

Dielectric Behavior and Transport Properties of Electrospun Polyvinylidene Fluoride Nanofiber Membrane

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ABSTRACT

Poly (vinylidene fluoride) (PVDF) is a chemical resistance polymer with high ferroelectric, piezoelectric and pyroelectric properties. PVDF has been chosen due to its unique properties compared with others in the polymers family and is used in a variety of sensors and transducers. A PVDF nanofiber membrane with relatively uniform morphology was prepared by an electrospinning technique. The surface morphology of the electrospun PVDF nanofibers was observed by scanning electron microscopy (SEM). The microstructure of electrospun PVDF nanofibers was characterized by Fourier Transform Infrared spectroscopy (FTIR) in the range 400 to 4000 cm^{-1} . The functional groups were identified in the membrane. Infrared vibrational spectroscopy (FTIR + Raman) curves revealed a ferroelectric β -phase in the un-annealed membrane intrinsically. It showed that the electrospinning technique induce crystalline and polar β -phase by applying an electric field to the PVDF polymer solution during high solution jet stretching. The membrane (7 mm x5 mm) with full-face copper electrodes was produced to form a capacitor for testing.

Keywords

PVDF, Nanofiber, Membrane, Pressure sensors.

Introduction

In the recent past, flexible electronic technology has been getting attention for potential applications in foldable and portable devices [1]. Poly vinylidene fluoride (PVDF) exhibits the finest electroactive properties, namely piezo, pyro, ferroelectricity, and optoelectronic. As a result, PVDF and its copolymers are attractive materials for increasing the number of possible organic microelectronics applications, such as electro-optic transducers, waveguides, sensors, actuators, energy harvesting, electro-optic memory, biomimetic robotics, and tissue engineering [1-5]. PVDF is a highly polar material, where concerning carbon atoms in the unit, the hydrogen atoms are positively charged, and the fluorine atoms are negatively charged. The repeat unit of $(-\text{CH}_2-\text{CF}_2)$ or $(\text{CH}_2\text{CF}_2)_n$, in which the carbon-hydrogen bonds with the electrically

polar carbon-fluorine, can take up several stable configurations. PVDF can be formed into at least four different polymorphous phases which depends on the film preparation conditions. Two forms β (or I) and α (or II) are of particular importance. In the form α , PVDF is non-piezoelectric, the bonds are in a trans-gauche-trans-gauche configuration, and the molecules are stacked, giving a nonpolar unit cell. The α phase can be converted into β form by stretching or electrically poling with an appropriate electric field. All-trans configuration in the β form exists in the molecular groups, molecules assembling to provide a polar unit cell.

Based on the above-cited applications, it is warranted to investigate the dielectric and ac transport properties of this vital polymer. Dielectric spectroscopy is a powerful tool to research molecular dynamics and relaxation processes in complex materials. Furthermore, limited systematic research has been performed on PVDF electrospun membrane. Thus, the present work's main aim

is to characterize dielectric and conduction mechanisms in PVDF membranes.

Experimental

Fabricating electrospun membrane

PVDF was dissolved in the solution of dimethylacetamide (DMA, analytical standard, Fisher Scientific) to yield a polymer solution with a concentration of 20 wt. %. It was mechanically stirred for 3 hours at a constant speed of 100 rpm on a hot plate set to 60°C. Electrospinning of PVDF solution was carried out with an Invenso lab apparatus. A constant voltage of 15 kV with positive and negative polarity was applied to the stainless needle of 18 gauge located 18 cm from the grounded collector plate. The flow rate of the solution for all samples was set to 6 mL·h⁻¹, and the time of electrospinning was around 60 minutes. Ambient temperature during electrospinning was around 25°C and humidity of around 60% were used. The produced fibers were collected on the aluminum foil. Prior to AC studies the electrospun fiber membrane were removed from aluminum foil and coated with copper tape with conductive adhesive so as to form a full-face electrode capacitor.

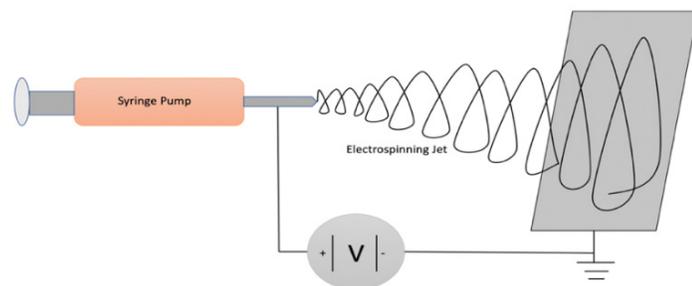


Figure 1: The basic equipment structure of the Electrospinning technique.

Surface Microstructure

The surface morphology of the electrospun PVDF nanofiber membrane was analyzed using scanning electron microscope (Joel). The fibers were coated with gold before they were examined using SEM at an accelerating voltage of 2 kV with 5000X magnification.

Optical Characterization

Raman spectral analysis in the range 250-2250 cm⁻¹ was carried out by using a Raman spectroscopy system (Enwave Optronics Inc.) operating at 785nm laser wavelength. Fourier Transform Infrared Spectroscopy (FTIR) was collected in the range 400 to 4000 cm⁻¹. The surrounding medium was air, and all the measurements were performed at room temperature.

Electrical Characterization

LabVIEW interfaced Quadtech LCR Bridge network was used to conduct the dielectric study. The real and imaginary parts of the dielectric constants (ϵ' and ϵ'') are obtained by measuring terminal parallel capacitance C_p and loss tangent at a measured frequency of 100 Hz to 1000 kHz using LCR meter, and measurements were taken during a thermal heat run with the aid of a temperature

controller. A thermocouple is installed near the sample, and the temperature can be measured using a digital multi-meter. The details of the system are described elsewhere [6]. The real part (ϵ'), imaginary part (ϵ'') of the dielectric constant were determined as:

$$\epsilon' = \frac{C_p d}{\epsilon_0 A},$$

$$\epsilon'' = \tan\delta \cdot \epsilon',$$

$$\sigma_{ac} = \omega \epsilon_0 \epsilon''$$

where C_p is the parallel capacitance of the sample at a signal frequency, $\tan\delta$ is the dielectric loss; A is the electrode area of the copper electrode, d is the thickness of the sample, $\epsilon_0 = 8.854 \times 10^{-12}$ F/m is the permittivity of vacuum.

Results and Discussions

Microstructure characterization

Figure 2 shows a typical SEM image of electrospun PVDF nanofiber membrane. The fibers are randomly oriented forming a web with only few beads formed during electrospinning.

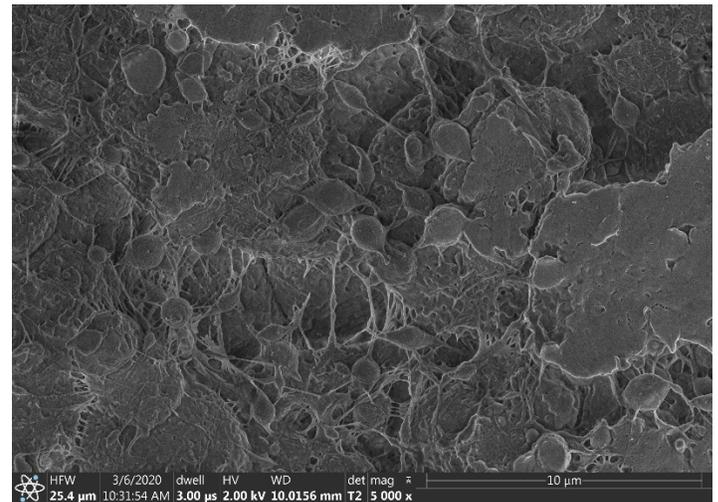


Figure 2: Representative SEM image of fibrous membrane.

Infrared vibrational spectroscopic characterization

From the recorded Fourier Transform Infrared (FTIR) and Raman spectra in the range, 300 to 2000 cm⁻¹ and functional groups were identified in the PVDF electrospun membrane, see Figure 3. Infrared vibrational spectroscopy (FTIR) revealed ferroelectric β -phase in the un-annealed membranes intrinsically around 845 cm⁻¹ as depicted in Figure 3 [7-8].

Dielectric investigations

Figure 4 (a-b) shows the dielectric constants ϵ' , the dielectric loss constant ϵ'' , of electrospun nano PVDF membrane. In ferroelectrics, these parameters (ϵ' , ϵ'') can increase with an increase in temperature however, it is found to decrease in parameters. This type of behavior may be due to a large number of pores present in the electrospun nanofiber membrane. The decrease in loss with increasing temperature is an advantage in conduction that could be detrimental to the piezocapacitive response since it relies on the material behaving as a dielectric.

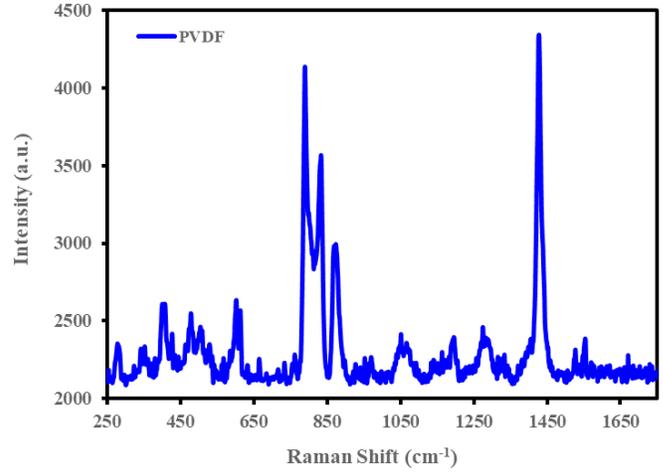
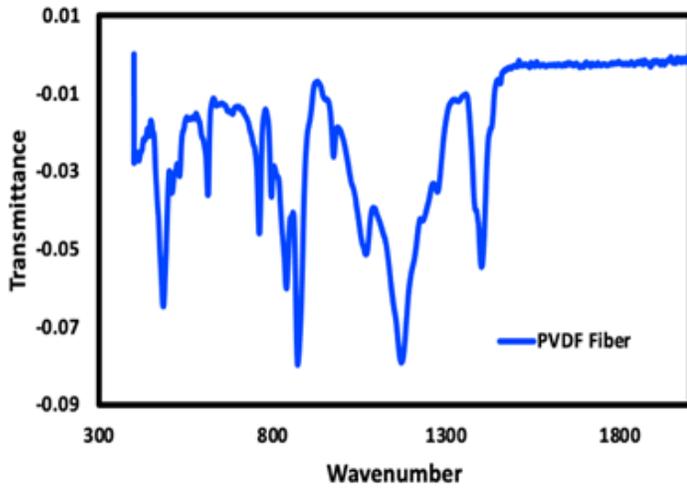


Figure 3: (a) FTIR spectra and (b) Raman spectra measured with a Raman system equipped with 785nm wavelength laser.

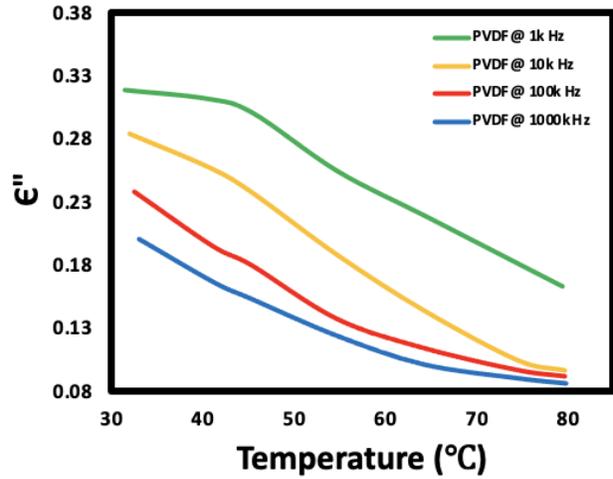
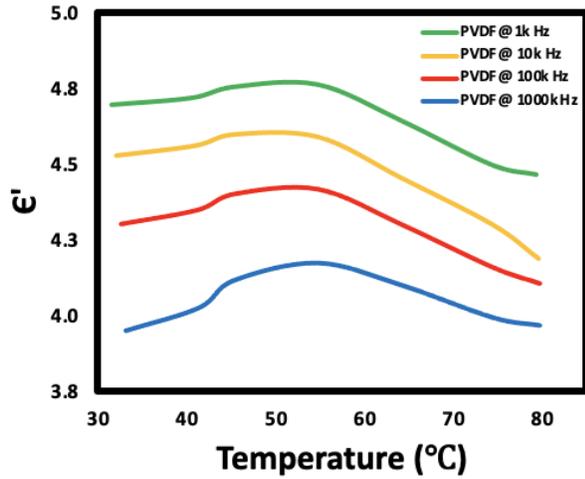


Figure 4: (a) The variation of dielectric constants ϵ' , (b) the dielectric loss constant ϵ'' with temperature.

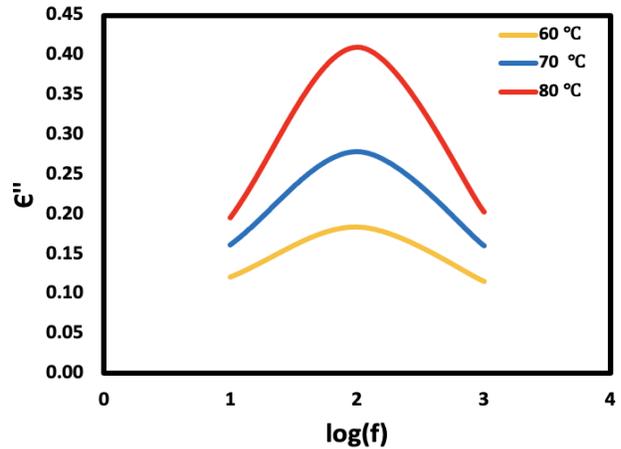
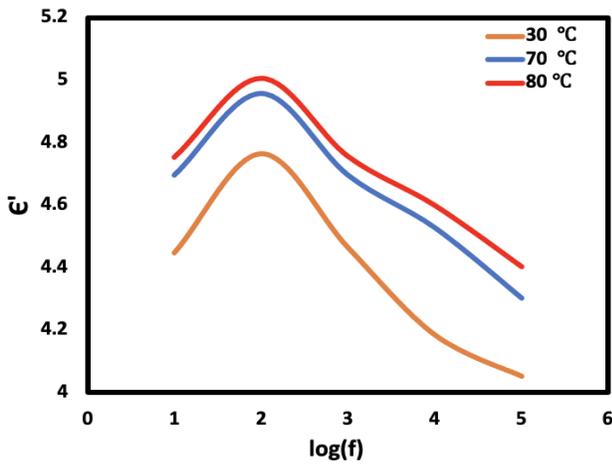


Figure 5: The real part (ϵ'), imaginary part (ϵ'') of the dielectric constant versus the frequency at different temperatures.

Furthermore, the expansion of pores due to heat treatment results in a decrease in interfacial polarization and leads to the reduction in dielectric constants. The pore content decreases the interfacial area between the polar phase and air present in the pores, thus lowering the value of dielectric constants of the electrospun PVDF nanofiber membrane.

The real part (ϵ'), imaginary part (ϵ'') of the dielectric constant versus frequency at different temperatures is illustrated in Figure 4. It is well known that the dielectric constant of PVDF is due to the presence of free dipoles within the matrix, which is responsible for the polarization [9]. At lower frequencies, the free dipoles in PVDF chains follow the orientation of the electric field at the same pace. In contrast, at higher frequencies, dipoles reorientation is out of phase with respect to field reversal. The result is the decrease of PVDF dielectric constant with increasing frequency, as depicted in Figure 4. The high value of the dielectric constant at lower frequencies may be influenced by Maxwell-Wagner-Sillar (MSW) interfacial effect [10]. The decrease in the interfacial polarization at higher frequencies lowers the imaginary part of the dielectric constant (loss). From figure 4, it can also be observed that dielectric loss (imag. Dielectric constant) is also temperature-dependent. It increases with an increase in temperature at a higher pace. This behavior may due to dielectric dipolar relaxation processes [11].

The ac conductivity with the variation of frequency and temperature is illustrated in Figure 6. The ac conductivity is described in the literature according to the correlated barrier-hopping model (CHB) [12]. This model includes the analysis based on the hopping of carriers between the neighboring sites separated by columbic barrier. Apart from this, it also depends on various parameters such as frequency of applied signal and temperature.

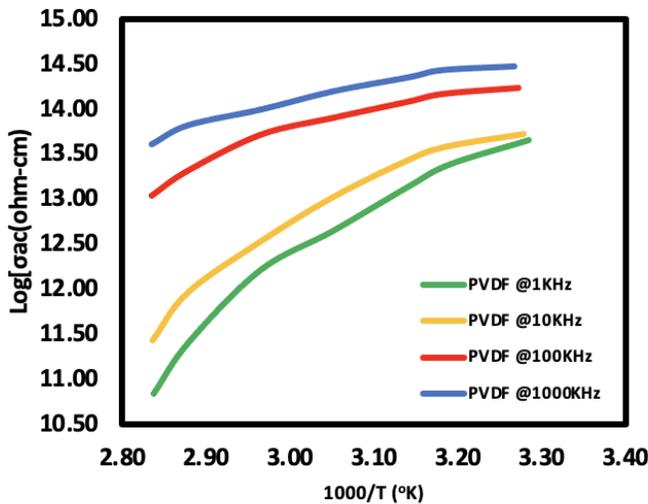


Figure 6: Temperature dependence of the AC conductivity for different frequency's. The frequency dependence of AC conductivity is expressed by the well-known Jonscher universal law with the assumption that dc conductivity is much less than AC conductivity (Figure 6).

$$\sigma_{AC}(\omega) = A\omega_s$$

where A is a constant that determines the strength of polarizability and 's' is the frequency exponent.

The frequency component 's' is dependent on temperature and was found to be less than 1 as shown in Figure 7.

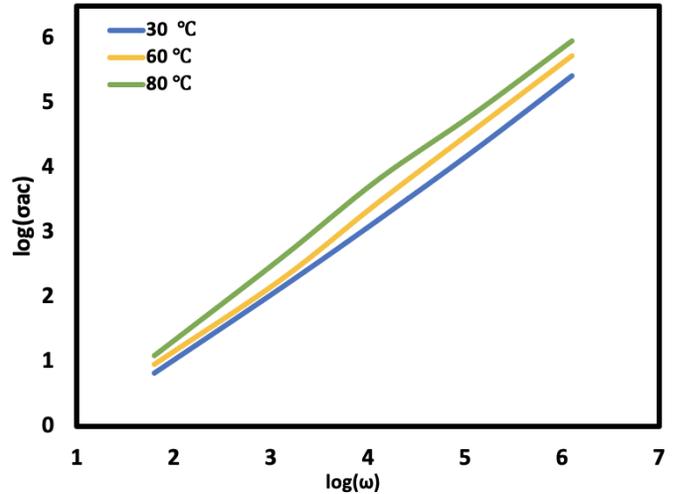


Figure 6: Frequency dependence of AC conductivity at various temperatures.

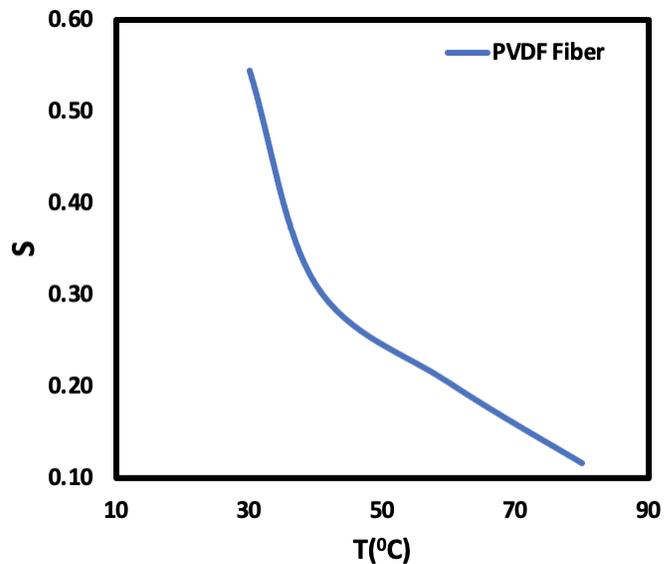


Figure 7: Temperature dependence of frequency exponent (s) of PVDF membrane.

The ac conductivity shows (Figure 6) strong temperature dependency. As the temperature increases, the charge carriers are thermally activated; the free volume increases; and more vacant sites are created for ions' motion, which in turn enhances the conductivity. The activation energies were calculated from AC conductivity analysis. The activation energies were calculated

from dependence AC conductivity on temperature. The activation energy determines from the slope of logarithmic conductivity plotted as a temperature function (T). It varies more or less linearly with the 1000/T as shown in Figure 5. Thus, to determine the activation energy, the experimental data was fitted into the well-known Arrhenius equation:

$$\sigma_{AC} = \sigma_0 \exp(-E_A/kT)$$

where E_A is the activation energy of thermal conduction process that takes place in the composites, k is Boltzmann constant and T is the temperature. The different values of activation energies was observed at a different frequency of the signal applied. The value of activation energy was found to vary from 2.008 to 6.176 eV at 100 Hz.

Conclusions

In summary, dielectric and electrical characterization of PVDF membrane have been examined over a wide range of frequencies (100 Hz-1 MHz) and temperatures 20°C -150°C). Furthermore, in this study, good quality and homogeneous porosity electrospun PVDF nanofiber membrane have been fabricated. via electrospinning. It is proposed that the pore content decreases the interfacial area between the polar phase and air present in the pores, thus lowering the value of dielectric constants of the electrospun PVDF nanofiber membrane as compared with PVDF film fabricated via the solution casting technique [6]. Maxwell-Wagner interfacial polarization is found to be active at lower frequencies.

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