Journal of Polymer Science and Engineering 2025, 8(1), 11818.
https://doi.org/10.24294/jpse11818

Article

Solvent effects on the synthesis of piezoelectric membranes, based on nanofibers of the polyvinylidene polyfluoride polymer

María Gabriela Bryden Guerra, Leeyuand Oscar Cuan Miranda*

Universidad Autónoma de Chiriquí, David Chiriquí 0427, Panama
*** Corresponding author:** Leeyuand Oscar Cuan Miranda, leeyuand.cuan@unachi.ac.pa

CITATION

Guerra MGB, Miranda LOC. Solvent effects on the synthesis of piezoelectric membranes, based on nanofibers of the polyvinylidene polyfluoride polymer. Journal of Polymer Science and Engineering. 2025; 8(1): 11818. https://doi.org/10.24294/jpse11818

ARTICLE INFO

Received: 7 April 2025
Accepted: 20 May 2025
Available online: 5 June 2025

Abstract: The qualitative and quantitative characteristics of piezoelectric membranes manufactured with the polymer polyvinylidene fluoride, through the electrospinning (TEH) technique were compared. We fabricated microfiber membranes of polyvinylidene fluoride (PVDF) using the electrospinning technique in Methyl Ethyl Ketone (MEK) solution at a ratio of 2:1 and compared them with those manufactured by other authors, who used Dimethylformamide (DMF) as a solvent. During the process, a potential difference of 15.0 kV was applied and the viscoelastic solution of PVDF was maintained at a temperature of 60 °C. The working hypothesis was based on analyzing the influence of the polymer solute on two specific properties: (1) the diameter of the microfibers of the PVDF polymeric material, synthesized through TEH and; (2) the formation of the rotational crystalline structure of the polymer, specifically in the beta (β) piezoelectric phase. The following techniques were used to characterize the synthesized samples: (1) Scanning electron microscopy (SEM), with which we were able to record the diameter of the microfibers between 85 and 113 nm. (2) X-ray diffraction (XRD), where the samples generated dispersions at $2\theta = 18.3°$, 19.9° and 20.6°, which indicated that the crystalline structure obtained is typical of the alpha (α) and beta (β) piezoelectric phases. (3) Raman spectroscopy, with which a spectrum with wave number (k) between 800 cm^{-1} and 840 cm^{-1} was determined, which supported the changes we caused in the internal structure of the polymer, using the DMF/MEC mixture as the polymer solvent. The characterization of the samples obtained allowed us to discover that the properties of PVDF microfiber membranes are affected by the solvent used in the synthesis process. When comparing membranes that used only DMF as a solvent with our membranes manufactured with the DMF/MEC solvent, a higher concentration of the piezoelectric beta (β) structural phase was generated in the latter, which have greater application in power-generating devices.

Keywords: microfibrous membranes; dimethyl formamide; methyl ethyl ketone; piezoelectric structures; electrospinning

1. Introduction

Currently, piezoelectric materials have a wide range of applications in science and engineering. Some of these materials are constructed from polymers, specifically based on the creation of micro- or nanometric fibers using the electrospinning technique, which offers multiple advantages and unique properties compared to other synthesis techniques. For this reason, there is a field of research focused on optimizing the piezoelectric properties of these materials. This research analyzes the effect of the variables involved in the synthesis process, which are usually related to their macroscopic piezoelectric properties, and which will impact their potential applications.

Membrane technology is a relatively young and dynamic discipline that still has a significant empirical component. For this reason, it is currently difficult to find a specific definition of a membrane that provides a clear understanding of what we are referring to. This stems from the wide morphological, structural, and compositional variety of the different materials or devices grouped under the generic term "membrane." A commonly accepted definition is: "A membrane is a material region that acts as a barrier between two fluids and restricts or facilitates the movement of one or more components of the fluids through it" [1].

In this research, the polymer polyvinylidene fluoride was selected for its piezoelectric characteristics. Thin films of this material have a piezoelectric coefficient that can reach up to 6.7 pC/N (picocoulombs per newton), ten times higher than that observed with any other polymer.

When polyvinylidene fluoride (PVDF) is exposed to an electric field, it changes its shape. Since fluorine atoms are much more electronegative than carbon atoms, they take electrons from the carbon atoms to which they are bonded. This means that the carbon-fluorine (CF2) bonding groups in the chain will be highly polar, with a partial negative charge on the fluorine atoms and a partial positive charge on the carbon atoms [2]. Thus, when placed in an electric field, they will align. This causes the polymer to deform, with all its CF2 groups trying to align.

The electrospinning technique is widely used to manufacture fibers ranging in size from microns to nanometers. This technique is based on the principle of coaxial stretching of a polymer's viscoelastic solution by applying electrostatic forces [3].

Currently, due to the rise of nanoscale materials, the technique has become popular due to its low cost and simple execution; the research focus has shifted toward aspects such as the morphology of the fibers produced and understanding the influence of process variables on their properties. Many researchers characterize the manufactured micro- and nanofibers using techniques such as Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and Raman spectroscopy.

The development of the technique begins with obtaining a solution composed of a polymer completely diluted in the solvent(s) chosen to work with. Polymers are dielectrics because, in the presence of an electric field, they can be considered an arrangement of microscopic electric dipoles composed of positive and negative charges. Their centers do not coincide perfectly. They are held in place by atomic and molecular forces and can only change their position slightly in response to strong external electric fields, which explains why the solution stretches during the process [4].

The polymer mixture is placed in the syringe, which is pressed until a drop, called a Taylor cone, is observed suspended at the tip of the capillary tube. At this point, a high voltage is applied to the dissolved polymer. If the electrostatic force and surface tension of the solution are balanced, a constant flow of solution originates from the Taylor cone. The solution flow travels a linear distance of 1 to 2 centimeters, known as the flow length [5], then experiences a spiral motion (flexural instability), resulting in the elongation (hundreds of times) and refinement of the fiber due to plastic deformation. The end of the polymer solution flow path is a collection screen where the fibrous membrane is formed.

The characterization of PVDF microfiber membranes was primarily performed using surface analysis techniques. Structural characterization of surfaces typically includes X-ray diffraction (XRD) and SEM. In addition, physical and chemical characterization methods such as Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) are commonly used.

The Applied Physics Research Center (CIFA) at the Autonomous University of Chiriquí uses the electrospinning (ELH) technique to create piezoelectric microfiber membranes based on piezoelectric polymers such as PVDF. For this reason, we propose conducting a study to qualitatively and quantitatively compare piezoelectric membranes manufactured using the electrospinning technique using different synthesis processes, specifically solvent changes, which are N-dimethylformamide (MDF) and methyl ethyl ketone (MEK).

Its piezoelectric properties are evident when the material is mechanically stretched to orient the molecular chains and polarity (under a strong electric field that induces a net dipole moment) under tension [6].

There are several forms of PVDF, which depend on how the chains are formed, whether with trans (T) or gauche (G) links. These forms are expressed by phases, which are:

- Phase alpha (TGTG)
- Phase beta (TTT)
- Phase gamma (TTTGTTTG)

2. Materials and methods

Among the basic components for the manufacture of polymeric membranes is Polyk 1006 (a commercial version of PVDF), which is a granulated form of polyvinylidene fluoride.

Two solvents were used in the process: N-N demethylformamide with a molar mass of 73.09 g/mol, chemical formula $HCON(CH_3)_2$, brand MERK (REF-Merk site) and acetone from the same supplier, with a molecular mass of 58.08 g/mol, chemical formula CH_3COCH_3. The materials mentioned here were used directly, that is, no additives were applied to modify them.

2.1. Membrane preparation

Figure 1. System consisting of a magnetic stirrer and thermometer, which allowed the sample to be homogenized and its temperature measured to control the variable.

The preparation process for our samples, based on PVDF microfiber membranes

(MMF-PVDF), involves two phases: preparation of the viscoelastic solution and application of the electrospinning technique. Both were performed at the Center for Applied Physics Research (CIFA) (**Figure 1**).

2.2. Preparation of the viscoelastic solution

To prepare the PVDF viscoelastic solution, 2.00 g of granulated PVDF was added to a screw-top glass container, followed by 5.60 g of Dimethylformamide (DMF) and 2.50 g of Methyl Ethyl Ketone (MEC) (**Figure 2**).

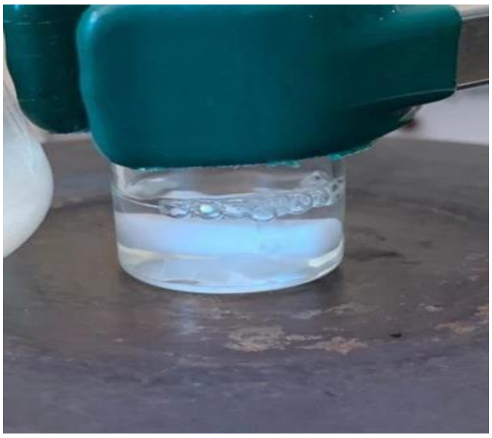

Figure 2. PVDF and ECM mixture before homogenization.

3. Application of the electrospinning technique

The electrospinning technique was applied with a constant output voltage of 15.0 kV at room temperature. The needle fluid output was maintained constant throughout the procedure; the A-99 Razel stepper motor injector was set at 1.73 mL/h. Humidity and temperature values were obtained using a Habor Hab5884Y67 humidity meter. The average values for humidity and temperature were (68 ± 4)% and (28.7 ± 1.6) ℃, respectively.

This technique took two hours for the electrospinning process to be completed, since it had to wait for the volume of the solution subjected to the technique to be exhausted and this allowed obtaining better membranes as shown in **Figure 3**.

Figure 3. PVDF sample, with DMF/MEC as the solvent, inside the syringe, ready to begin the electrospinning technique.

Characterization equipment

To identify the properties of the manufactured membranes, characterization techniques were performed in conjunction with the Materials Science, Engineering, and Bioengineering Laboratory at the University of Texas at Dallas (USA).

In the analysis process for the molecular structure of the PVDF sample, which presents modification and the unmodified one, the Nicolet Almega XR Raman was used, which has a laser wavelength of 780 nm (Annex No. 10). Similarly, the XRD analysis was obtained using the Rigaku Ultima III XRD equipment (40 kV, 44 mA, Rigaku Co. X-ray Diffraction, Tokyo, Japan), with a Cu kα source, with a wavelength of 0.15418 nm. The diffractometer was recorded in a range of $2\theta = 10°$ and $2\theta = 50°$, where a 0.1° scan was first performed, at a rate of 20°/min to calibrate and reference the X-ray spectrum. Subsequently, it was measured at 0.02°, at a rate of 3°/min at room temperature.

Finally, to determine the morphology of the PVDF microfibers, it was characterized by means of SEM, SEISS SUPRA-40, and its diameter was measured using the digital image processing program ImageJ, which is in the public domain, developed by Wayne Rasband (NIH) and programmed by Java.

4. Data analysis methodology

To obtain the microfiber diameters, images collected using the SEM technique were used. These were analyzed using ImageJ, which allows measurements to be calibrated using a reference parameter in the image to be processed. After acquiring the diameter measurements, they were entered into the graphical analysis program Origin Pro (produced by OriginLab Corporation and runs on Microsoft Windows) to create the diameter frequency histogram. This program was also used to construct the absorbance and diffraction spectra graphs obtained from the Raman and XRD characterization data, respectively.

Full Pro-Suite software was used to determine the Miller indices, which are necessary to identify the geometric configuration of the PVDF phase crystal systems. The program works with XRD characterization data.

The calculation of the quantity of β phase obtained from the fabricated samples was carried out using the Fityk program. This program creates Gaussian curves, blocking the peaks at the previously identified diffraction angles of the PVDF crystalline phases. Using the three Gaussian curves, the program performs a fit, resulting in a corrected unified curve. This curve is used to calculate the area representing the quantity of β piezoelectric phase.

5. Results and discussion

The macroscopic and microscopic properties of the fabricated membranes were characterized. At the macroscopic level, their mechanical properties were determined, and at the microscopic level, their piezoelectric crystalline phase was determined. These properties were compared with results obtained by other authors using other PVDF solvents.

The MEC allowed obtaining viscoelastic solutions of PVDF (**Figure 4**), with optimal characteristics for the application of the electrospinning technique, where it could be seen that the drops of the polymeric solution were stretched at the tip of the needle, generating a conical geometric shape, typical of the Taylor cone, giving rise to PVDF fibers, which were uniformly deposited in the electrified collector of the electrospinning apparatus.

Figure 4. Homogenized solution.

The synthesized PVDF microfiber membranes presented the following characteristics (**Figure 5**):

- Uniform distribution of microfibers:
- Low porosity;
- Stable thickness in the synthesized samples
- Tamper resistance

Figure 5. Collection of the membrane formed during the electrospinning process.

6. SEM morphological characterization

Figures 6 and **7** show a comparison of the samples we manufactured with the PVDF/DMF/MEC solution and the one produced by Obaldia et al. [7] using the PVDF/DMF solutions. For the microfibers made with PVDF/DMF/MEC and DMF/PVDF, average diameters were (99 ± 31) nm and (104 ± 37) nm, respectively.

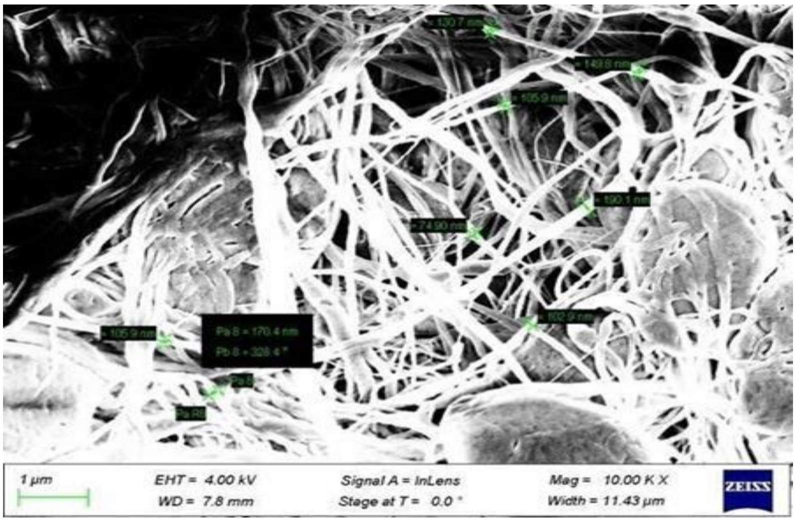

Figure 6. Sample prepared with the PVDF/DMF/MEC solution.

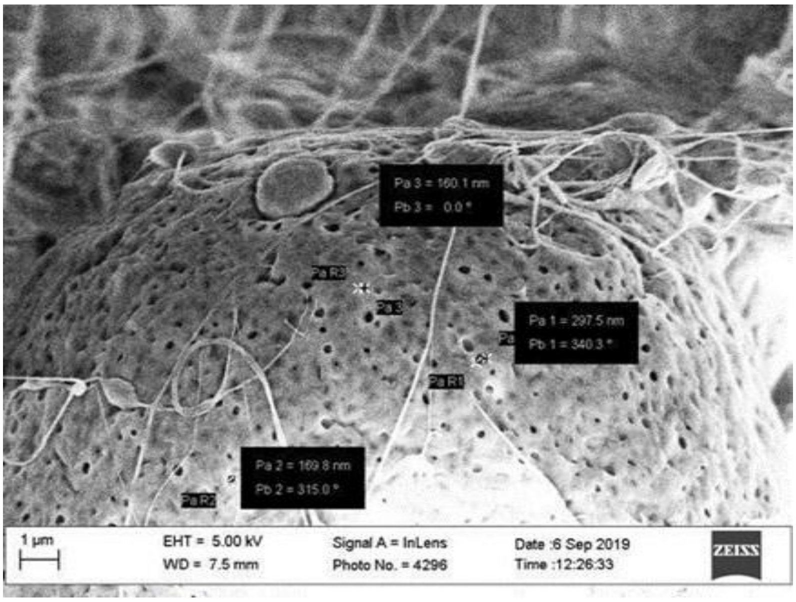

Figure 7. Sample prepared with the PVDF/DMF solution [7].

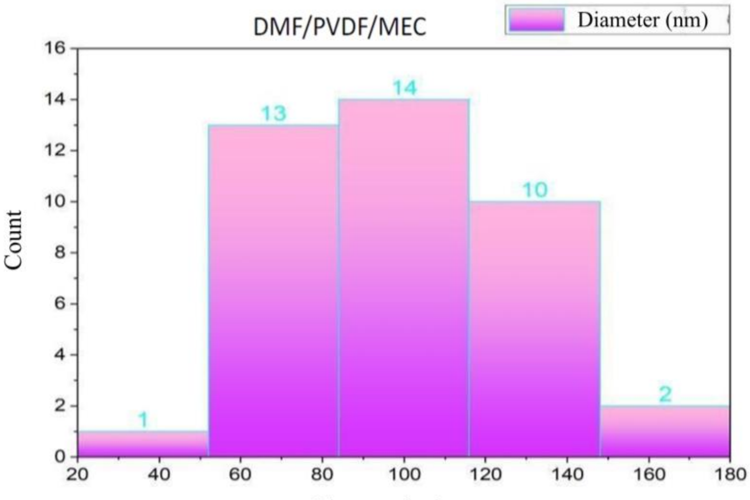

Figure 8. Frequency distribution of fiber diameters.

Figure 8 shows the microfiber diameter distributions for samples made with the PVDF/DMF/MEC and PVDF/DMF solutions. This analysis was performed using ImageJ, an image-processing software program that allows distance measurements to be calibrated using the scale shown in the figure above.

Microfibers made with the PVDF/DMF/MEC solution show diameter distributions less than 150 nm, with a trend in the diameter range between 69 nm and 129 nm. Meanwhile, microfibers made with the PVDF/DMF solution have distributions up to 200 nm, with a trend in the range of less than 150 nm. The decrease in the diameter size of the microfibers is related to the presence of rotational β structure [8], since during the application of the electrospinning process, the fibers created in the electric field experience alterations in the rotational structure of the polymer. The SEM results show that the PVDF/DMF/MEC solution causes a decrease in the diameter of the fibers.

It can be indicated that the microfibers made with the PVDF/DMF/MEC solution show diameter distributions less than 150 nm, with a trend in the diameter range between 69 nm and 129 nm. While the microfibers that were made with the PVDF/DMF solution have distributions up to 200 nm, with a trend in the range of less than 150 nm. The decrease in the diameter size of the microfibers is related to the presence of β rotational structure [8], since during the application of the electrospinning process, the fibers created in the electric field experience alterations in the rotational structure of the polymer. The SEM results show that the PVDF/DMF/MEC solution causes a decrease in the diameter of the fibers.

7. Structural characterization by Raman spectroscopy

As mentioned above, PVDF can be found in four different crystalline phases: α, β, γ, y, δ. The chain formation for the α, y, δ phases is shown in **Figure 9**. The most common phase is α, as it is the one obtained directly upon melting the crystal. The zigzag planar conformation of the β phase can induce a significant dipole moment [9]. The structural differences between the α and β phases are caused by the rotation of the monomers. This rotation is associated with the distinct polarities that distinguish the two phases of the polymer. Raman spectra identify the regions that show the changes in polarity characteristic of each phase.

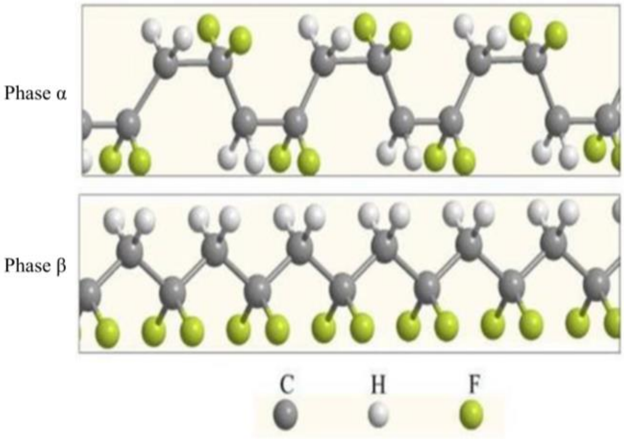

Figure 9. Chain formation for phases α and β [7].

The absorbance spectra for the samples prepared with both solutions are shown in **Figures 10** and **11**. We continue to compare them with those made by Obaldia et al. [7].

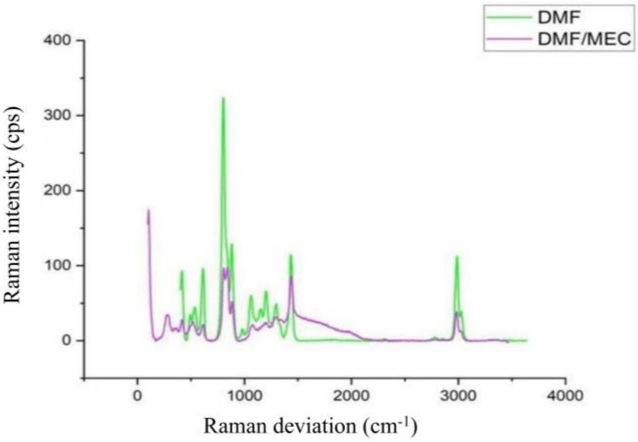

Figure 10. Absorbance spectrum of the samples.

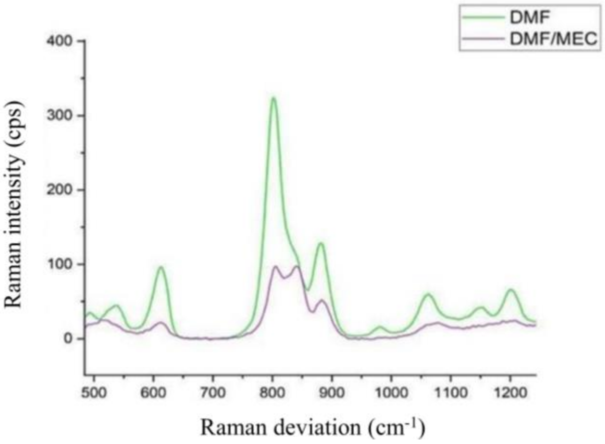

Figure 11. Expanded absorbance spectrum.

Figure 10 shows the specific vibration region (2940 cm^{-1} to 3020 cm^{-1}) for the hydrocarbon compounds C=H [10]. Bands were present for both samples in the region around 2985 cm^{-1}. The DMF/MEC sample comprises a band of moderate intensity in the region from 1600 cm^{-1} to 1710 cm^{-1} [10], characteristic of the ketone group. **Figure 10** shows the unnormalized band. The normalized Raman spectra are recorded in **Figure 11**. The characteristic bands of the α, and β phases can be identified at 794 cm^{-1} and 839 cm^{-1}, respectively. For the sample made with DMF/MEC, there is no dominant phase, since the intensities presented for the α and β phases of the polymer are similar. The differences in Raman intensities between both samples may be due to the fact that the sample concentrations are not the same, as this is one of the factors that affects this parameter [10]. These results show that the conformation of PVDF chains changed from an β phase with TransGauche-Trans-Gauche (TGTG) formation to an α phase with Trans-Trans formation where the hydrogen and fluorine atoms are located on opposite sides of the PVDF backbone.

Structural characterization by XRD

Figure 12 shows the diffraction spectrum for the membrane fabricated with the DMF/MEC solution. The diffracted peaks at $2\theta = 18.3°$ are observed, characteristic of the crystalline phase (**Figure 13**). The diffracted peak at 20.6° corresponds to the presence of the crystalline phase **(Figure 14**).

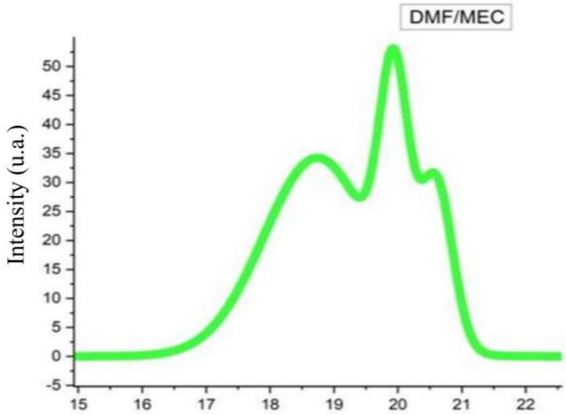

Figure 12. Diffraction spectrum of the sample with DMF/MEC solution.

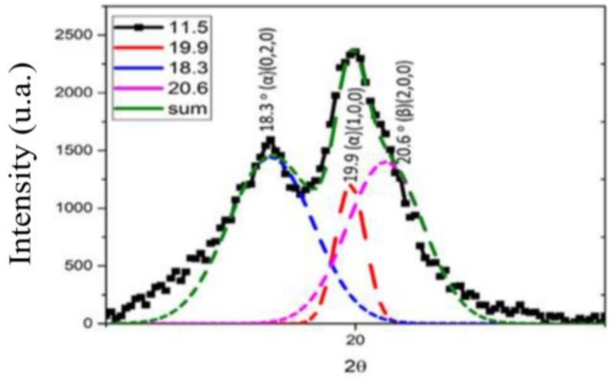

Figure 13. XRD. Calculated areas of the 2θ diffraction angles at 18.7°, 19.9°, and 20.6° of the modified PVDF microfiber membrane sample using DMF/MEC.

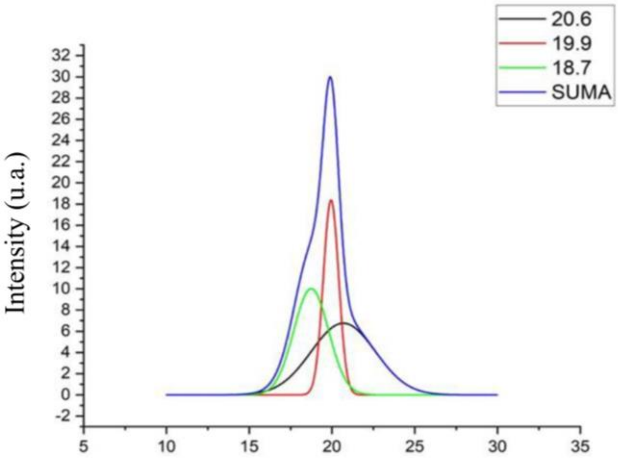

Figure 14. XRD. Calculated areas of the 18.3°, 19.9°, and 20.6° diffraction angles of the modified PVDF microfiber membrane sample using DMF/PVDF [7].

To geometrically determine the crystalline state of PVDF, it is common to relate the unit cell parameters to the spacing between the lattice planes using the expressions shown in **Table 1** [11].

Table 1. Expressions of crystal systems.

Crystalline system	**Expression for**
Monoclinic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d^2} = \frac{1}{\mathrm{sen}^2\beta}(\frac{h^2}{a^2} + \frac{k^2 sen^2\beta}{b^2} + \frac{l^2}{c^2} + \frac{2hl\cos\beta}{ac}$

where d is the spacing between planes, a, b, and c are the unit cell parameters, and h, k, l are the Miller indices, β is the unit cell angle.

The Miller indices, unit cell parameters, and unit cell angles were determined using FullPro Suite software for the monoclinic and orthorhombic crystal systems. The values of the unit cell parameters were also verified through calculation. The spacing between the planes was obtained using Bragg's law equation. The results shown in the table indicate the presence of reflections in the (200) plane, typical of orthorhombic unit cells in the β phase for the peak at 2θ = 20.6°, and reflections in the (020) and (100) planes, corresponding to the monoclinic unit cells of the α phase, for the peaks at 2θ = 18.3° and 19.9°. These results coincide with those obtained from the analysis of samples prepared with DMF as a solvent [7].

The β-phase content in the sample was determined using the Fityk program by fitting the region where the diffraction peaks of 18.7°, 19.9°, and 20.6° are located. This analysis was performed on membranes prepared with the DMF/MEC solution. The fitting with this program allowed the width and intensity of the Gaussian curves to be manipulated once the peaks were locked.

As can be seen in **Figures 13** and **14**, an area of 80.6 u 2 was obtained for the sample manufactured with the DMF/MEC solution. While the result of the area for the analysis of the sample made with DMF as the solvent was 4300 u 2 and 80.6 u 2 [7]. This result indicates that a greater amount of beta rotational structure was obtained for the sample made with DMF as the solvent.

8. Conclusions

Using the electrospinning technique with a viscoelastic solution consisting of DMF and ECM, with a concentration of 2.5 g of ECM per 5.6 g of DMF, PVDF microfibrous membranes were manufactured.

The results obtained using various characterization techniques show that:

1) The fabricated microfiber membranes contain the β-crystalline phase of the PVDF polymer.

2) SEM micrographs of the membranes revealed the formation of microfibers. Some irregularities within the microfiber structure, described in the literature as beads, were present.

3) The diameter distribution histogram obtained through image analysis showed a fiber diameter of (99 ± 31) nm for the sample prepared with DMF and MEK as solvent; while the fiber diameter obtained with DMF was (104 ± 37) nm.

4) Using Raman spectroscopy, specific vibrations in the hydrocarbon compound

region were detected, as bands appeared in the vicinity of 2985 cm^{-1}, which remained constant in the samples prepared with DMF and DMF/MEC solvents.

5) For the sample prepared with DMF/MEC, a moderate band was identified in the region corresponding to the ketone group, ranging from 1600 cm^{-1} to 1710 cm^{-1}.

6) In the DMF/MEC sample, bands of intensity were observed that allowed the identification of α and β crystalline phases of the polymer.

7) The characteristic intensity bands of α and β phases in the DMF/MEC samples did not allow the identification of a dominant phase because they recorded similar intensities.

8) XRD identified the geometric formations of the polymer's crystalline state, monoclinic and orthorhombic, in the samples containing DMF and DMF/MEC.

9) The amount of the polymer's β rotational structure obtained for the DMF-made sample was greater than that obtained for the DMF/MEC sample.

Author contributions: All authors contributed equally to this work. All authors have read and agreed to the published version of the manuscript.

Acknowledgments: We would like to thank the Materials Science, Engineering, and Bioengineering Laboratory at the University of Texas at Dallas (USA) for their collaboration, where characterization techniques were performed. We would like to thank Elida De Obaldía and Daniel Villareal, who have access to this equipment. We would also like to thank the Autonomous University of Chiriquí for providing its facilities at the Applied Physics Research Center, with the support of Pablo Weigandt.

Conflict of interest: The authors declare no conflict of interest.

References

1. Romero JM. Transformation of Thermoplastic Materials, 1st ed. IC Editorial; 2013.
2. Duque Sánchez L, Rodríguez L, López M. Electrospinning: the age of nanofibers. Revista Iberoamericana de Polimeros. 2013; 14(1): 10-27.
3. Abu Alhassan Z., Burezq YS, Nair R, et al. Polyvinylidene difluoride piezoelectric electrospun nanofibers: Review in synthesis, fabrication, characterizations. Journal of Nanomaterials. 2018. doi: 10.1155/2018/8164185
4. Sánchez LM, Rodriguez L, López M. Electrospinning: The era of nanofibers. Revista Iberoamericana de Polímeros. 2013; 14(1): 10-27.
5. Asmatulu R, Khan WS. Synthesis and Applications of Electrospun Nanofibers. Elsevier; 2019. doi: 10.1016/C2017-0-00516-5
6. Billmeyer FJ. Polymer science. Reverté; 1975.
7. Obaldia E, Miranda A, Boya A. Synthesis and characterization of piezoelectric membranes based on the polymer polyvinylidene fluoride, using the electrospinning technique. Revista de I + D Tecnológico. 2021; 17(1): 122-131.
8. Castkova K, Kastyl J, Sobola D, et al. Structure-properties relationship of electrospun PVDF fibers. Nanomaterials. 2020; 10(6): 1221. doi: 10.3390/nano10061221
9. Ruan L, Yao X, Chang Y, et al. Properties and applications of the β phase poly(vinylidene fluoride). Polymers. 2018; 10(3): 228. doi: 10.3390/polym10030228
10. Adamo T. Understanding Raman Spectroscopy Principles and Theory. TRACES Centre. 2021. Available online: https://www.utsc.utoronto.ca/~traceslab/PDFs/raman_understanding.pdf (accessed on 5 April 2025).
11. Pérez J. X-ray diffraction. Introduction. Universidad Politécnica de Cartagena; 2015.