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Investigation of the Effects of Working Parameters in Electrospinning Technology on Morphology of Polymeric Nanofiber Membranes Using Reference Polymers

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In this study, polymeric membranes were prepared by electrospinning technique using different biocompatible polymers such as polycaprolactone (PCL), polyvinylalcohol (PVA) and polyacrylonitrile (PAN). The morphological effects of electrospinning technique on nanofiber membranes obtained by keeping the voltage, working distance and feed flow properties constant between each other were investigated. Structural (FTIR-Fourier Transform Infrared Spectroscopy), morphological (SEM-Field Emission Gun Scanning Electron Microscope) and mechanical (Tensile) analyzes were performed on the polymeric membranes produced and the material properties were determined. The effects of the morphological characterization of the obtained polymeric membranes on electrospinning operating parameters and the use of membranes that will result from these effects in sectors such as health, filtration, defense, textile and agriculture.

Keywords: Polymer, electrospinning, nanofiber membrane, morphological, SEM

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1. Introduction

"Nanotechnology" concept; It is a combination of the words nano and technology. Technology is the body of information used to produce useful products and to design new products. Nano means "dwarf" in Greek. Expressions defined by nano represent one billionth of any measure. For example; Nanometer refers to one billionth of a meter (1 nm = 10^{-9} m). When nanostructures are viewed in terms of length, they correspond to systems of approximately 10-100 atoms (10^{-9} meters). Any size (length, width or thickness) between 100 and 1 nanometers (nm) (1/10 million meters to 1/1 billion meters) is expressed for materials covered by nanotechnology.

It can be defined as fibers of one micron in diameter and below. Today, nanofiber can be produced from many ceramic and polymer materials using various production

methods. Fibers produced from polymer solution and polymer melt at sizes below micro meters using various methods are called nanofibers [1-5].

Today, there are many nanofiber production methods. If we list them:

- Fibrillation,
- Meltblowing,
- Bicomponent,
- Spunbond
- Electrospinning method

Electrospinning method is the process of transforming the fluid into nano-sized fibers by applying a voltage of kV to viscous liquids at very small flow rates. Polymer solution or melt is used as viscous liquid in its application. The solution arriving at the tip of the medical syringe at uniform flow forms a spherical droplet under the influence of surface tensions, and here, under the effect of electrical forces, it is tapered (Taylor cone) and transferred as nanofibers to the grounded collector at a certain distance [6,7]. Figure 1.1. shows the working principle of electrospinning.

Figure 1.1. *Electrospinning working principle [7]*

Electrospinning method can be affected by a number of variables. These parameters are; They can be classified as solution properties, controllable variables and environment parameters. It is among the solution properties such as viscosity, conductivity, surface tension, molecular weight of polymers. The effect of solution properties is difficult to ignore. Because the change of a parameter generally affects the other solution properties. Controlled variables are flow rate, electric field strength, distance between needle tip and collector plate, needle tip design, and geometry with the arrangement of the collector plate. Ambient parameters are temperature, humidity and air velocity.

The concentration of the polymer solution plays a large role in fiber formation during the electrospinning process. Four critical concentrations should be considered, from low to high.

• When the concentration is very low polymeric nanoparticles will be obtained. Meanwhile, due to the low viscosity of the solution and high surface tensions, instead of electrospinning, electrospray is formed.

• When the concentration is slightly higher, the bead structure and blend of fibers will be obtained.

• When the concentration is suitable, smooth nanofibers can be obtained.

• If the concentration is too high, spiral-shaped microstrips can be observed instead of nanoscale fibers.

Molecular weight of the polymer also has an important effect on fiber morphologies obtained by electrospinning. In principle, molecular weight reflects the entanglement of polymer chains in solutions. Smooth fibers can be obtained by increasing molecular weight. When the molecular weight is increased a little more, microstrips can be observed. However, for electrospinning, molecular weight is not always effective if intermolecular interactions can be supported by oligomers.

Solution viscosity is an important factor in calculating fiber morphology. It has been proven that continuous and smooth fibers cannot be obtained at very low viscosity, and too high viscosity causes difficulties in spraying jets from solution. Therefore, it is a requirement to have a suitable viscosity for electrostatic spinning. Generally, solution viscosity can be adjusted by varying the polymer concentration of the solution. Viscosity, polymer concentration and polymeric molecular weight are interrelated parameters.

Surface tension is a very important factor in electrospinning as a function of solvent mixtures of the solution. According to the researches, it has been observed that different solvents reveal different surface tensions. By improving the concentration, reducing the surface tension of the solution can lead to the conversion of droplet fibers into smooth fibers. Basically, surface tension determines the upper and lower limits of electrospinning when all other conditions are idealized.

Increasing the solution conductivity or charge density can be used to produce smoother fibers with fewer beads. Generally, natural polymers are generally poly-electrolytic and ions increase the charge-carrying ability of the polymer jet, causing high voltage under the electric field.

One of the most studied parameters among controllable variables is the applied voltage. Only when the applied voltage is higher than the threshold voltage charged jets begin to fly through the Taylor cone. At low voltages, the drop hangs on the tip of the needle, producing a jet spheroid-free spin that would be a Taylor cone. As the voltage

increases, the volume of the drop at the needle tip decreases, causing the Taylor cone to retract. When the voltage is increased a little more, the jet starts to circulate without a visible Taylor cone on the edge of the needle tip. Many particle structures can be observed under these conditions. As a result, the effect of voltage on the diameters of the formed fibers can be mentioned.

The flow rate of the polymer solution in the syringe is another important process parameter. In general, a low flow rate is recommended for the polymer solution to reach polarization in sufficient time. When the flow rate is too high, coarse-diameter particulate fibers will be formed instead of fine-diameter smooth fibers. This is due to the short drying time and low stretching force before the collector reaches the plate.

During electrostatic spinning, collector plates often act as a conductive substrate for collecting charged fibers. With the need to transfer fibers, various plates have evolved. These plates; a) wire mesh, b) pin, c) grid, d) parallel or grid bar, .e) rotating bars or cylinders, f) liquid bath and the like.

The distance between the collector plate and the syringe is known to affect fiber diameter and morphology. In short, when the distance is short, the fibers will not have enough time to solidify before reaching the collector plate. If the distance is too great, particulate fibers can be obtained. One of the important physical properties of fibers obtained by electrostatic spinning is solvent-induced dryness. It is therefore important to set the optimal distance.

Environmental parameters such as humidity and temperature can also affect fiber diameters and morphology. Increasing the temperature causes the fibers to form low diameter. This reduction in diameter is due to the decrease in viscosity of the high temperature polymer solution. Low moisture can cause the solvent to dry completely and increase the evaporation rate of the solvent. Increasing moisture results in the formation of small circular pores on the surface of the fibers. More moisture increase causes pores to merge.

When the concept of fiber in general is considered, the term "nano" refers to the size of the fiber diameter. One of the most important techniques developed to form fibers is the electrospinning method. With this production method, it is possible to obtain nano-sized, low weight and high mechanical strength biocompatible materials. Electrospinning technique is the process of converting fluid into nanoscale fibers by giving a kV tension to viscous liquids at very small flow rates [8-14]. The effects of working parameters on nanofiber and bead formation in electrospinning technique are shown in Figure 1.2.

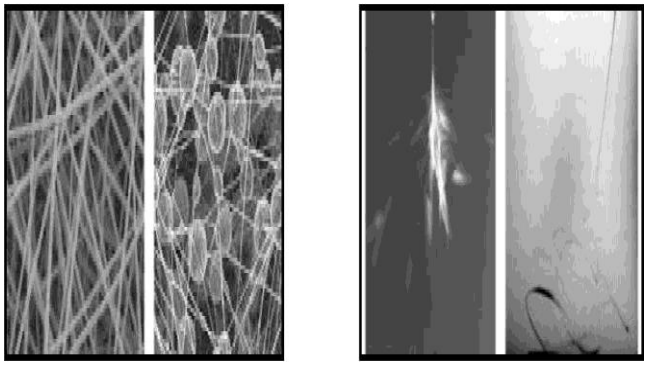

Figure 1.2. *Effects of working parameters on nanofiber and bead formation in electrospinning technique [15]*

Applying high voltage to the polymer solution is the key point of the electrospinning process. When voltage is applied, the electric field obtained affects the stretching and acceleration of the jet. The distance between the needle tip and the collector plate will determine the distance at which the jet will occur and affect the intensity of the electrostatic forces. At this distance, fiber formation occurs, the solvent is removed and the fiber solidifies, the time of storing the fiber in the collector takes place in the meantime. Feed rate is an important parameter affecting the speed of the jet and the material transfer rate [16]. Figure 1.3. shows cone formation in foals in electrospinning technique.

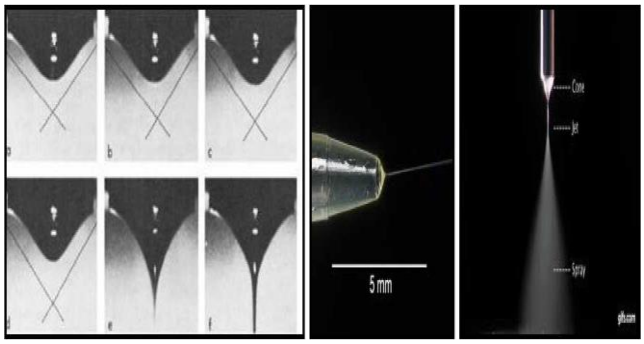

Figure 1.3. *Foal cone formation in electrospinning technique [17]*

In this study, electrospinning working parameters will be applied by using various polymers and it is aimed to investigate the effects on the morphology of polymeric membranes.

2. Material and Method

2.1. Material

Mw: 80.000 g/mol polycaprolactone (PCL) polymers, Mw: 85.000-124.000 g/mol polyvinyl alcohol (PVA) and commercial polyacrilonitrile (PAN), distile water, dimetilyformamide (DMF), chloroform, wax paper are used. Sigma-Aldrich brand was preferred as reference.

2.2. Method

2.2.1. Preparation of nanofiber membrane solutions

Table 2.1. Nanofiber membranes were obtained by using electrospinning technique by applying the values in Table 2.2. Production stages of polymeric membranes are

2.2.2. Characterization studies

FTIR structural analysis was determined using Jasco 6600, America, generated as a graph obtained over the 400-4400 cm^{-1} region. Tissues placed in the holders were examined and photographed with a ZEISS EVO SEM microscope. During the examination of the diameter and dimensions of the produced composite nanofibers, images magnified at x6000 times were examined for SEM analysis at 7 kV potential. The average diameter thickness of the nanofibers was measured on high resolution SEM photographs using Image j (National Health Organization) software. The mechanical (tensile) test was carried out by cutting the electrospun mats 1x5 cm in length according to the ASTM standard and repeating them 3 times under 500 Newton load.

3. Result and Discussion

3.1. FTIR analysis

When the functional groups of PCL, PVA and PAN polymers are examined, they overlap with the peaks in the FTIR graphs in Figure 3.1. FTIR graph of nanofiber membranes is given in Figure 3.1.

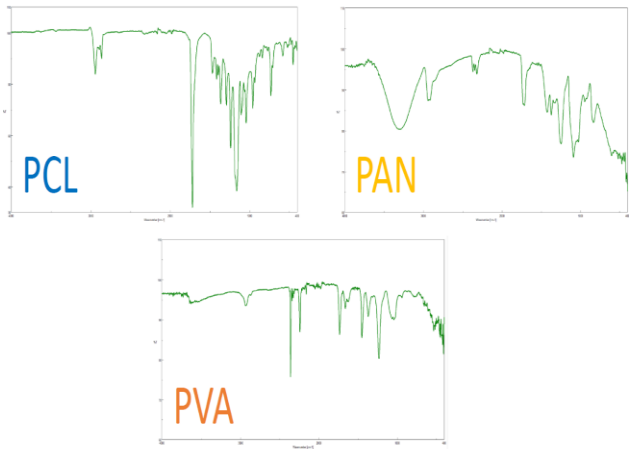

Figure 3.1. *FTIR plot of nanofiber membranes*

3.2. SEM analysis

Nanofiber formation was observed in all samples. PCL, PVA and PAN polymers were used by applying among themselves, one of the working parameters of electrospinning was variable. For this reason, when nanofiber membranes were examined, the thinnest nanofiber structure in the study was revealed in the 10% PVA sample [18-20]. Thinner nanofibers and a homogeneous morphology were obtained by only decreasing the voltage value. In Figure 3.2., there are SEM morphological images of nanofiber membranes.

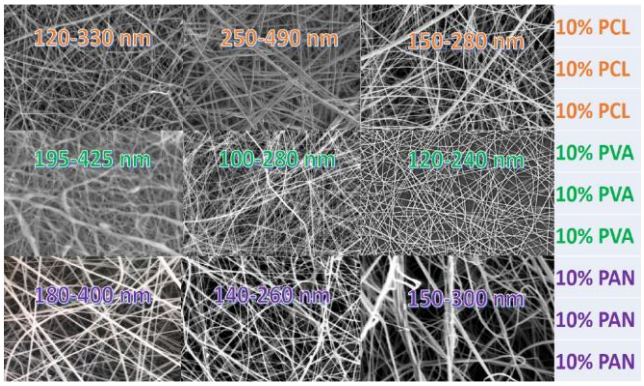

Figure 3.2. *SEM morphological images of nanofiber membranes*

3.3. Tensile test

All samples were prepared according to ASTM standards and each polymer sample was tensile strength values determined by taking arithmetic averages by performing a three-center retraction test among themselves. When we examine these samples in general, the highest tensile strength value in the study was determined in the 10% PCL sample. In the production of PCL membrane, only the

feeding flow is increased [20-24]. This increase caused a linear increase in tensile strength. Figure 3.3. shows the tensile test values of nanofiber membranes.

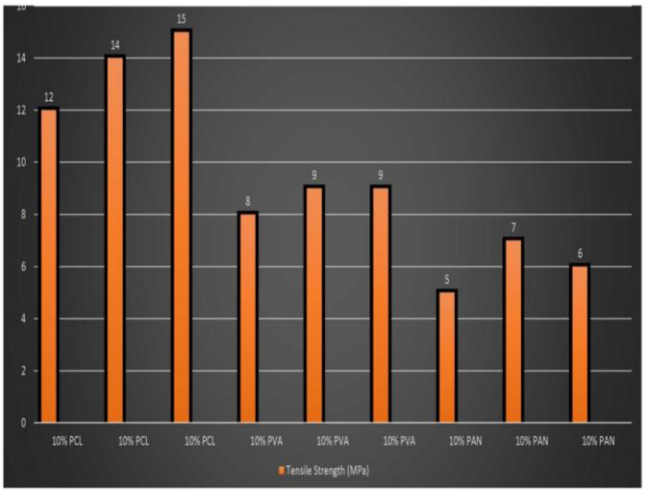

Figure 3.3. *Tensile strength values of nanofiber membranes*

4. Conclusion

In this study, purposeful membrane production was carried out using PCL, PVA, PAN polymers by electrospinning method. Nanofibers were obtained by applying two constant variable values as voltage, flow rate and working distance among PCL, PVA, PAN polymers. Voltage, flow and working distance cause significant changes on fiber morphology. It is related to mechanical properties according to morphological images. Mechanical strength increases and decreases according to the parameter change. The polymeric membranes obtained are aimed to be used for purposes in sectors such as health, filtration, defence, textile and agriculture.

References

[1] McNeil, S. E. (2005). Nanotechnology for the biologist. *Journal of leukocyte biology*, *78*(3), 585-594.

[2] Poole Jr, C. P., & Owens, F. J. (2003). *Introduction to nanotechnology*. John Wiley & Sons.E. Bulus, Fırat Üniversitesi Yüksek Lisans Tezi, (2017)

[3] Bulus, E., Sahin, Y. M., Darici, H., & Sener, L. T. Investigation of the Cellular Behavior of Polycaprolactone-Hydroxyapatite Tissue Materials Produced with Bioprinter, International Journal of Scientific and Technological Research, 5(1), 148-161. ISSN (online) 2422-8702.

[4] Cui, S., Kim, T. H., & Ham, U. (2020). Influence of the Tip Shape on Scanning Tunneling Luminescence Spectra: Implications for Nanomaterial Characterization. *ACS Applied Nano Materials*.

[5] Bulus, E., Mansiroglu, D. S., Ismik, D., Sahin, Y. M., Oktar, F. N., Gunduz, O., & Gokce, H. (2018). Bioceramic synthesis and characterization to be used in major tissue engineering applications. In 2018 Electric Electronics, Computer Science, Biomedical Engineerings' Meeting, EBBT 2018 (pp. 1–4). Institute of Electrical and Electronics Engineers Inc.

[6] He, C. H., Shen, Y., Ji, F. Y., & He, J. H. (2020). Taylor series solution for fractal Bratu-type equation arising in electrospinning process. *Fractals*, *28*(01), 2050011.

[7] Altinkok, C., Karabulut, H. F., Tasdelen, M. A., & Acik, G. (2020). Bile acid bearing poly (vinyl chloride) nanofibers by combination of CuAAC click chemistry and electrospinning process. *Materials Today Communications*, *25*, 101425.

[8] Buluş, E., Buluş, G. S., & Yakuphanoğlu, F. (2020). Production of polylactic acid-activated charcoal nanofiber membranes for COVID-19 pandemic by electrospinning technique and determination of filtration efficiency. *Journal of Materials and Electronic Devices*, *4*(1), 21-26.

[9] Buluş, E., Bulus, G. S., & Yakuphanoglu, F. (2020). Production and Characterization of Novel Nature-Friendly Organic Fertilizer Covers Based on Nanotechnology for the Agricultural Sector. *JOURNAL OF MATERIALS AND ELECTRONIC DEVICES*, *5*(1), 12-16.

[10] Ismik, D., Mansuroglu, D. S., Buluş, E., & Sahin, Y. M. (2020). The Use of Chitosan Nanoparticles Obtained by Ionic Gelation Method as a Drug Delivery System. *JOURNAL OF MATERIALS AND ELECTRONIC DEVICES*, *5*(1), 6-11.

[11] Bulus, E., Bulus, G. S., & Yakuphanoglu, F. (2020). Production and Characterization of Rechargeable Composite Nanofiber Membranes. *JOURNAL OF MATERIALS AND ELECTRONIC DEVICES*, *4*(1), 32-37.

[12] Duymaz, B. T., Erdiler, F. B., Alan, T., Aydogdu, M. O., Inan, A. T., Ekren, N., … Gunduz, O. (2019). 3D bio-printing of levan/polycaprolactone/gelatin blends for bone tissue engineering: Characterization of the cellular behavior. European Polymer Journal, 119, 426–437. https://doi.org/10.1016/j.eurpolymj.2019.08.015

[13] Buluş, E., Sakarya Buluş, G., & Şahin, Y. M. (2020). Production and Characterization of Nanotechnological Tape for Wounds Caused by Diabetes. JOURNAL OF MATERIALS AND ELECTRONIC DEVICES, 5(1), 20-24.

[14] Altinkok, C., Karabulut, H. F., Tasdelen, M. A., & Acik, G. (2020). Bile acid bearing poly (vinyl chloride) nanofibers by combination of CuAAC click chemistry and electrospinning process. *Materials Today Communications*, *25*, 101425.

[15] Celebioglu, A., & Uyar, T. (2020). Electrospinning of cyclodextrins: hydroxypropyl-alpha-cyclodextrin nanofibers. *Journal of Materials Science*, *55*(1), 404-420.

[16] Wang, D., Yue, Y., Wang, Q., Cheng, W., & Han, G. (2020). Preparation of cellulose acetate-polyacrylonitrile composite nanofibers by multi-fluid mixing electrospinning method: Morphology, wettability, and mechanical properties. Applied Surface Science, 510, 145462.

[17] Keaswejjareansuk, W., Wang, X., Sisson, R. D., & Liang, J. (2020). Electrospinning process control for fiber-structured poly (Bisphenol A-co-Epichlorohydrin) membrane. *AIMS Materials Science*, *7*(2), 130.

[18] Wu, Y. K., & Liu, Y. (2020). Fractal-like multiple jets in electrospinning process. *Thermal Science*, *24*(4), 2499-2505.

[19] Li, Y., Dong, A., & He, J. (2020). Innovation of Critical Bubble Electrospinning and Its Mechanism. *Polymers*, *12*(2), 304.

[20] Sarkar, K., Gomez, C., Zambrano, S., Ramirez, M., de Hoyos, E., Vasquez, H., & Lozano, K. (2010). Electrospinning to forcespinning™. *Materials today*, *13*(11), 12-14.

[21] Thompson, C. J., Chase, G. G., Yarin, A. L., & Reneker, D. H. (2007). Effects of parameters on nanofiber diameter determined from electrospinning model. Polymer, 48(23), 6913-6922.

[22] Zhang, F., Zuo, B., Fan, Z., Xie, Z., Lu, Q., Zhang, X., & Kaplan, D. L. (2012). Mechanisms and control of silk-based electrospinning. *Biomacromolecules*, *13*(3), 798-804.

[23] Tan, S. H., Inai, R., Kotaki, M., & Ramakrishna, S. (2005). Systematic parameter study for ultra-fine fiber fabrication via electrospinning process. Polymer, 46(16), 6128-6134.

[24] Padmanabhan, T., Kamaraj, V., Magwood Jr, L., & Starly, B. (2011). Experimental investigation on the operating variables of a near-field electrospinning process via response surface methodology. *Journal of manufacturing Processes*, *13*(2), 104-112.