

Influence of molecular weight on dielectric properties and piezoelectric constant of poly(vinylidene fluoride) membranes obtained by electrospinning^{*})

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Abstract: A significant influence of the molecular weight on the dielectric properties and piezoelectric constant of poly(vinylidene fluoride) (PVDF) membranes obtained by electrospinning was demonstrated. Electrochemical impedance spectroscopy and d_{33} meter were used to evaluate dielectric properties and piezoelectric constant respectively. The presence of the β -phase was determined by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The membranes with the lowest molecular weight (180,000 g/mol) possessed the best dielectric properties. They also had the highest piezoelectric constant (21 pC/N) and dielectric constant (2.9 at 50 Hz) as well as the highest β -phase content (80.25%).

Keywords: piezoelectric constant, poly(vinylidene fluoride), electrospinning, molecular weight.

Wpływ masy cząsteczkowej na właściwości dielektryczne i stałą piezoelektryczną membran poli(fluorku winylidenu) otrzymanych metodą elektroprzędzenia

Streszczenie: Wykazano istotny wpływ masy cząsteczkowej na właściwości dielektryczne i stałą piezoelektryczną membran poli(fluorku winylidenu) (PVDF) otrzymanych metodą elektroprzędzenia. Do oceny stałej piezoelektrycznej i właściwości dielektrycznych stosowano, odpowiednio, miernik d_{33} i spektroskopię impedancyjną. Obecność fazy β określono za pomocą spektroskopii w podczerwieni z transformacją Fouriera (FTIR) i dyfrakcji rentgenowskiej (XRD). Membrany o najmniejszej masie cząsteczkowej (180 000 g/mol) charakteryzowały się najlepszymi właściwościami dielektrycznymi. Miały również największą stałą piezoelektryczną (21 pC/N) i stałą dielektryczną (2,9 przy 50 Hz) oraz największą zawartość fazy β (80,25%).

Słowa kluczowe: stała piezoelektryczna, poli(fluorek winylidenu), elektroprzędzenie, masa cząsteczkowa.

Poly(vinylidene fluoride) (PVDF) is a semicrystalline polymer with an excellent piezoelectric and dielectric properties, thus it is very useful in electronics as sensors, actuators and capacitors [1, 2]. It has a repeating unit of $-\text{CH}_2\text{CF}_2-$ monomer which acts as a dipole due to the fluorine's highest electronegativity in the periodic table. The arrangement of these repeating units in PVDF directly controls the net dipole moment and orientation of dipoles.

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There are three well-known PVDF crystalline phases, α , β and γ , where α -phase is the most common in melt crystallization. High temperature and pressure are the only factors that induce the γ -phase to develop whereas the β -phase is produced via poling or annealing at high pressure. Due to the orientation of all dipole chains in the same direction, the β -phase PVDF with high dipole moment induces strong spontaneous polarization in a unit cell, which is a desirable feature of pyro-, ferro- and piezoelectric properties [3–5]. Besides, Martion *et al.* reported higher piezoelectric constant of the PVDF membrane with the greatest β -phase content than the membrane with lower β -phase content [6]. Thus, most of researchers focused on creating high β -phase content in PVDF by using different methods, such as mechanical stretching, additives, electrospinning and electrical poling [7].

Recently, the electrospinning process allows for synthesis of PVDF membranes which increased the formation of β -phase [6, 8]. In addition, it is an easy and inexpensive method of producing ultrafine fibers with sizes ranging from a few micrometers to hundreds of nanometers [9, 10]. Moreover, electrospun nanofibers have one-dimensional morphology, high surface area, extraordinary length and high porosity.

Since recognizing the effect of intrinsic characteristics such as molecular weight and crystal structure are crucial to obtain high piezoelectric constant and dielectric properties of PVDF, in this study we focused on the influence of the molecular weight of PVDF on these properties.

EXPERIMENTAL PART

Materials

Poly(vinylidene fluoride) (PVDF) with molecular weights of 180,000; 275,000; 530,000 and 1,000,000 g/mol were purchased from Sigma-Aldrich whereas R&M Chemicals provided *N,N*-dimethylformamide (DMF) and acetone.

Methods

PVDF granules were dissolved in a 70:30 volumetric ratio of DMF and acetone to produce solutions of PVDF with various molecular weights at a concentration of 13 wt%. PVDF solutions were swirled thoroughly for 12 hours at 70°C. DMF and acetone both have high dielectric constant in the range of 20.7–30.7, so it makes them suitable for electrospinning. The electrospinning parameters were established to be 13 kV applied voltage, 15 cm distance between collector and needle, 2.5 ml/h PVDF solution flow rate, 5 ml syringe and 20-gauge needle were used.

The JSM-7800F field emission scanning electron microscope (FESEM), which delivers images at very high magnification and resolution (1.3 nm at 30 kV), was used to study the morphology of PVDF membranes. All membrane samples were cut into squares with a length of 3 cm and the average membrane diameter of the electrospun PVDF was measured on 30,000 \times magnified FESEM images. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) were used for examination of the crystalline phases of PVDF. ATR-FTIR measurements were taken from 1500 to 400 cm^{-1} using the

Perkin-Elmer Spectrum 100 apparatus in attenuated total reflection (ATR) mode. The Bruker D8 Advance X-Ray Diffractometer was employed for XRD, with a step size (2θ) of 0.02°, current and voltage of 40 mA and 40 kV respectively. The area and thickness of electrospun membranes were measured and after sandwiching between two stainless steel electrodes their dielectric properties were specified using electrochemical impedance spectroscopy (EIS) at ambient temperature. The dielectric constant, ϵ' , and dielectric loss, $\tan \delta$, were calculated from complex impedance EIS data using Equations 1–3 [11].

$$\epsilon' = \frac{t}{\omega A \epsilon_0} \frac{Z''}{Z'^2 + Z''^2} \quad (1)$$

$$\epsilon'' = \frac{t}{\omega A \epsilon_0} \frac{Z'}{Z'^2 + Z''^2} \quad (2)$$

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (3)$$

where:

t – thickness of the electrospun membrane, A – cross-sectional area of the membrane, ω – angular frequency, ϵ_0 – permittivity of free space, Z' – real part of the impedance and Z'' – imaginary part of the impedance.

Finally, the piezoelectric constants of the electrospun PVDF membranes were measured using commercial quasi-static d_{33} meter (90-2030, APC International, Ltd) at 50 Hz frequency. This instrument is able to directly measure the d_{33} values of piezoelectric materials.

RESULTS AND DISCUSSION

FESEM images of electrospun PVDF membranes with various molecular weight and the same concentration are shown in Figure 1. The membranes had high porosity and linked pores. The high fiber porosity increases the surface area. Furthermore, due to the interaction of electrostatic forces between the needle and the collector during electrospinning, the PVDF membrane comprised of uniform fibers rather than beads [12, 13]. Table 1 illustrates the calculated fiber diameters; it is shown that as the PVDF molecular weight increased, the average diameters of electrospun fibers increased as well. The 180,000 g/mol PVDF membrane had the least average fiber diameter of 72.84 nm while the 530,000 g/mol PVDF membrane had the greatest one. The molecular weight increase from 180,000 to 530,000 g/mol led to the increase of the diameter of electrospun fibers by almost 41%, from

Table 1. Average fiber diameters, fraction of β -phase and piezoelectric constant of the electrospun PVDF membranes

PVDF molecular weight, g/mol	Fiber diameter, nm	F_{β} %	Piezoelectric constant, d_{33} , pC/N
180,000	72.84	80.25	21.0
275,000	113.42	62.89	15.9
530,000	175.24	66.53	17.0
1,000,000	136.13	54.42	14.5

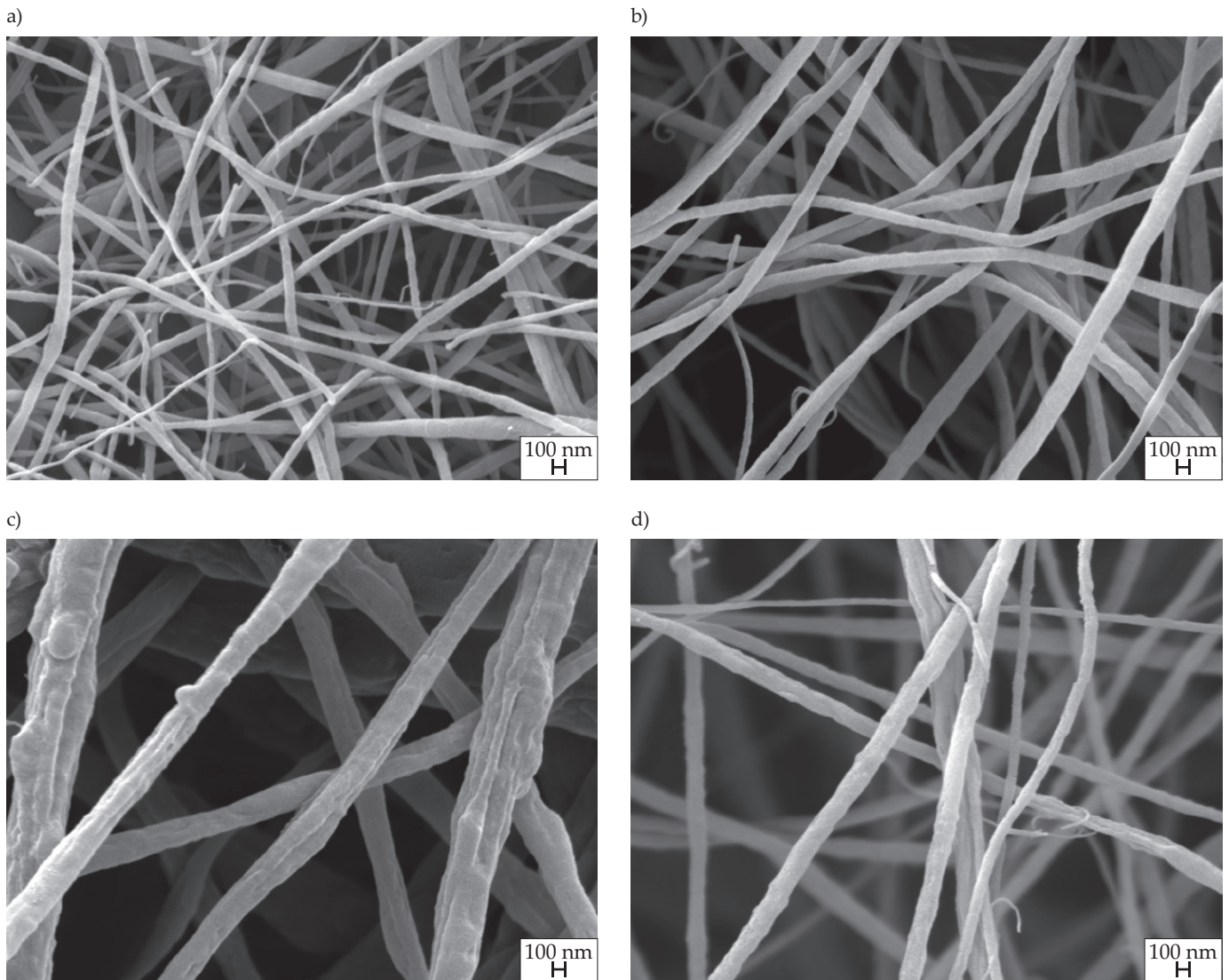


Fig. 1. FESEM images of electrospun PVDF membranes of: a) 180,000 g/mol, b) 275,000 g/mol, c) 530,000 g/mol, d) 1,000,000 g/mol; all images are reported at scales of 100 nm

72.84 nm to 175.24 nm, while increasing the molecular weight up to 1,000,000 g/mol resulted in thinner fibers. The width of the diameter of 530,000 g/mol PVDF membrane was caused by an unstable electrical force during the fabrication of electrospun PVDF [2].

As shown in the ATR-FTIR spectra in Figure 2, two kinds of crystalline phases appeared in electrospun PVDF: α -phase and β -phase. The β -phase was present most frequently in all samples of electrospun PVDF. Therefore, the β -phase was successfully obtained by electrospinning without the need to do post-treatment such as drawing and annealing. The β -phase crystals existing in a material [2, 14–15] leads to efficient piezoelectricity and dielectric properties. At 614, 763 and 970 cm^{-1} , the characteristic bands corresponded to the α -phase [2, 9]. Besides, the absorption peaks at 482, 510, 599, 840, 1275 and 1400 cm^{-1} corresponded to the β -phase [1, 6, 8, 16–18].

The absorption band at 763 cm^{-1} was associated with the rocking vibration while CH_2 twisting was associated at 970 cm^{-1} . At 1400 cm^{-1} , PVDF membranes presented

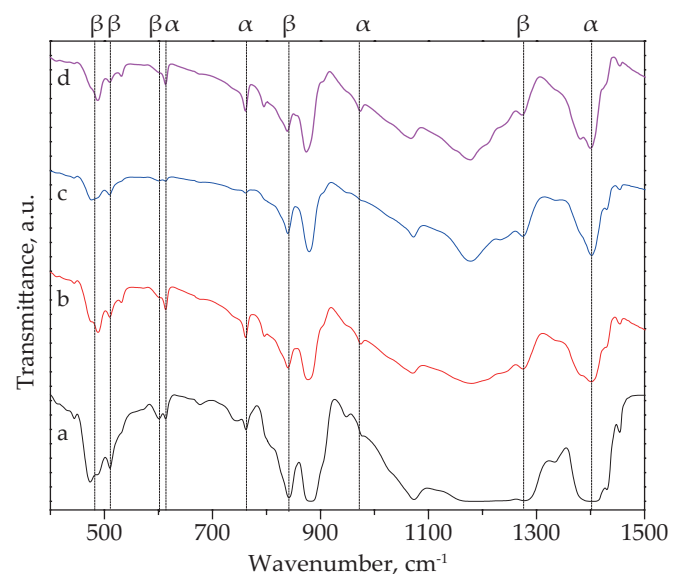


Fig. 2. FTIR spectra of PVDF membranes with molecular weight: a) 180,000 g/mol, b) 275,000 g/mol, c) 530,000 g/mol, d) 1,000,000 g/mol

sharp absorption which implied an in-plane bending vibration of $-\text{CH}_2$ [19]. A combined form of CH_2 rocking and CF_2 asymmetric stretching vibration was assigned to the band at 840 cm^{-1} , while a CF_2 bending was allocated to the band at 510 cm^{-1} [20–21]. Moreover, the fraction of β -phase, F_{β} , could be determined by FTIR data (Table 1). The largest β -phase content (80.25%) characterized the 180,000 g/mol PVDF membrane and decreased with increasing molecular weight. Thus, this indicates that molecular weight influenced the development of the β -phase in PVDF during electrospinning.

XRD results (Figure 3) show the existence of both α - and β -phase in electrospun PVDF membranes. The α -phase of PVDF had peaks at 18.4° (020) and 20.13° (110) while the β -phase of PVDF had peaks at 20.8° (110) and 20.0° (110) [2, 22–27]. 180,000 g/mol PVDF membrane had a diffraction peak at $2\theta = 21.0^\circ$, equivalent to the overlapping (110) and (200) reflections of β -crystals with low intensity diffraction peak at 18.4° . For electrospun membrane, notably electrospun PVDF with a molecular weight of 530,000 g/mol, the peak at 18.4° decreased in intensity. Then, the peak intensity at 20.0° for the 180,000 g/mol PVDF membrane was more precise than the peak intensity at 20.8° . However, there was no peak corresponding to β -phase at 20.8° for the 1,000,000 g/mol PVDF membrane [28]. Moreover, the electrospun 180,000 g/mol PVDF membrane was distinguished from the other membranes with the sharpest peak at $2\theta = 20.0^\circ$ and 21.0° , which indicated the membrane greater β -phase content. As a result, the calculated β -phase fraction (F_{β} , Table 1) was verified. Therefore, the molecular weight of electrospun PVDF that produces the maximum β -phase content is 180,000 g/mol.

Figures 4a and b illustrate the dielectric constant, ϵ' , and dielectric loss, $\tan \delta$, as a function of frequency. It can be established that the dual dielectric properties of

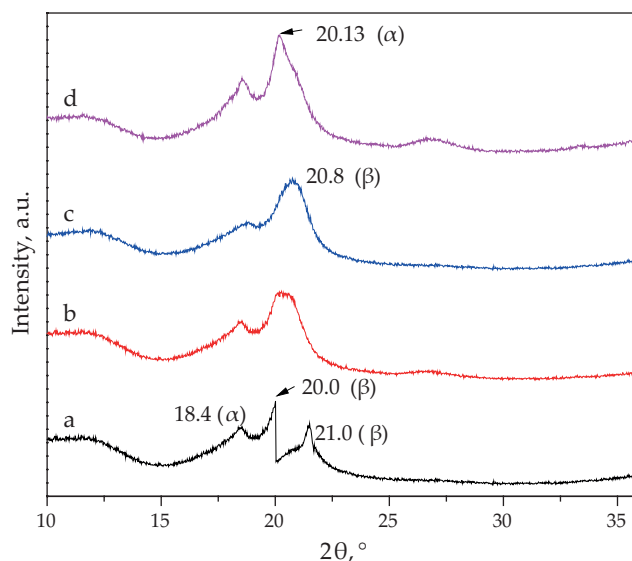


Fig. 3. XRD graph of PVDF membranes with: a) 180,000 g/mol, b) 275,000 g/mol, c) 530,000 g/mol, d) 1,000,000 g/mol

all membranes decreased with increasing of frequency. It is the result of dipoles orientation movement in the crystalline-amorphous of PVDF [29]. The ϵ' of all membranes was exceptionally high in the low frequency region, as seen in Figure 4a, however, as the frequency was risen, the dielectric constant dropped due to the inability of the electric dipole to cooperate with the change of electric field applied. Moreover, the ϵ' of these electrospun PVDF membranes against the frequency exhibited and evident reduction around 150 Hz until the end of the frequency (100 kHz). The ϵ' at frequency of 50 Hz for all the samples was decreased which is consistent with the F_{β} content in electrospun PVDF membranes, indicating that the molecular weight influences the dielectric constant. Thus, 180,000 g/mol PVDF is the optimum molecu-

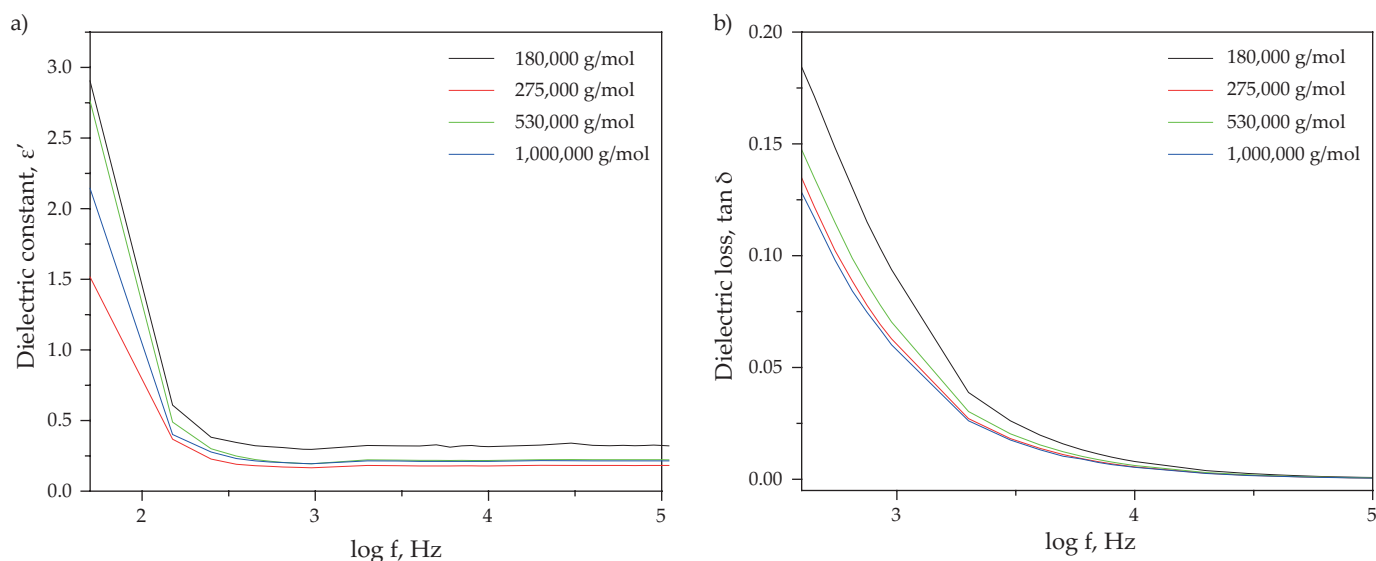


Fig. 4. The dielectric constant (a) and the dielectric loss (b) of electrospun PVDF membrane at ambient temperature with various molecular weights

lar weight to get a high dielectric constant. The crystalline β -phase of PVDF is most likely responsible for the significant effect of the ϵ' [20, 29].

Dielectric loss is defined as the amount of power loss in dielectric material under the influence of the applied voltage of the field. It can change with frequency, temperature, composition, orientation, pressure and molecular structure of a material. As shown in Figure 4b, the dielectric loss, $\tan \delta$, curves of the electrospun PVDF membranes decreased with an increase of frequency. However, all the samples showed constant $\tan \delta$ values throughout the frequency at the range 1–100 kHz. For all membranes, energy dissipation was extremely low for $\tan \delta$ calculated below 0.2. Because the dipoles responsible for polarization could no longer follow the oscillation of the electric field at these frequencies in the presence of alternating current, the $\tan \delta$ continued to drop down with frequency [29]. Additionally, the $\tan \delta$ curves of the electrospun PVDF membranes were comparable and there was just a minor difference at the high frequency. Consequently, the dissipation factor of PVDF membranes is unaffected by their molecular weight.

Finally, the piezoelectric constant, d_{33} , was measured and listed in Table 1. With 21 pC/N, the electrospun 180,000 g/mol PVDF membrane demonstrated the highest piezoelectric constant while the lowest piezoelectric constant belonged to the electrospun 1,000,000 g/mol PVDF membrane (14.5 pC/N). The d_{33} of PVDF membranes are consistent with changes of ϵ' and $\tan \delta$, showing that the lowest molecular weight has the highest d_{33} , ϵ' and $\tan \delta$ since it has the highest β -phase content. Thus, the crystalline β -phase is responsible for the increase of piezoelectric constant in PVDF. The β -phase is the most attractive conformation with the greatest polarity, hence, a piezoelectric effect depending on their molecular structure [14–15].

CONCLUSION

PVDF membranes with a high β -phase content were successfully synthesized using electrospinning process. PVDF molecular weight affected membrane morphologies and its decrease reduced the average fiber diameter. The molecular weight greatly impacted the dielectric properties and piezoelectric constant. The studied PVDF membrane with molecular weight of 180,000 g/mol showed the highest β -phase content and had the highest dielectric properties and piezoelectric constant.

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