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Dielectric Behaviour of PVDF Thin Films

Anjana Jain*, P. N. Rashmi, S. Jayanth Kumar, J. C. Swaroop

CSIR- National Aerospace Laboratories, Bangalore - 560017, INDIA.

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ABSTRACT

Piezoelectric polymer PVDF poly (vinyledene fluoride) films play an important role in sensor and actuator applications. PVDF exists in four different phases α, β, γ and δ, out of which β-phase is most suitable for piezoelectric applications. The present work concerns the development of α-PVDF films, which are then converted to β-phase by appropriate thermo-mechanical treatment. The films are characterized for structural and surface morphological studies to investigate the presence of β-phase through X-ray diffraction, and scanning electron microscopy. These films are electroded and poled to align the dipoles and acquire piezoelectric properties.

Being dielectric material, dielectric properties of PVDF has been studied in detail. As PVDF is flexible, light weight, chemically inert, tough and creep resistant, it has added advantages to put on curved surfaces. In the present study, various parameters of PVDF such as Permittivity, Tanδ, Capacity (pF), Impedance (Ω), Modulus, Conductivity(S/cm), Specific Resistance (Ωcm) are obtained using dielectric spectrometry. Results are well match with literature value. These properties are useful for super capacitor applications.

Keywords: *PVDF, Dielectric spectroscopy, Impedance, Permittivity, Capacity, Modulus, Conductivity*

1. INTRODUCTION

Poly(vinylidene fluoride), PVDF, is a semi crystalline and thermoplastic polymer which is used in many industrial applications such as capacitor dielectrics and transducer materials [1]. Since PVDF involves fluorine atoms with high electro-negativity, it has high electric dipole moment. Therefore motion of the molecules, which has been excited by electric field and heat, can be analyzed through dielectric measurements [4, 10]. The molecular chains, which are entangled in α-phase PVDF film, are rearranged along the draw axes and hence, the polymer shows anisotropic physical behavior [19–21]. However, in general the polymers are oriented by using various deformation methods. The most common of these are, uniaxial or biaxial drawing and rolling [20-23]. The alignment of molecular dipoles in the field direction cannot take place instantaneously when an electric field is applied. The dielectric properties and the dielectric relaxation behavior of polymers are directly affected by their molecular structure and morphology. Thus, research related to dielectric properties are frequently used in the study of molecular dynamics of polymers. Another reason for the use of this technique in studying dipolar polymers is that the dielectric measurement allows the analysis over wider range of frequency (10^{-4} Hz to10^{14}Hz) than mechanical measurements [20,22,24]. So dielectric properties such as impedance, admittance, dielectric constant (or dielectric permittivity), modulus, capacitance, conductivity etc have been investigated in the present paper and these values are compared with the literature values.

2. EXPERIMENTAL DETAILS

PVDF film with 0.095mm thickness and 1780kg/m^3 of density were prepared from solvent cast method. The film obtained was in α-crystalline phase, which can be drawn into thin film by thermo mechanical process at pre-determined temperature so that β-phase with all trans conformation is obtained. These films were then characterized using XRD and SEM to find out the structural and surface morphological properties of the material. X-ray Diffraction patterns were recorded with Bruker AXS D8 Advance X-ray diffractometer with Cukα radiation, operated at 40 kV, 40 mA, SEM was recorded by using Joel scanning electron microscope and dielectric properties was measured by using Novocontrol Alpha-N high resolution dielectric analyzer.

3. RESULTS & DISCUSSIONS

Figure 1 shows the XRD pattern of α & β phase PVDF film. The diffraction pattern in the 2θ range 10 to 60° was recorded and the sample is rotated at

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*Corresponding Author:
Email: janjana@nal.res.in
Phone: +91 9448682877

the scan speed of 1^o/minute. The indexing is done using unit cell dimensions a=4.96, b=9.64, c=4.62 Å for α-phase and a=8.58, b=4.91, c=2.56 Å for β-phase reported by Hasegawa et al [16] and most intense reflection (110) was concentrated to check the phase.

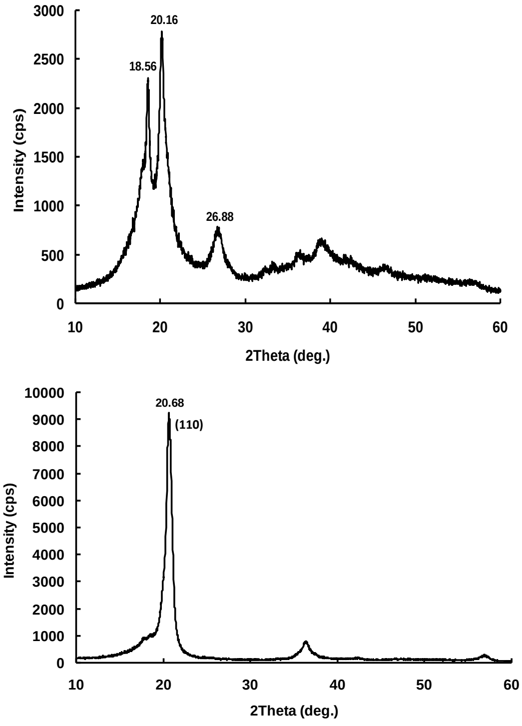


Figure 1: The XRD of α & β phase PVDF

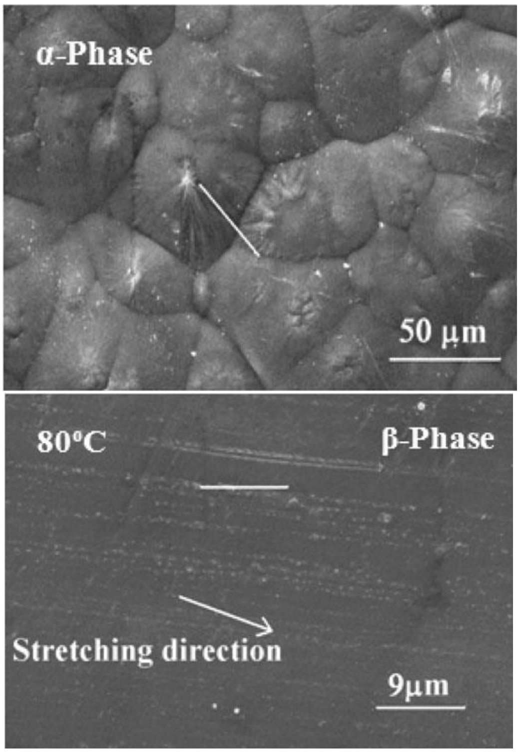


Figure 2: SEM of α & β phase PVDF

Figure 2 represents the SEM feature of α & β phase PVDF film. The α-phase shows grain like structure after hot stretching this grain like feature disappears and the surface shows fibril like structure which indicates the stretching direction. Further, β-phase PVDF films were electroded on both sides using silver ink to make it conductive, and poled to align the randomly oriented dipoles to attain the piezoelectric properties. The piezoelectric charge coefficient d_{33}, was measured using PM300 Piezometer. Figure 3 shows circuit diagram of the dielectric analyzer.

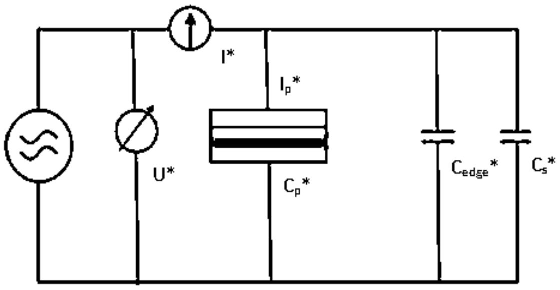


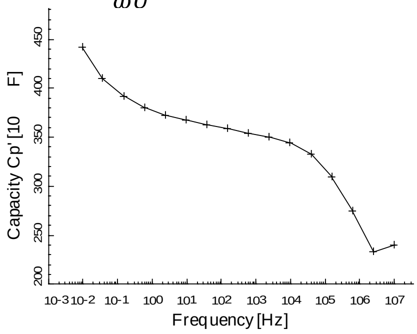
Figure 3: Circuit of dielectric analyzer [20].

- C_p* denotes parallel capacitance of the sample
- C_s denotes the additional stray capacitance due to external sample cell
- C_{edge} is an additional capacitance due to stray electric field at boundaries
- U* and I* is the voltage and current respectively at the sample cell
- ω is frequency

Dielectric Properties of PVDF

- The sample **capacity** is related to the measured voltage and current as shown in equation (1) [20].

$$C_P^* = -i\,\frac{I^*}{\omega U^*} - C_{edge} - C_s \rightarrow (1)$$

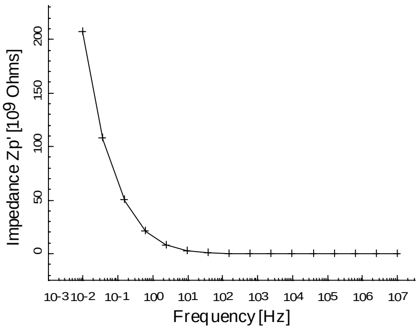


The sample capacity is directly dependent on frequency and decreases as frequency is increased. In the frequency range 10^{-1} to 10^4 Hz, capacity is nearly same, but it decreases very fast outside this range as capacitance of a sample capacitor is inversely proportional to its thickness.

- For round plate capacitor sample **impedance** is given by equation (2) [20].

$$Z_s^* = \frac{1}{Y_P^*} = -\frac{i}{\omega C_p^*} \qquad \rightarrow (2)$$

Z*s= Impedance
Y*P =admittance

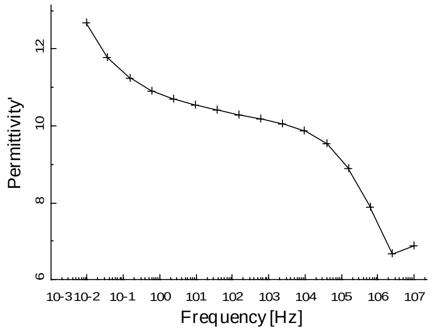


This instrument covers an impedance range from 10^{-1} Ω to 10^{14}Ω. Above graph verifies high impedance of the material at low frequencies (<10^{-1} Hz.). And as the frequency increases impedance decreases first and then becomes nearly constant.

- **Relative permittivity** can be expressed in complex dielectric constant form as ε* related to the complex sample capacity by equation (3) [20]

$$\varepsilon *= \varepsilon' - i\varepsilon'' = \frac{C_P^*}{C_0} \quad \rightarrow \quad (3)$$

C_0 =Empty cell capacity
ε'= real part permittivity
ε" = imaginary part permittivity



The permittivity shows continuous variation with the frequency, indicating that dielectric constant of material depends largely on the frequency. The permittivity of material decreases with increase in frequency over entire frequency spectrum. With large slope at frequencies below 1Hz and above 10 kHz, the slope is very small in the 1-10 kHz frequency range. Thus, giving nearly same permittivity in this frequency range.

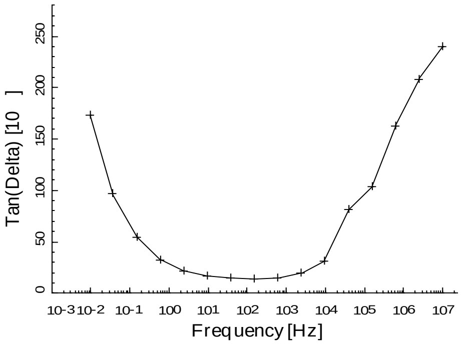
Sample cell consisting of round parallel plates with diameter D and spacing d, C_0 is calculated by equation (4) [20]

$$C_0 = \epsilon_0 \frac{\Pi\left(\frac{D}{2}\right)^2 - A_{spacer}}{d} \quad \rightarrow (4)$$

where, A_{spacer} denotes average area inside the sample capacitor occupied by the spacer material.

- Equation (3) consists of real part which is dielectric constant and the imaginary part which is the dielectric loss. The ratio between the dielectric losses with the dielectric constant is quantified as **tanδ**. It is given by [20].

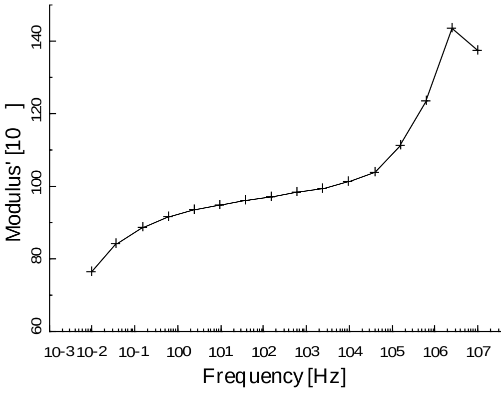
$$\tan\delta = \frac{\in''}{\in'} \rightarrow (5)$$



From the above graph, PVDF samples have high ratio of losses to dielectric constant at low frequencies as well as high frequencies. This ratio is least in the frequency range 1Hz to 10^4Hz, giving the preferable frequency range of operation. With a resolution in tanδ < 10^{-5}, value obtained for PVDF is 0.015 at 1 KHz.

- Complex **dielectric modulus** can be expressed by equation (6) [20].

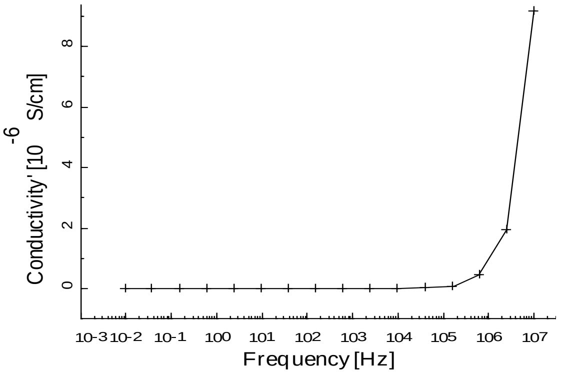
$$M^* = M' + iM'' = \frac{1}{\in^*} \rightarrow (6)$$



As the frequency increases the modulus also increases gradually. But at very high frequency (around 10^7 Hz) PVDF ruptures.

- **Specific conductivity** σ* is related to the dielectric constant by equation (7) [20]

$$\sigma^* = \sigma' - i\sigma'' = i2\pi f \varepsilon_0(\varepsilon^* - 1) \rightarrow (7)$$

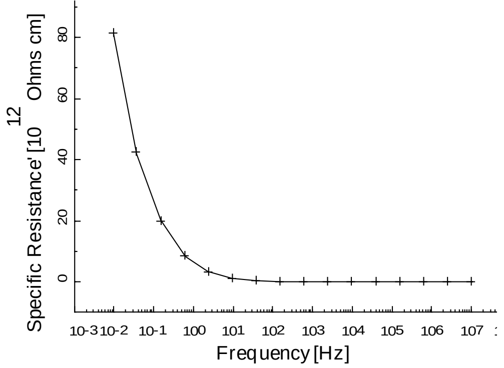


Above graph shows variation of PVDF conductivity at different frequencies. Like other dielectric materials PVDF also has negligible conductivity. The graph also shows nearly flat curve below 10^5Hz. But as the frequency increases to 10^5Hz, the conductivity increases abruptly.

- **Specific resistance** of material is calculated by equation (8) [20]

$$\rho = \frac{1}{\sigma'} \quad \rightarrow (8)$$

Resistivity and conductivity have a reciprocal relationship. So, is apparent from their graphs v/s frequency for PVDF, as well.



PVDF shows a high resistivity at low frequency around 10^{-3} Hz, but as frequency increases the resistivity decreases and it settles to low value at frequency 1Hz and further increase in frequency doesn't affects the resistivity.

Table 1: Comparison of literature values and experimental values of PVDF.

PVDF Film Property	Literature Value	Experimental Value
Relative Permittivity	12-14	13
Tan @1kHz	0.02	0.015
Capacity @ 1kHz	380 pF	310 pF
Conductivity S/cm	$10^{-5} – 10^{-16}$	10^{-6}

Specific applications of dielectric materials [21]

- Studies on the molecular dynamics of liquids, liquid crystals and polymers
- Charge transport in semiconductors, organic crystals, ceramics etc
- Monitoring of chemical reactions or polymerization processes
- Structural properties like phase compositions, phase transitions and crystallization process
- Non- linear electrical and optical effects.

4. CONCLUSION

Dielectric behaviour of PVDF has been obtained by dielectric spectroscopy (DS) and variation of parameters such as Permittivity, Tanδ, Capacity, Conductivity, Impedance, Modulus, and Specific resistance with frequency has been studied. The values obtained from experiments are matching well with the literature values. Experimentally measured parameters for PVDF film give Impedance of 120Ω, Modulus of $5x10^{-3}$ N/m^2 and Specific resistance > 3Ω cm. Further, PVDF can be used for lithium ion battery and super capacitor applications.

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