

Influence of Molecular Weight on the Morphology and Structure of Electrospun Polyvinylidene Fluoride (PVDF)

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Abstract. Polyvinylidene fluoride (PVDF) reveals outstanding properties such as lightweight, high flexibility and temperature independence material compared to other polymers. In this study, PVDF as a function of molecular weight was prepared by using an electrospinning method in order to study the influences of the molecular weight of the PVDF membrane on the morphology. Analytical techniques such as field emission scanning electron microscope (FESEM), Fourier transform infrared (FTIR) and X-ray diffraction (XRD) were used to characterize the electrospun PVDF membranes. FESEM was used for morphology characterization and also to measure the diameter of fibers while XRD and FTIR were employed to examine crystalline phase membranes. The lowest molecular weight has the smallest average diameter of fibers. Besides, a combination of both α -phase and β -phase crystalline was showed by XRD and FTIR results. This is because the crystalline phases and membrane morphology depend on the polymer molecular weight. In this research, it was found that the largest β -phase fraction for the electrospun PVDF membrane is 80.25 % with a molecular weight at 180,000 g/mol.

Introduction

For the previous decades, a tremendous increase in the usage of PVDF membrane for several applications such as in some biomedical materials, electrical components and filtration membranes [1, 2, 3]. PVDF has been widely analyzed as it comes by with high flexibility, lightweight and temperature independence material.

PVDF is a semi-crystalline polymer with five well-known crystalline phases which are α , β , γ , δ and ϵ phases. Among all the five crystalline phases, PVDF tends to produce α -phase, β -phase and γ -phase. The α -phase is a regular crystalline phase that is found in a PVDF melt while the γ phase does not form except at high temperatures and pressures. Besides, the β -phase PVDF is obtained by methods poling or annealing at very high pressure. However, the β -phase exhibits great electrical characteristics including piezoelectric, pyroelectric and ferroelectric properties [4].

Therefore, many researches work on change α -phase to β -phase crystalline or directly produce β -phase. Based on the previous study, PVDF membrane was successfully prepared by using electrospinning method which in turn increased the formation of β -phase [5]. Nevertheless, important to assess of PVDF's internal features as with molecular weight and crystal structure.

The polymer's molecular weight also has an impact on the deformation and flow of polymer solution as well as on the dissolution of a polymer in the solvent at a temperature [6]. Thus, PVDF have been developed using various method with different molecular weight for numerous applications. For example, Haponska *et al.* [7] were prepared PVDF by the immersion precipitation method while Zhao *et al.* [8] synthesized PVDF through a solution casting method and a quenching treatment. In this work, PVDF with different molecular weight by using electrospinning was studied. The effects of molecular weight on membrane morphology and structure were investigated.

Experimental

Materials. Polyvinylidene fluoride (PVDF, Mw = 180,000, 275,000, 530,000 and 1,000,000 g/mol) from Sigma-Aldrich were used as received while N, N-dimethylformamide (DMF) and acetone were purchased from R&M Chemicals.

Synthesis of Electrospun PVDF Membrane. Electrospun PVDF of multiple molecular weight was synthesized by using the electrospinning method. PVDF solutions were synthesized by dissolving PVDF granule in the mixed solvents of dimethylformamide (DMF) and acetone with 70:30 volumetric percentages. Both solvents have a high dielectric constant in the range of 20.7 – 30.7 therefore better suited for electrospinning. The PVDF solutions with four different molecular weight were prepared at a concentration of 13 wt% and stirred well at 70 °C for 12 hours in a beaker. During electrospinning, the homogenous PVDF solution was then ejected by using a plastic syringe. The experimental conditions for electrospinning, which including applied voltage, distance between needle and collector, flow rate, needle size, temperature were standardized at 13 kV, 15 cm, 2.5 ml/h, 20-gauge needle and ambient temperature.

Characterization of Electrospun PVDF Membrane. The field emission scanning electron microscope (FESEM); JSM-7800F that provides images at a very high magnification & resolution (1.3nm at 30kV) has been used to appraise the morphology of the PVDF membranes with different molecular weight by electrospinning. Before the observations, all the samples were cut off with a maximum size of 3 cm × 3 cm. The average membrane diameter of the electrospun PVDF was measured on 30,000 x magnified FESEM images.

An analysis of the polymer crystalline phase was performed using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The XRD was undertaken as a qualitative crystal structure evaluation for all samples using a Bruker D8 Advance X-Ray Diffractometer with a step size (2θ) of 0.02° and 57.6 s scan step time. The current and voltage used were 40 mA and 40 kV, respectively. The samples were analyzed in the 2θ range of 10 to 35 degree. The FTIR measurements were performed from 1,900 to 400 cm^{-1} at room temperature in a Perkin-Elmer Spectrum 100 apparatus in attenuated total reflection (ATR) mode.

Results and Discussion

Figure 1 illustrates the FESEM images of electrospun PVDF membranes fabricated from a different types of molecular weight with the same concentration by using the electrospinning process. The observed electrospun membranes exhibited high porosity and fully interconnected pores. The porosity of fibers is an advantage, especially in nanofiber membranes, because it will increase the surface area. Moreover, based on the FESEM images, the PVDF membranes produced also have a uniform and non-beaded fibers because of the electrostatic force between needle and collector during electrospinning [9, 10]. Table 1 presents the calculated fiber diameter. It was observed that the average diameters of electrospun fibers were increased with increasing the PVDF molecular weight. At low molecular weight, the electrospun PVDF membrane holds the smallest average fiber diameter of 72.84 nm whereas PVDF of 530,000 g/mol possesses the largest average fiber diameter. An increment of molecular weight of PVDF from 275,000 g/mol to 530,000 g/mol causes an increase of approximately 21 % in the diameter of electrospun fibers from 113.42 nm to 175.24 nm while a further increase of the molecular weight to 1,000,000 g/mol leads to thinner fibers as shown in Figure 2. The widespread diameter distribution may be due to an unstable electrical force [3].

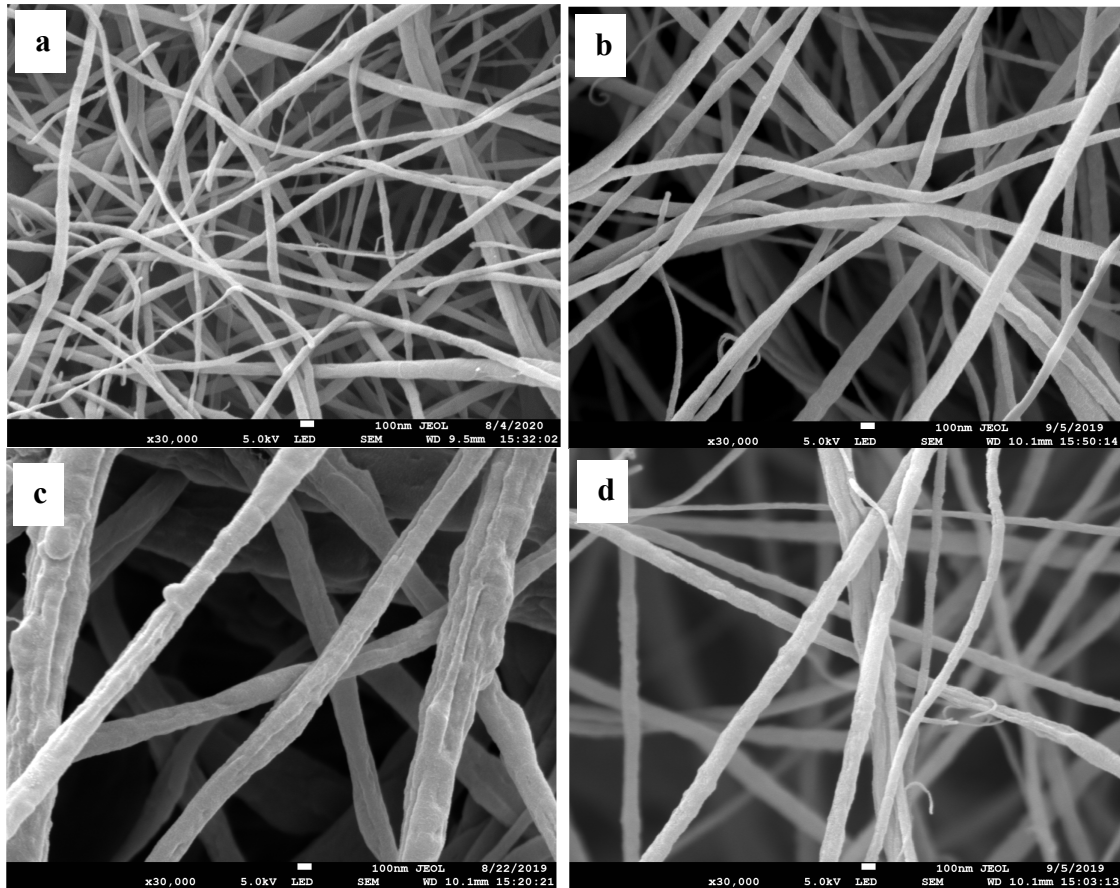


Figure 1. FESEM images (30,000X) of electrospun PVDF membranes prepared using molecular weight (a) 180,000 g/mol (b) 275,000 g/mol (c) 530,000 g/mol (d) 1,000,000 g/mol (scale bar: 100 nm).

Table 1. Average diameter and fraction of β -phase of the electrospun PVDF membranes with different molecular weight.

Samples PVDF/molecular weight [g/mol]	Fiber diameter [nm]	F_{β} [%]
180,000	72.84	80.25
275,000	113.42	62.89
530,000	175.24	66.53
1,000,000	136.13	54.42

In the ATR-FTIR spectra as shown in Figure 3, the absorption peaks of α -phase appear at 763 and 1402 cm^{-1} . Then, the peaks at 470 cm^{-1} , 510 cm^{-1} , 840 cm^{-1} and 1276 cm^{-1} , which were associated with the β -phase [11, 12, 13]. Meanwhile, Figure 3 was obvious to be observed that the highest peak at 1402 cm^{-1} from spectra electrospun PVDF (Mw = 180,000 g/mol). Therefore, in one step of the electrospinning process, β -phase crystalline in electrospun PVDF membrane can be developed without any additional steps such as drawing, poling and annealing. These FTIR absorption bands follow Beer-Lambert law. The fraction of β -phase can be determined by the following equation by using the typical absorption bands of α and β -phases at 763 cm^{-1} and 840 cm^{-1} :

$$F(\beta) = \frac{X_{\beta}}{X_{\alpha} + X_{\beta}} = \frac{A_{\beta}}{1.26A_{\alpha} + A_{\beta}} \quad (1)$$

where X_{α} and X_{β} are α and β phases crystalline mass fractions while A_{α} and A_{β} refer to 763 cm^{-1} and 840 cm^{-1} absorption waves. The results of β -phase fraction are shown in Table 1. PVDF membrane

with a molecular weight, 180,000 g/mol has the highest β -phase fraction, 80.25 %. A rocking vibration in the PVDF chain is defined by the 763 cm^{-1} absorption peak [14]. The absorption band at 470 cm^{-1} related to the bending and wagging vibration of CF_2 groups [15].

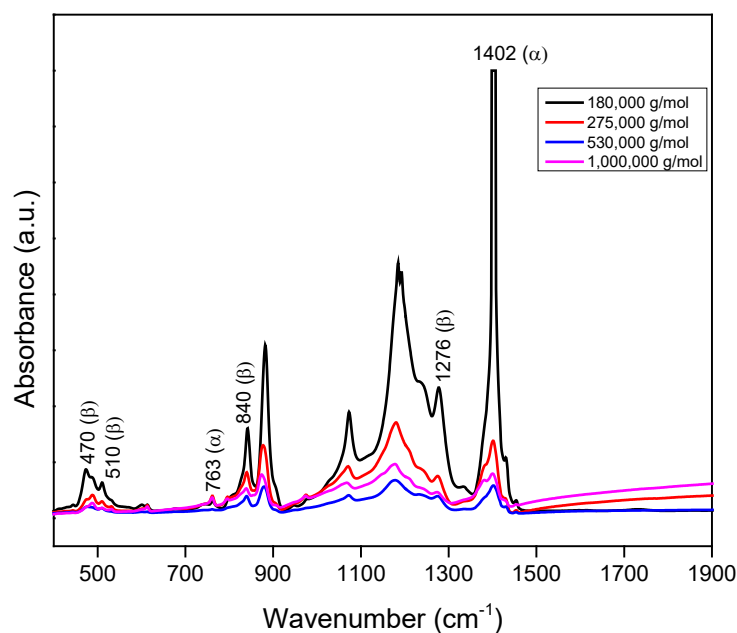


Figure 3. FTIR spectra of PVDF membranes with different molecular weight.

The XRD patterns, as shown in Figure 4, indicate the coexistence of both α and β -phases of the electrospun PVDF membranes with four different types of molecular weight which act as a manipulated variable in this research. The peaks at 2θ corresponding to 18.4° (0 2 0) and 20.13° (1 1 0) were assigned to the α -phase of PVDF whereas the β -phase of PVDF located at 20.8° (1 1 0) and 20.0° (1 1 0) [16-21]. The peak at 18.4° is equal to the α -phase diminished in intensity for electrospun membrane especially for electrospun PVDF (530,000 g/mol). As seen from Figure 4, the peak intensity of the β -phase at $2\theta = 20.0^\circ$ for sample PVDF membrane (180,000 g/mol) more accurate compared with the β -phase peak intensities at 20.8° . However, β -phase at 20.8° was absent for electrospun PVDF (1,000,000 g/mol) while from XRD diffractions, the broad peak around 20° appeared for electrospun PVDF membrane with molecular weight 275,000 g/mol. The wide peak within about 20° intersected the α -phase and β -phase peaks correspond to the amorphous area of the PVDF [22]. In addition, for the samples shown in Figure 4, the electrospun PVDF membrane with the lowest molecular weight is differentiated from the other membranes with the highest sharp peak at $2\theta = 20.0^\circ$, which points out more β -phase crystalline content in the membrane. Hence, this result supported the calculated β -phase fraction, $F(\beta)$ from Table 1. Therefore, the optimum molecular weight of electrospun PVDF is 180,000 g/mol to produce the highest β -phase crystalline content. Besides, FTIR and XRD demonstrate that β -phase crystalline formation is caused by the electrospinning process.

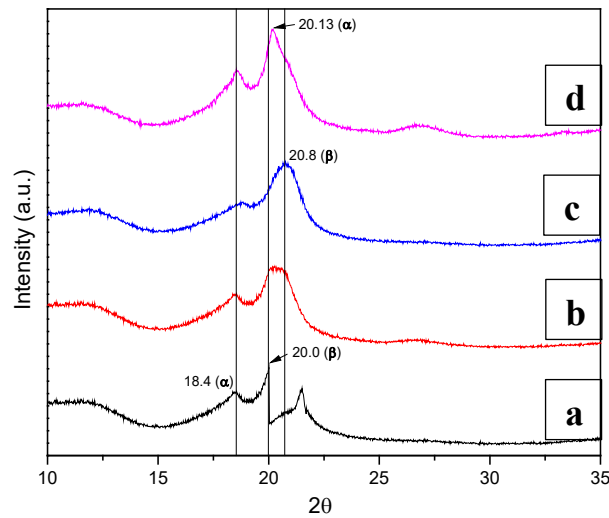


Figure 4. X-ray diffractograms of electrospun PVDF membranes with (a) 180,000 g/mol (b) 275,000 g/mol (c) 530,000 g/mol (d) 1,000,000 g/mol.

Conclusion

In this paper, the PVDF membranes with different molecular weight and membranes with the predominant β phase were fabricated. The electrospinning process has successfully produced the formation of β -phase crystalline in PVDF membranes based on FTIR and XRD results. Based on both results, it was observed that the membranes are impacted by the molecular weight of polymer as well as PVDF with the smallest molecular weight showed the highest fraction β -phase. FESEM images demonstrated that PVDF molecular weight influences membrane morphologies.

Acknowledgment

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