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Effects of Annealing Temperature and Solvent Dipole Moment on the Formation of β -Phase of PVDF

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ABSTRACT
PVDF polymer is known for its lightweight, superior mechanical qualities, resistance to chemicals and electricity, and processability. PVDF-based energy harvesting systems can withstand greater vibration due to their excellent chain flexibility. This study aims to create thin films with high β phase content using DMSO, an organic solvent with a higher polarity index and dipole moment than DMF. Raman and FTIR spectroscopy are used to measure the material and describe dielectric characteristics at different temperatures and frequencies. The study aims to optimize the annealing temperature to achieve the maximum β-phase content, which was found to be 100°C. Polarization-Electric field (P-E) curves are characterized using a Sawyer-Tower circuit, determining key ferroelectric parameters like remnant polarization and saturation polarization. The study found that the remnant polarization value was maximum for the sample with the maximum β content (annealed at 100°C)

Keywords: *PVDF, Polarization, dielectric, permittivity, thinfilms*

INTRODUCTION
Since the discovery of piezoelectricity in poly(vinylidene fluoride) (PVDF), there has been a strong focus on processing the semi-crystalline polymer and at least five distinct polymorphs, a, b, g, and d. Processing parameters, such as mechanical, thermal, electrical, and chemical treatments, affect the final properties of PVDF, including electroactivity, dielectric and mechanical properties, antifouling behavior, and cellular behavior. FTIR has been widely used in characterizing PVDF, but reports in existing literature often have conflicting characterization results, especially in the electroactive b and g phases. Two main reasons for this divergence are that many directly assigned the FTIR bands at around 840 and 510 cm to the b and g phases without providing sufficient evidence. This work analyzes the FTIR vibrational bands of PVDF materials fabricated by different processes with detailed XRD (X-ray diffraction) characterization to identify the structural a, b, and g phases [1-3].

By examining the results in this work and extensively reviewing published research reports in the literature, a universal phase identification procedure using only the FTIR results is proposed and validated. This procedure can differentiate the three phases by checking the bands around 763 and/or 614, 1275, and 1234 cm for the a, b, and g phases, respectively. The rule for assignment of the 840* and 510* cm bands is provided for the first time and an integrated quantification methodology for individual b and g phase in mixed systems is also demonstrated [4].

The procedure for the identification of a, b, and g phases using the FTIR vibrational spectrum is proposed and demonstrated with an integrated quantification methodology for individual b and g phase for PVDF materials made of various a, b, and g phase compositions. Both FTIR and XRD data have been utilized to validate and identify the phases of various PVDF polymeric systems. Secondary crystallization as a source of structural evolution has been extensively investigated on various polymers, including ethylene/octene copolymers, PEEK, and polycarbonate. These secondary crystals are small clusters of organized neighbouring chain segments forming bundle-like or fringed-micellar structures with virtually no or few re-entry foldings. The kinetics governing this secondary crystallization differ from those relative to primary crystallization, with an ,

important aspect being the progressive increase in conformational constraints within the residual amorphous fraction due to a crosslinking-like effect. This conformational entropy reduction leads to an increase in the melting point of the secondary crystals with aging time [5-7].

This paper focusses on fabricating the PVDF thin films with high content of β phase by using the organic solvent DMSO having high polarity index (7.2) and high dipole moment (4.1) compared with DMF (6.4 and 3.86)

2.Materials and Methods

Initially, polyvinylidene fluoride (PVDF) is dissolved in dimethyl sulfoxide (DMSO), a solvent with a high dipole moment, to form a homogeneous solution. This solution is then subjected to magnetic stirring, typically at elevated temperatures, to ensure complete dissolution and uniform mixing. Once the solution is adequately prepared, it is cast onto clean glass substrates using a cube applicator to form thin films of uniform thickness. The cast films are then dried to remove any residual solvent, resulting in solid PVDF thin films with an approximate thickness of 30 μm. These films are subsequently annealed in a hot air oven at various temperatures 80°C, 100°C, 120°C, 140°C, and 160°C for a duration of 16 hours. The annealing process plays a critical role in influencing the crystalline phase composition of the PVDF films, particularly in promoting the formation of the electroactive β-phase, which is essential for enhancing the piezoelectric and dielectric properties of the material. After annealing, the prepared samples are ready for further structural and electrical characterization,

3.Result and Discussion

3.1 Xrd Analysis

The X-ray diffraction (XRD) analysis in the study was conducted to observe the crystallinity and phase evolution of PVDF (polyvinylidene fluoride) thin films annealed at different temperatures: 80°C, 100°C, 120°C, 140°C, and 160°C are 18.79nm, 19.03nm, 19.67nm, 20.6 and 21.3nm respectively Shown from fig 1-5. The main outcome of the XRD measurements was the calculation of crystallite size at these annealing temperatures, which showed a progressive increase. It indicates that increasing annealing temperature enhances crystallite growth in PVDF films, likely contributing to changes in phase composition and crystallinity. However, the optimal β-phase formation crucial for piezoelectric applications peaked at 100°C, as verified through complementary FTIR and Raman analysis [8].

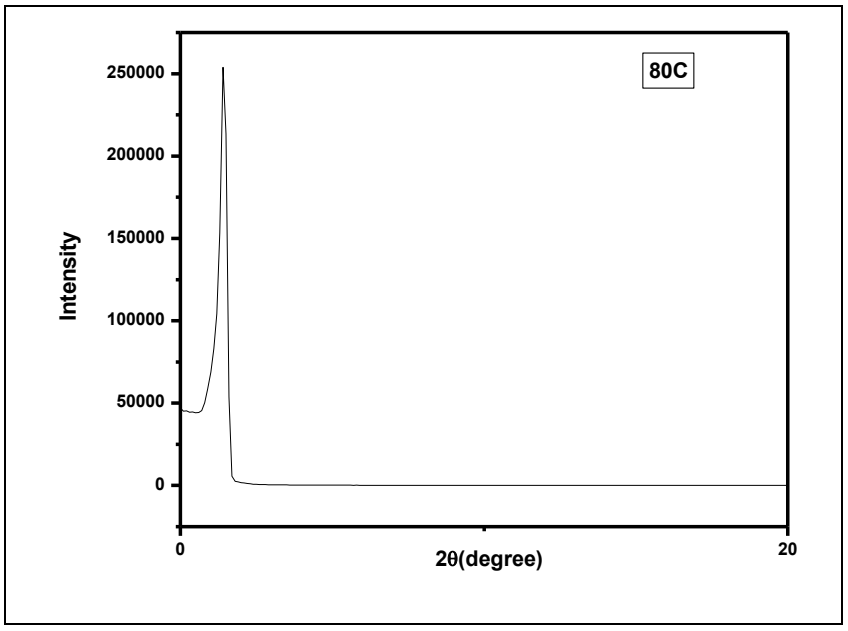

Figure 1 Shows the XRD peak of 80C

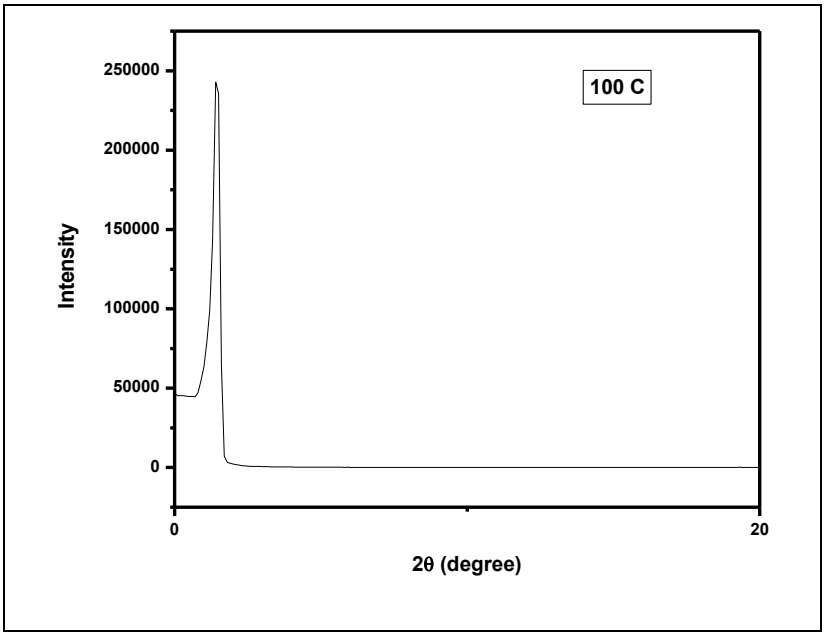

Figure 2Shows the XRD peak of 100C

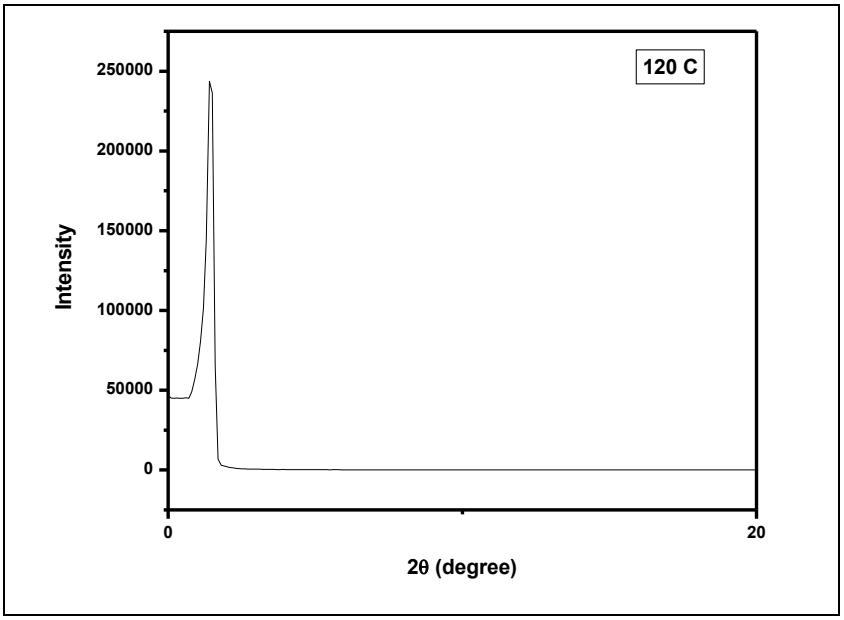

Figure 3Shows the XRD peak of 120C

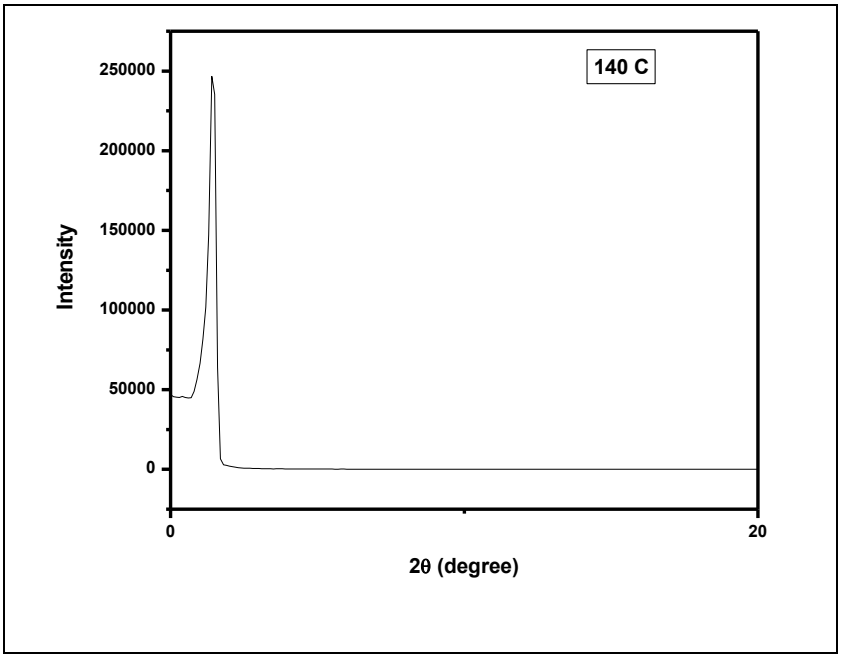

Figure 4Shows the XRD peak of 140C

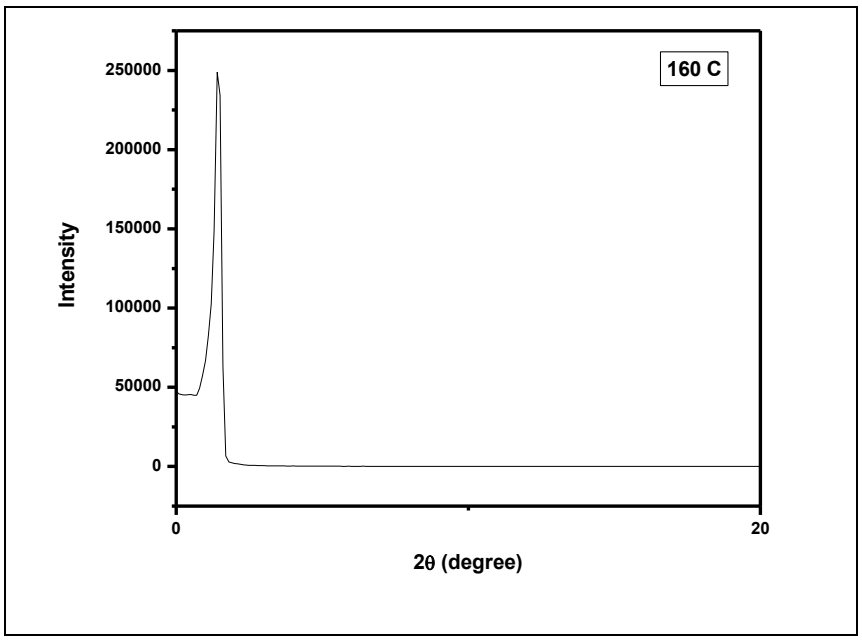

Figure 5Shows the XRD peak of 160C

FT-IR Analysis

The study presents FTIR absorbance spectra of PVDF powder and films annealed at various temperatures, revealing varying peak intensities and positions. The spectra qualitatively quantified the α, β, and γ phases by comparing relative peak intensities. The β-phase peaks were most intense at 100°C, indicating maximum β-phase content. Other annealing temperatures showed weaker β peaks or increased α and γ signatures, suggesting partial transformation or loss of the β-phase. FTIR confirmed that 100°C is the optimal annealing temperature for β-phase enrichment, aligning with Raman and dielectric results. This spectroscopy was central to confirming that annealing PVDF at 100°C optimizes the formation of the electroactive β-phase, critical for high-performance applications like sensors and energy harvesters [9,10].

Phase percentage of α, β and γ phases were evaluated from the characteristics absorption peaks of the FTIR spectra. A maximum β phase percentage of 89% was attained for the PVDF thin film annealed at 100°C. FT-IR spectra is shown in fig.6 and the fraction value is mentioned in table.1

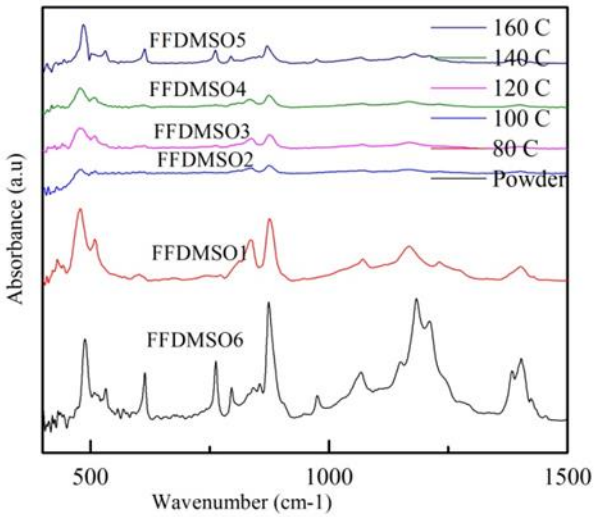

Figure 6 FT-IR Spectra of Different annealing temperatures.

Table:1 Shows the Fraction of β Value.

Sample	Fraction of β
80 C	87.71
100 C	89.79
120 C	85.04
140 C	78.66
160 C	38.70

3.3 Raman Analysis

Raman studies were conducted to identify and quantify crystalline phases in PVDF thin films, evaluate the effect of annealing temperature on the formation of the electroactive β-phase, and support findings from FTIR analysis. The Raman spectra showed in fig.7 has distinct vibrational peaks corresponding to different crystalline phases of PVDF, with the β-phase, which is highly polar and piezoelectrically active, showing strong Raman signals at specific characteristic wavenumbers. The intensity of β-phase peaks was maximized at 100°C, confirming this as the optimal annealing temperature for promoting β-phase formation [11,12]. The quantified the relative phase content using characteristic Raman peaks for α, β, and γ phases. Raman analysis confirmed that 100°C treatment yielded the highest β-phase content, aligning with FTIR results and dielectric property trends. This dual confirmation strengthens the conclusion that annealing at 100°C maximizes functional properties in PVDF films. The Raman spectroscopy studies played a critical role in validating structural phase transformation with thermal treatment, identifying the ideal annealing temperature, and supporting the broader conclusion that solvent dipole moment and thermal history significantly affect PVDF's functional performance.

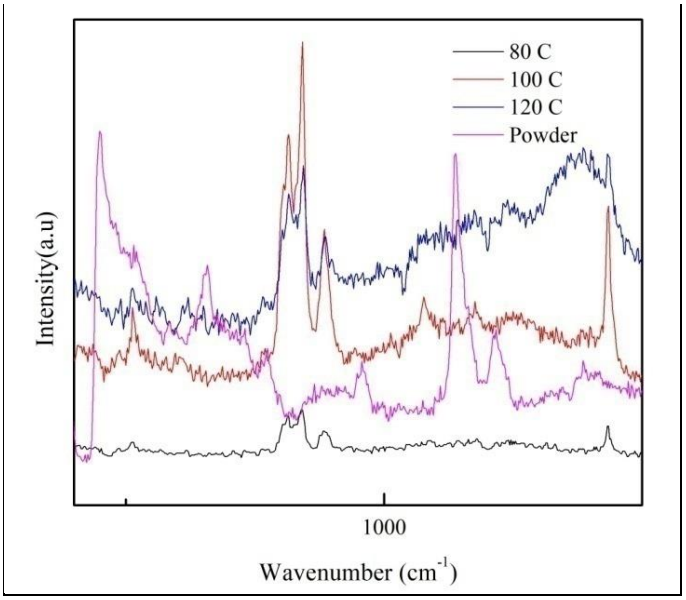

Figure 7 Shows the Raman Spectra of different annealing temperatures

3.4 Dielectric Studies

Dielectric permittivity measures a material's ability to store electrical energy in an electric field. The maximum dielectric permittivity (13.3) occurred for the sample annealed at 100°C, which had the highest β-phase content in shown in fig.8. The formation of the polar β-phase is enhanced at moderate annealing temperatures, resulting in increased dielectric constant. At higher temperatures, there may be transformation into less polar phases or degradation of crystalline order, thereby reducing permittivity [13].

Dielectric loss quantifies energy dissipation as heat in a dielectric material under an alternating electric field. The lowes t tanδ values were observed at 140°C (0.02299) and 160°C (0.02295), is tabulated in 2 correlating with low β-phase content and dielectric permittivity is shown in fig.9. Annealing at 100°C produces an optimal structure with enhanced polarization response and manageable energy dissipation. Excessive annealing may reduce both dielectric response and energy storage efficiency due to phase changes or thermal degradation [14].

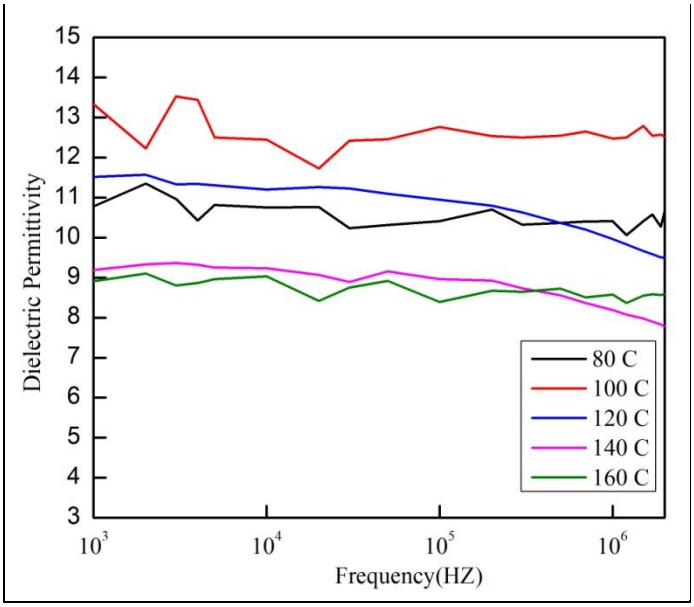

Figure 8 Shows the dielectric permittivity of different temperatures

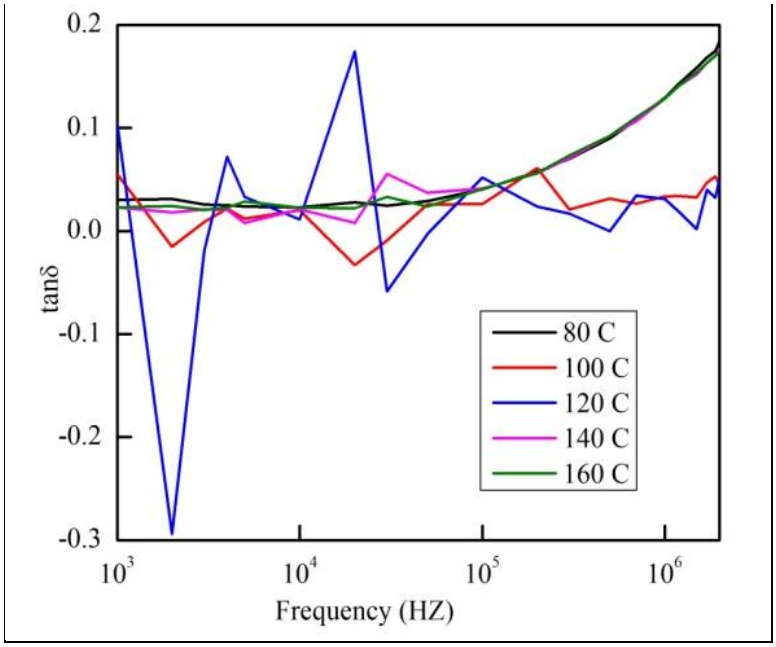

Figure 9 Shows the dielectric loss of different temperature

3.5 Magnetic Studies

The fabricating thin films of PVDF with a high content of the β-phase, the most polar and piezoelectrically active crystalline phase of PVDF. It optimize the annealing temperature to achieve the maximum β-phase content, which is found to be 100°C. This optimization is crucial as the piezoelectric response in PVDF is directly related to the amount of β-phase present. Polarization-Electric field (P-E) shown in fig.10-15 curves were characterized using a Sawyer-Tower circuit, determining key ferroelectric parameters like remnant polarization and saturation polarization. The study found that the maximum remnant polarization value (0.304 μC/cm²) was found for the sample with the maximum β content (annealed at 100°C) shown at fig.15 and values were denoted in table.2. P-E loop analysis also provides evidence of the switchable polarization in the material, a hallmark of ferroelectricity, a prerequisite for piezoelectricity in polymers like PVDF. The results suggest optimized conditions for piezoelectric performance.

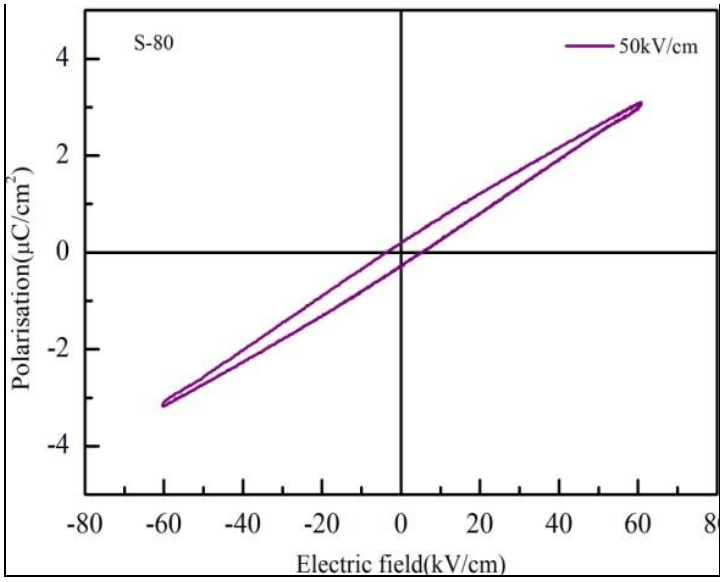

Figure 10Shows the P-E loop of 80C

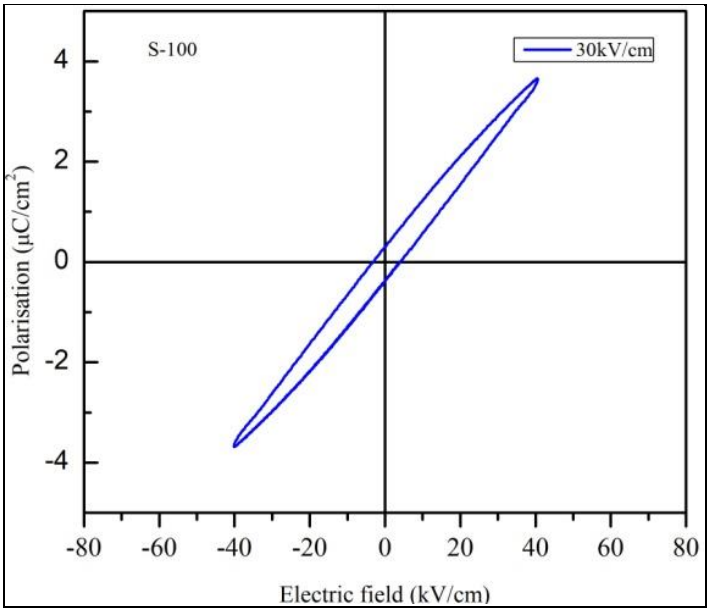

Figure 11Shows the P-E loop of 100C

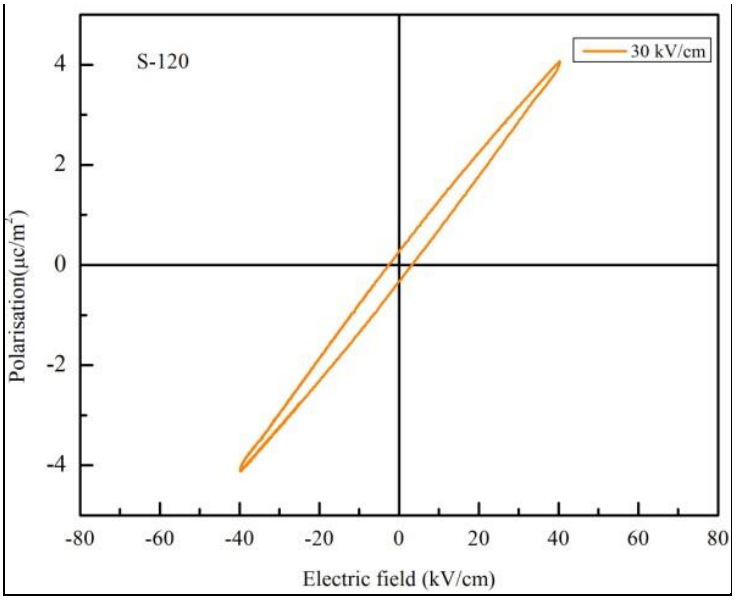

Figure 12Shows the P-E loop of 120C

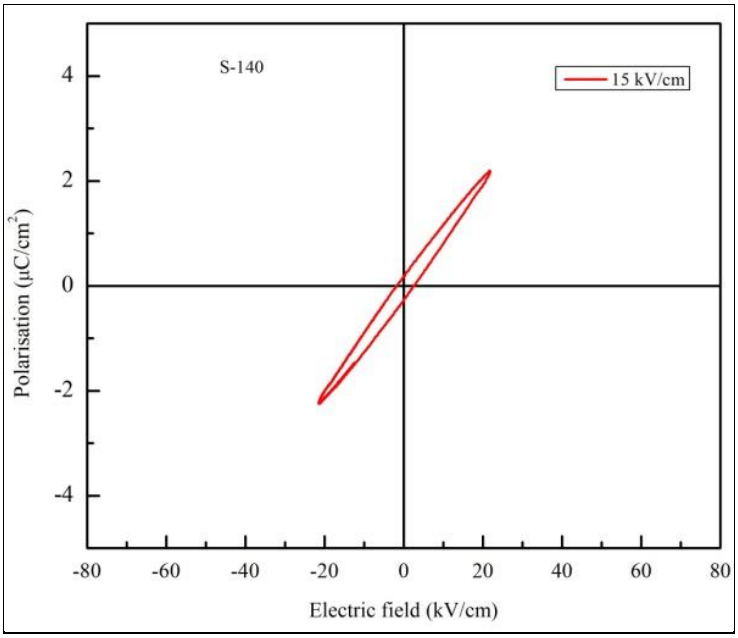

Figure 13Shows the P-E loop of 140C

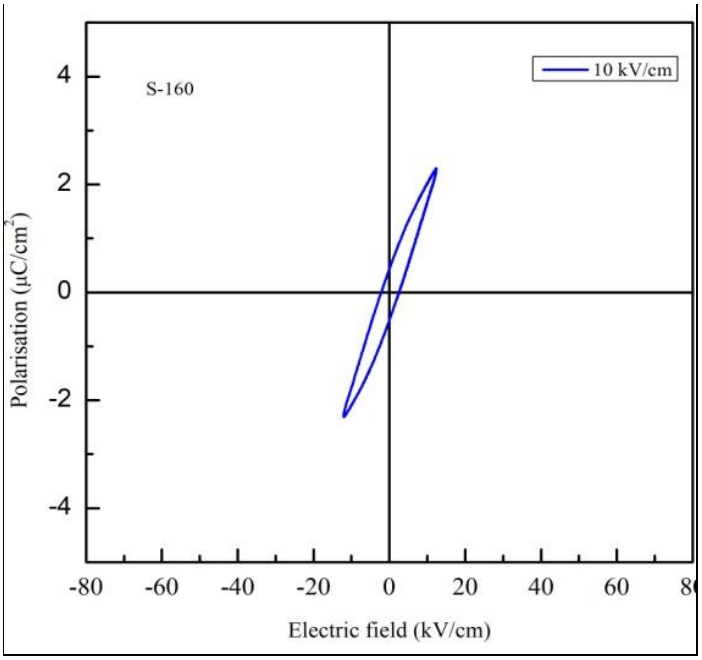

Figure 14Shows the P-E loop of 160C

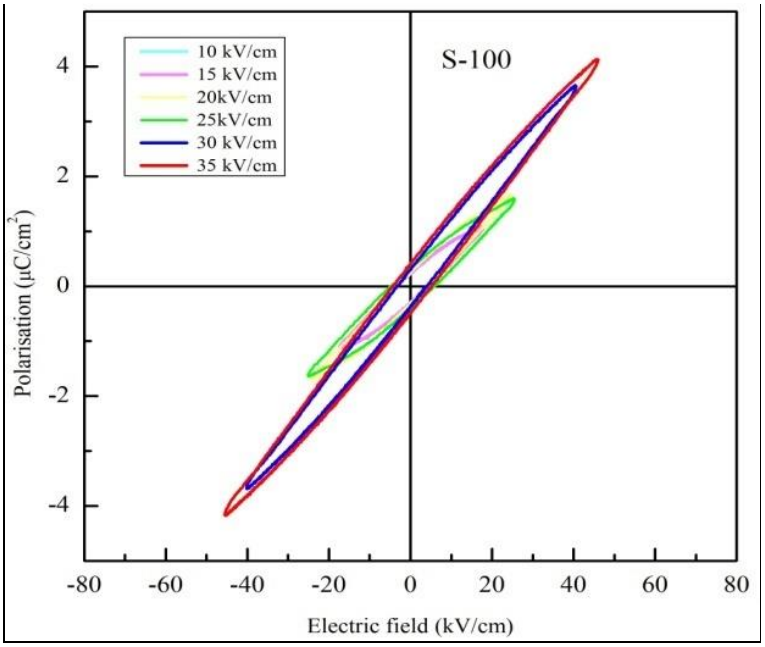

Figure 15 Shows the P-E loop of 100C at different voltage

Table: 2 Shows the Value of dielectric permittivity, dielectric loss and remnant polarisation and saturation polarisation.

Sample	Dielectric permittivity	Dielectric loss(tanδ)	Remnant Polarisation (Pr) (μC/cm2)	Saturation Polarisation (Ps) (μC/cm2)
80 C	10.7	0.03019	0.169	3.12
100 C	13.3	0.05524	0.304	3.66
120 C	11.5	0.10381	0.242	4.07
140 C	9.2	0.02299	0.147	2.21
160 C	8.9	0.02295	0.110	2.19

4.CONCLUSION

PVDF thin films of thickness 30 μm were fabricated and annealed at different temperatures. The annealing temperature for achieving the maximum β-phase content was optimized at 100°C. The α, β, and γ phases in all the PVDF thin films were quantified using FTIR and Raman spectroscopy. The dielectric permittivity reached its maximum value of 13.3 for the sample with the highest β-phase content. Additionally, the remnant polarization peaked at 0.304 μC/cm² for this same sample, confirming that 100°C is the ideal annealing temperature to enhance the piezoelectric and dielectric properties of PVDF films.

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