voltage, and distance from needle's tip to collector. The parameter that affected the diameter the most was the weight percent; the weight percent and the diameter having a directly proportional relation. Even though the jet was stable for each one of the solutions tested, only three of them gave flawless fibers: ethanol with 8% wt PVP (3 ml/h feed rate, 15 cm distance to collector, 6 kV voltage), DMF with 14% wt PVP (0.5 ml/h feed rate, 20 cm distance to collector, 6 kV voltage), and ethanol with DMF in a weight ratio 70/30 and 8% wt PVP (5 ml/h feed rate, 17 cm distance to collector, 6 kV voltage). The corresponding mean diameters were 1.6 μm , 1.22 μm , and 1.35 μm . For all these successful fibers, a mechanical characterization was performed in a AFM to determine the Young's modulus. The results were 40.08 MPa, 8.8 MPa, and 32.78 MPa, for the elastic modulus for ethanol, DMF, and ethanol-DMF, respectively. The standard deviations varied from 15% to 50% of the mean value, which is acceptable in these kinds of experiments in which

there is a lot of uncertainty due to the random deposition of fibers. Being the value of ethanol the greatest, and the one of the combination of ethanol and DMF still bigger than the one with DMF only, for better mechanical properties, ethanol must be used as the solvent in PVP solutions.

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