



Production and characterization of membranes containing PCL and PVP obtained by simultaneous and blends electrospinning

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Abstract: Electrospinning can easily produce nano- and micrometer-diameter polymeric fiber membranes. The hydrophilicity of poly (ϵ -caprolactone) (PCL) membranes can be improved blending it with another polymers. PCL has biocompatibility and an excellent in vitro and in vivo release mechanism, however, it has limited applications when faster degradation is required. In this work, two blends membranes containing PCL and polyvinylpyrrolidone (PVP) and one membrane containing simultaneously fibers of PVP and PCL were produced by electrospinning. The membranes received morphological characterization by scanning electron microscopy (SEM). The contact angle measurements were used to investigate the wettability of the materials. Fourier Transform Infrared Spectroscopy (FTIR) was used to depict the chemical composition of the materials. The PCL/PVP membrane with a 1:1 ratio (w/w, of the polymer solutions) stood out among the others, because in addition to an increase in wettability, it presented a better balance between the characteristics of these two polymers.

Keywords: Poly (ϵ -caprolactone). Polyvinylpyrrolidone. Electrospinning. Hydrophobicity. Hydrophilicity.

Introduction

The use of biomaterial-based fibers has received attention for biomedical applications in the areas of tissue engineering¹ or regenerative medicine². Polymeric membranes can be produced by nano- and micrometer fibers using electrospinning technique, in a relatively inexpensive and easy mechanism³.

Electrospinning is a technique in which a viscous polymer solution is intended to force through an electric field to form fibers on a grounded metal surface. The produced fibers from this process are deposited continuously, forming a membrane with high surface area to volume ratio, porous, and flexible⁴.

Poly(ϵ -caprolactone) (PCL) is a semicrystalline polymer with high mechanical properties and biocompatibility, presenting potential properties for use as biomaterial^{5,6}. This polymer is widely used in electrospinning processes^{1,7,8} because it is a non-toxic material and *in vitro* and *in vivo* biocompatibility. PCL is a hydrophobic material and it has limited applications for devices which require a faster degradation⁹.

Polyvinylpyrrolidone (PVP) has in its main molecular structural highly hydrophilic groupz (pyrrolidone) and a hydrophobic groups (alkyl) being a hygroscopic and non-toxic biopolymer¹⁰.

The association of PCL with another polymer, producing polymer blends, can be carried out using using the electrospinning technique, improving PCL hydrophilicity. Kim and collaborators (2013) produced scaffolds by electrospinning using a PCL/PVP blend. The authors produced fibers with good chemical interaction between polymers with potential applications in tissue engineering¹¹.

In this study, PCL has been combined with PVP in different ways such as conventional electrospinning using PCL and PVP blending solutions, and simultaneous electrospinning of PCL and PVP solution in order to improve the wettability of the PCL fibers.

Materials and methods

Materials

PCL (molecular mass: 80,000 g.mol⁻¹) and PVP (molecular mass: 1,300,000 g.mol⁻¹) were purchased from Sigma-Aldrich. Chloroform

and acetone were purchased from Labsynth Products for Laboratories Ltda. Ethyl alcohol was purchased from The Scientific Synergy, and methyl alcohol was purchased from Neon Comercial Ltda.

Membranes production by solution electrospinning

The PCL solution was prepared by the mixture of chloroform and acetone solvents (1:1 mass ratio), under mechanical stirring for 15 minutes at room temperature. Next, PCL 15.82% w/w was added into the flask and subjected to the mechanical stirring until complete solubilization of polymer for 2 hours.

The PVP solution was prepared mixing ethanol and water solvents (4:1 mass ratio) into the flask. The solvents mixture was mechanically stirred for 5 minutes. Then, PVP 8% w/w was added into the flask under mechanical stirring for 2 hours at room temperature.

The PCL/PVP blend solution was prepared by mixing the PCL and PVP solutions, previously described, into an unique flask in the proportion of 1:1 mass ratio. In order to mixture completely the polymers, it was applied a mechanical stirring during 2 hours. The solution prepared by this methodology was called the PP2 solution.

Another PCL/PVP blend solution was prepared as described in the literature¹² and it was called PP3. Chloroform and methanol were mixed into the flask in the proportion 3:1 (volume ratio), and PCL solution with 10% w/v was prepared. Another mixture solution was prepared with the same solvents and proportion to prepare the PVP solution with 30% w/v. After their preparation, the solutions were mixed at a ratio of 7:3 by volume. The PCL/PVP blend solution was mechanically stirred for 2 hours at room temperature called PP3 solution.

In the conventional electrospinning system, a single syringe was used to accommodate the polymeric solution, equipped with an infusion pump, high voltage source with 15 kV capacity, and a rectangular metallic collector cooper that was kept static. The simultaneous electrospinning system was equipped similarly to conventional electrospinning. The difference was in the use of two syringes that accommodated different polymeric solutions.

During electrospinning, the solvents evaporated, and the PCL, PVP,

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PP2, and PP3 solutions resulted in the PCL, PVP, PP2, and PP3 membranes, respectively. The membrane PP1 was produced by simultaneous electrospinning system with the PCL solution into a syringe and PVP solution into other syringe and resulted in the PP1 membrane.

The process parameters used were the capillary diameter of $\varnothing = 0.8$ mm, the flow rate of $Q = 8$ mL/h, the working distance of $Wd = 20$ cm, and the applied voltage of $V = 15$ kV. All these parameters were fixed. The environmental parameters were humidity and temperature of 57% and $T = 26^\circ\text{C}$, respectively.

Characterizations

Scanning Electron Microscopy (SEM)

Fibers micrographic images of PCL, PVP, PP1, PP2, and PP3 were obtained by scanning electron microscope – SEM (ZEISS, model Evo MA–15). The samples were coated with a thin layer of gold (5–10 nm) using a Sputter Coater (BAL–TEC, model SCD 050).

The fiber diameter measurements were carried out manually from SEM images using ImageJ software, and the mean values and standard deviations (mean \pm SD) were calculated following the procedure suggested in the literature¹³.

Wettability and Contact Angle

The contact angle measurements (θ) using a water drop (5 μL) on the materials surface evaluated the materials wettability. Digital microscope (TQC USB, TQC microscope) was used to monitor water drop behavior for 120 seconds. The contact angle measurements were obtained by ImageJ software. The tests were performed in triplicate at room temperature ($T = 26^\circ\text{C}$) and 57% humidity. In order to investigate the influence of membrane porosity, PCL, PVP, PP2, and PP3 films were prepared using the casting method.

Fourier Transform Infrared Spectroscopy (FTIR)

Spectroscopic analysis of the materials chemical composition was performed by Fourier Transform Infrared Absorption Spectrometer – FTIR (Spectrum 65, PerkinElmer), equipped with the accessory of Attenuated Total Reflection – ATR was used. The analyzed region was in the range of 4000 to 400 cm^{-1} .

Results and Discussions

Scanning Electron Microscopy (SEM)

All SEM images of this work were obtained with magnitudes at 1,000X and 10,000X with 10 and 1 μm scales, respectively. The diameters values were measured manually and represented as mean \pm SD, statistical distribution, and data distribution.

In Figure 1 is shown the SEM images of the PCL membrane that showed the behavior of the fibers with random direction and without the presence of pearls, which are considered defects in fibers produced by electrospinning¹⁴. This result corroborates with the SEM images obtained by Morais Segundo (2015) that produced the fibers using the same process parameters⁵. Besides, we observed by superficial characterization from the SEM image, the rough surface of PCL fibers; this effect may be related to the humidity during its formation^{15,16}.

PVP membrane morphology is shown in Figure 2 by the SEM images. The process parameters for its production were the same parameters used in the membrane PCL production; these parameters were not favorable for fibers production without beads. Figure 2.a and Figure 2.b are showed the presence of beads and beads-on-string in the fibers structure. However, we observed considerably thinner fibers than PCL fibers. Vongsetskul et al. (2015) prepared PVP solution using ethanol and water and investigated PVP fibers production by electrospinning using different voltage values. The author reported that higher voltages give finer PVP fibers, with a voltage of 16 kV was able to produce ultrafine fibers¹⁷. In this study, no optimization was done to eliminate the beads, because it was used as an indicator to locate the PVP fibers in the membrane morphology obtained by simultaneous electrospinning.

The SEM images in Figure 3 show the electrospun PVP and PCL fibers simultaneously (PP1). The morphology showed the PCL fibers identified by large fibers with a rough surface, as shown in Figure 1, and fine fibers identified the PVP fibers with beads that correspond to the same characteristic observed in Figure 2 attributed to PVP fibers. The mixture between PCL and PVP polymers into the PP1 membrane does not exist chemical interaction due to the electrospinning technique used, which can be a differential for specific applications.

The Figure 3 in (c), (d), (e), and (f) contains the fiber morphologies of the PP2 and PP3 membranes that were produced by the formation of PCL and PVP blends. In both materials, the production of beads-free fibers was obtained; this effect may have occurred due to the good chemical interaction between the PCL e PVP polymers, which had already been reported by the work authors that produced the PP3 membrane¹¹. In this research, we performed a different methodology from the literature to produce PP2 fibers, which resulted in the formation of finer and more uniform fibers than PP3 fibers, as can be seen in Figure 3d compared with the Figure 3f.

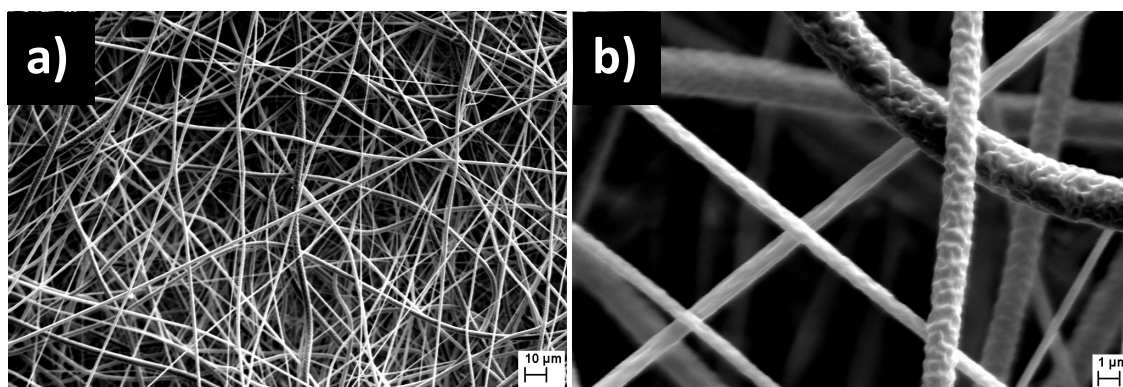


Figure 1– SEM images of the PCL membrane with magnitudes of 1,000X (a) and 10,000X (b).

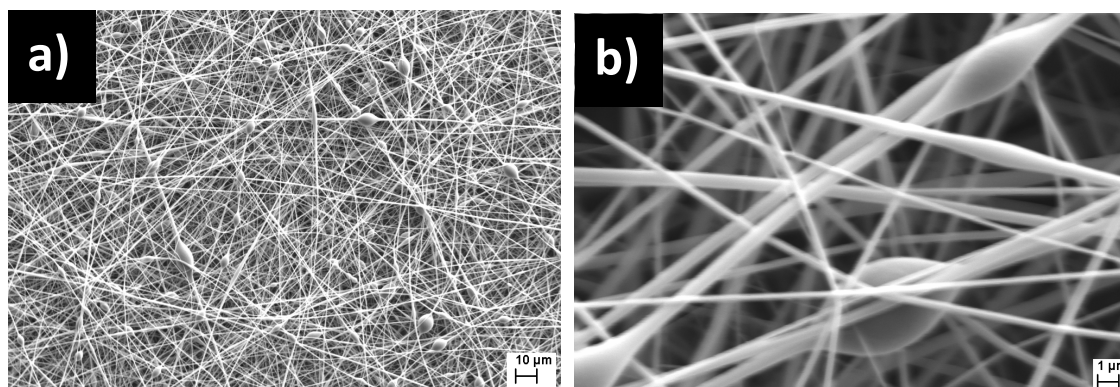


Figure 2 – SEM images of PVP membrane with magnitudes of 1,000X (a) and 10,000X (b).

Figure 3 in (c), (d), (e), and (f) In Figure 4 is shown the distribution of fiber diameters of PVP, PCL, PP1, PP2, and PP3. The diameters of PVP fibers were more uniform than the PCL fibers. PP3 fibers presented values more disperse of their diameters than the PP2 fibers. On the other hand, the PP1 fiber diameters had its distribution more strengthen due to the PCL fiber diameter participation that presented lower diameters values, as shown in Table 1. The diameters of fibers for PCL, PVP, PP1, PP2, and PP3 were 1.9 ± 0.5 , 0.4 ± 0.2 , 0.5 ± 0.5 , 1.8 ± 1.2 , and $4.0 \pm 1.0 \mu\text{m}$, respectively.

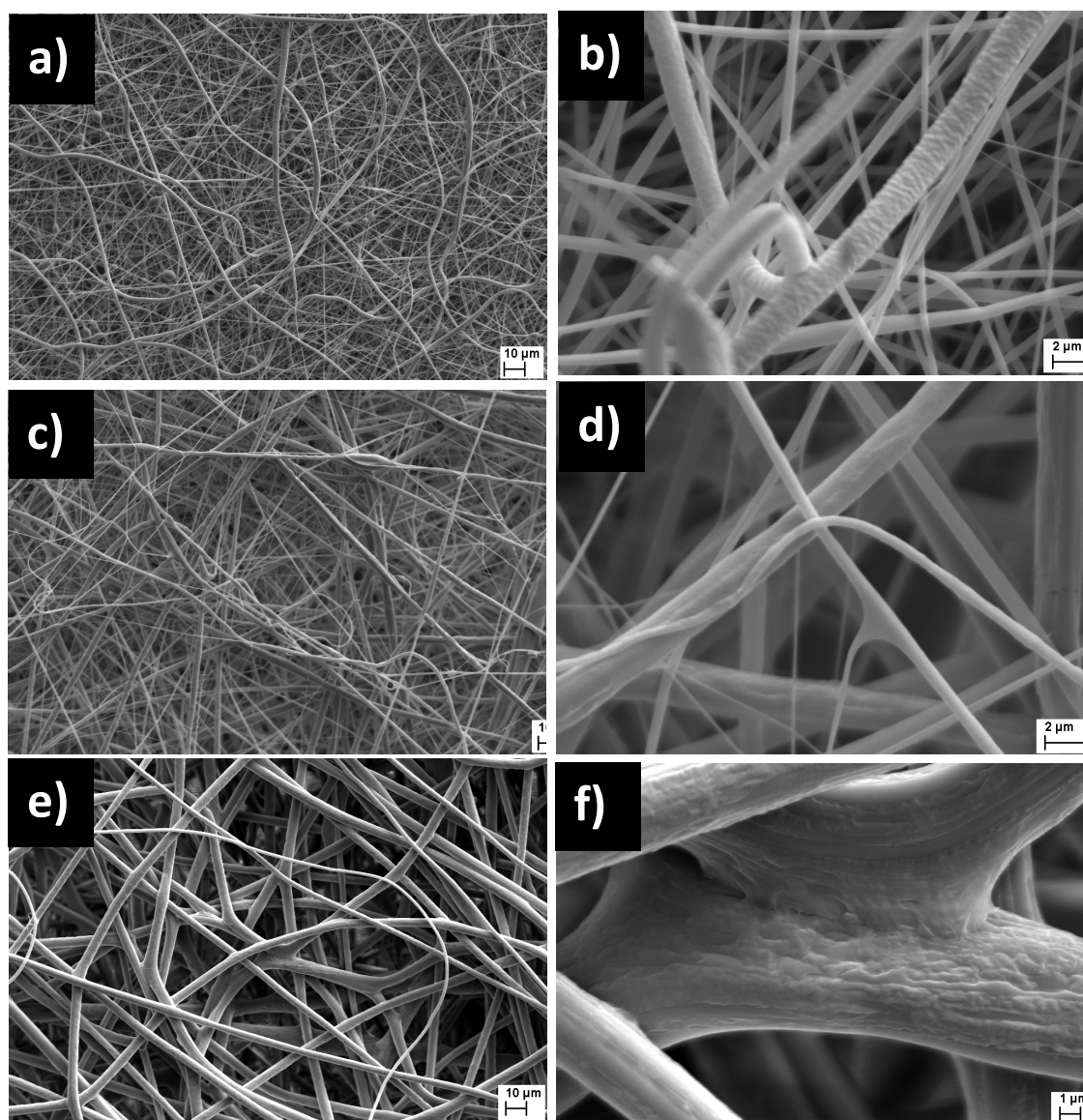


Figure 3 – SEM images of the membranes of PP1 (a and b), PP2 (c and d) and PP3 (e and f) with magnitudes of 1,000X and 10,000X, respectively.

Table 1 are listed the statistical data on the diameters of the electrospun fibers by different techniques. In the PP1 membrane, we observed the $D_{min} = 0.04 \mu\text{m}$ and $D_{max} = 3.30 \mu\text{m}$; both values corroborate with the D_{min} from PVP and D_{max} from PCL. Obviously, it is clear that the PVP fibers structural dimensions were smaller than the PCL fibers, as showed the Figure 4a and Figure 3b. The participation concomitantly of PVP and PCL fibers was confirmed due to their characteristic unique.

In addition, the PCL/PVP blended fibers into PP2 membrane showed better structural characteristics than the PCL/PVP blended fibers from the PP3 membrane described on literature. This improvement may have occurred due to a reduction in the amount of PCL in the solution blending.

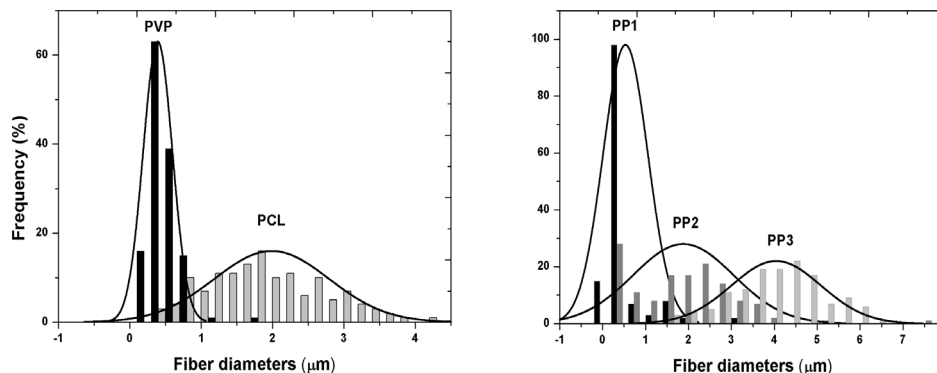


Figure 4 – Distribution curve of (a) PCL and PVP fiber diameters. (b) PP1, PP2, and PP3 fiber diameters.

Statistic data	FIBER DIAMETERS (μm)				
	PCL	PVP	PCL + PVP	BLENDS	
				PCL:PVP 1:1	PCL:PVP 7:3
Mean \pm SD	1.9 \pm 0.5	0.4 \pm 0.2	0.5 \pm 0.5	1.8 \pm 1.2	4.0 \pm 1.0
D_{max}	4.3	1.8	3.3	7.5	6.3
D_{min}	0.5	0.09	0.04	0.2	1.5

Table 1 – Fiber diameters obtained in different processing ways. Values are in micrometers (μm).

Wettability and Contact Angle

In order to compare the effect of wettability were prepared films of PCL, PVP, PP1, PP2, and PP3. Figure 5 is shown the wettability in Table 2 are listed the contact angle measurements (θ).

PCL is considered a hydrophobic polymer⁹, and the PCL membranes produced by electrospinning have their hydrophobicity increased by the presence of air due to membrane porosity⁵. Figure 5.e shows the water drop on the PCL membrane in an almost spherical shape with $\theta = 136.33 \pm 7.84^\circ$. On the PCL film, the water drop behavior in the half-moon shape (to see Figure 5.a) and its contact angle was $\theta = 79.88 \pm 3.25^\circ$. These results confirmed the air influence in the PCL membrane.

PVP has with the water a friendly relationship because of its hygroscopic property¹⁸. For this reason, it is considered highly hydrophilic. Figure 5b shows the water drop on the PVP film of scattered form with a contact angle of $\theta = 49.74 \pm 1.68^\circ$. The PVP membrane did not have its contact angle value due to the PVP membrane total water drop absorption. In this case, the opposite effect occurred with the water drop on the PCL membrane; due to the PVP membrane porosity, its absorption was slightly rapid and high.

The PP1, PP2, and PP3 membranes acquired the same PVP membrane effect, being highly absorbent to water. In contrast, the contact angles of the films of PP2 and PP3 were $\theta = 55.23 \pm 2.76^\circ$ and $\theta = 71.22 \pm 2.20^\circ$, respectively. The contact angle of PP3 film was larger than PP2 film due to an increase of PCL amount into PP3 film.

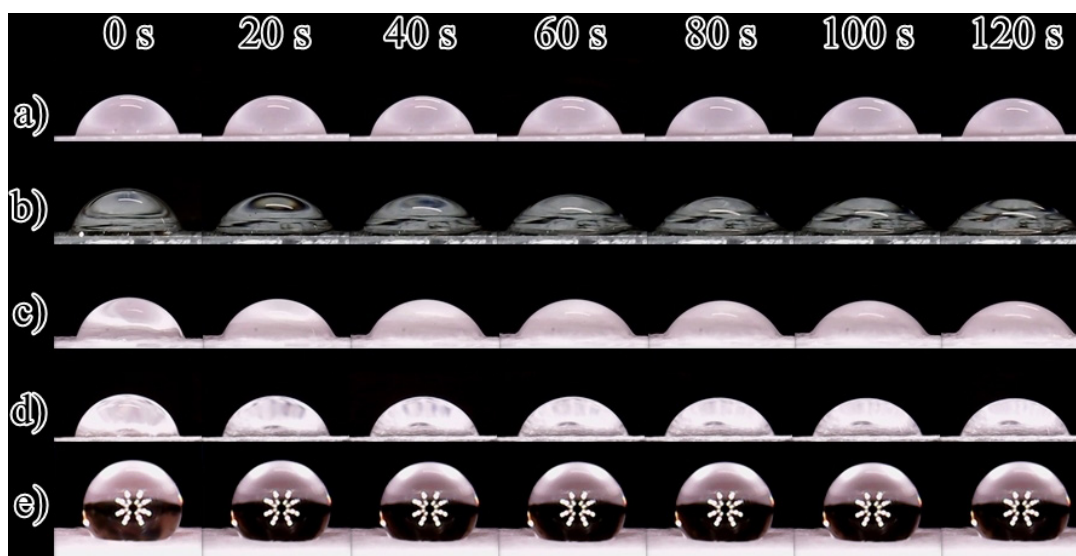


Figure 5 – Wettability of PCL (a), PVP (b), PP2 (c) and PP3 (d), and PCL membrane (e) films.

Material	Contact Angle	
	Film	Membrane
PCL	79.88 ± 3.25	136.33 ± 7.84
PVP	49.74 ± 1.68	---
PP1	NA	---
PP2	55.23 ± 2.76	---
PP3	71.22 ± 2.20	---

Table 2 – Contact angle of films and membranes of the studied materials.

Fourier Transform Infrared Spectroscopy (FTIR)

In Figure 6 are showed the FTIR spectra and their main bands that represent the vibrational modes of chemical composition of PCL, PVP, PP1, PP2, and PP3 membranes.

The PCL membrane bands are following the literature¹⁹. Positions at 2946 cm^{-1} and 2868 cm^{-1} are attributed to the asymmetrical and symmetrical stretching of CH_2 group. The bands at 1722 cm^{-1} correspond to the ester $\text{C}=\text{O}$ group, at 1293 cm^{-1} represents the stretching of $\text{C}-\text{C}$ and $\text{C}-\text{O}$ in the crystalline phase, and at 1162 cm^{-1} is attributed to the symmetrical stretching of $\text{C}-\text{O}-\text{C}$.

PVP membrane bands such as at 1644 cm^{-1} represent the stretching of the amide $\text{C}=\text{O}$ group, at 1287 cm^{-1} assigns to the amide $\text{C}-\text{N}$ stretching, at 1495 cm^{-1} corresponds to the CH_2 deformation of linear chain, and at 1422 cm^{-1} associates to the CH asymmetric deformation and CH_2 cyclic groups^{20, 21, 22}. The band at 3419 cm^{-1} represents the stretching of $\text{O}-\text{H}$ group due to its hygroscopicity.

Figure 6 shows bands around 3419 cm^{-1} , 1722 cm^{-1} , and 1644 cm^{-1} in the PP1, PP2, and PP3 membranes, which confirms PVP presence in the membranes and chemical interaction between the polymers. Moreover, it explains the rapid absorption of water, as shown in the wettability study. Therefore, the PP1, PP2, and PP3 membranes acquired the hygroscopic property of PVP.

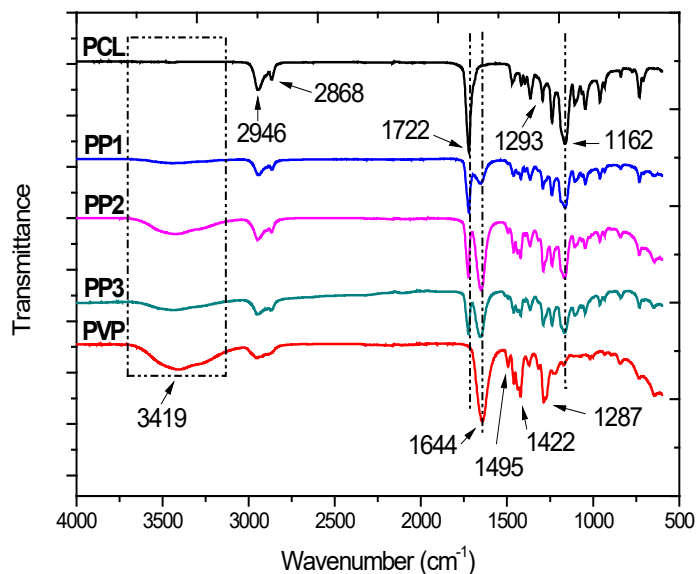


Figure 6 – FTIR spectra and positions of the PCL, PVP, PP1, PP2, and PP3 vibrational modes.

Conclusion

Electrospinning produced membrane containing PCL and PVP using different techniques of preparation. SEM images showed the morphology of PVP and PCL fibers and revealed nanometric dimensions for the PVP fibers. The PP1 membrane preserved the PCL and PVP fibers structural characteristics, and the fibers of PP2 and PP3 membranes presented different aspects. The presence of PVP into the PCL membrane considerably improved its wettability. The bands at 3419 and 1644 cm^{-1} confirmed PVP in the PP1, PP2, and PP3 membranes. The PP1 and PP2 membranes produced in this work have great potential for pharmaceutical and biomedical applications.

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