

Effect of Annealing and Time of Crystallization on Structural and Optical Properties of PVDF Thin Film Using Acetone as Solvent

Imtiaz Noor Bhatti^{1*}, M. Banerjee² and Ilyas Noor Bhatti³

¹(Nanoscience and Nanotechnology lab. School Of Physics, D.A.V.V. Indore, India)

²(Nanoscience and Nanotechnology lab. School Of Physics, D.A.V.V. Indore, India)

³(Laser Building, School Of Physics, D.A.V.V. Indore, India)

Abstract : In this report pure poly(vinylidene fluoride) (PVDF) films were prepared by casting method using acetone solvent. The crystallization of both α and β phase from acetone solvent by varying the time of crystallization has been described. This paper also describes the enhancement of β phase at different annealing condition. β phase dominant thin films were obtained when as cast thin films were annealed at 90 °C for 5 hours. The PVDF films with dominant α -phase were obtained, when time of crystallization is extend. From (X-ray diffraction) XRD and Fourier Transform Infrared Spectrum (FTIR) it is confirmed that the PVDF thin films, cast from acetone solution and annealed at 90 °C for 5 hours, have maximum percentage of β -phase. Presence of the crystalline α and β phases in each sample was confirmed by X-ray Diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). We found that of PVDF when crystallized from its acetone solutions led to the formation of β phase. UV-visible optical absorption analysis revealed a change in the optical gap and shift in absorption edge with annealing temperature.

Keywords: Annealing, casting, polymorphism, polar, PVDF

I. INTRODUCTION

The introduction Poly(vinylidene fluoride), PVDF ($\text{CH}_2\text{-CF}_2$) is a semi- crystalline polymer which has, in recent times , attracted the attention of scientists due to its pyro and piezoelectric properties. Another interesting property of PVDF is its polymorphism. PVDF exists in five crystalline phases- α phase which is nonpolar, while β , δ , γ and ϵ phases which are polar. Although PVDF has a simple chemical structure, it is well established that it can exhibit five different polymorphs depending on its processing conditions. These crystal forms involve three different chain conformations, namely: (1) all-trans (TTTT) planar zigzag for β -phase, (2) TGTG' for α and γ phases, and (3) T₃GT₃G' for δ and ϵ phases [1]. When PVDF chains are packed into crystal lattices, their dipoles are either additive, which leads to a net dipole as in β , γ and δ phases, or cancelled among themselves, resulting in no net dipole as in α and ϵ phases [1]. Among the three polar phases, the β -phase has the largest spontaneous polarization (p) per unit cell and thus exhibits the highest piezo-, pyro and ferroelectric activities, which endues PVDF with great potentials for various device applications[2]. However, the phases of a particular PVDF film depend on the method of preparation and post preparation treatments. Various methods have been used to prepare PVDF films, like melt casting, spin coating, solution casting, chemical vapor deposition etc. Post preparation treatments include mechanical stretching, stretching along with heating, electric poling, annealing etc.[3][4][5]. Many researchers intend to enhance the β phase of PVDF and it is frequently investigated worldwide.

Researchers had adopted different methods reported in literatures. The effect of filler like BiCl_3 FeCl_3 - CoCl_2 and MgCl_2 on the content of the α and β phases and the structural and physical properties of PVDF films is reported [6],[7]. These techniques normally induced undesired structural deformation giving rise to changes of the physical properties in the worse direction. Effect of annealing on phase transition in poly(vinylidene fluoride) films prepared using DMSO solvent.[8] When deposited from solutions PVDF commonly crystallizes in α and γ phase. The β phase has been found in solvent-cast thin films when a highly polar but toxic solvent, hexamethyl phosphoramidate, was used [5]. Solution casting method has become popular recently and has been established as a simple and versatile method for fabricate polymer thin films. The solvents used frequently by various researchers are highly polar solvents like DMF and DMSO. There is no report on the systematic study of PVDF films prepared using acetone as a solvent. This motivated us to investigate the possibility of preparing PVDF films by solution casting method using a less polar solvent like acetone.

This work was undertaken to investigate the crystalline phase variation in PVDF thin films under various conditions using acetone solvent. In the present study we have prepared PVDF films by solution casting method using acetone as solvent under two set of conditions. The preparation conditions have been varied to obtain two kinds of films. Then in post preparation treatment films were subjected to thermal annealing for five hour. An as-cast PVDF film is kept for reference study and three films annealed at different temperature from

each set are studied using XRD, FTIR and UV-Vis. spectroscopy. Finally effect of annealing and time of crystallization on structural and optical properties PVDF films have been studied and reported in this report.

II. METHODS AND PROCEDURE

Materials

PVDF powder used in the study obtained from Alfa Aesar Chemical Company and Acetone obtained from RFCL Limited (RENKEN). The double distilled water was prepared in laboratory.

Experimental

2.1 Sample Preparation

Crystallization from solution method is used for sample preparation. Films of PVDF were prepared by casting method. The solvent used was the pure acetone to dissolve the PVDF powder. PVDF was dissolved in the acetone at PVDF concentration, namely polymer/solvent weight ratio of 15 wt.% . Solution was heated at 60 °C for 30 minutes with continuous stirring to make it clear. The solution of dissolved polymer were cast on glass and dried at room temperature. Imposing condition on crystallization time PVDF films were casted under two sets.

2.1.1 Under Set-1 the films were cast on glass substrate. These films were dried rapidly at room temperature in 30 minutes.

2.1.2 Under set-2 the time of crystallization was increased. This was achieved by reducing the evaporation rate of solvent. The solution content kept in beakers covered with aluminum foil and kept undisturbed to drying. It took 25 days to completely dry and we obtained transparent PVDF self standing films (foil).

The films so produced were kept at room temp. for two weeks to ensure the complete removal of solvent traces . The films so produced were annealed at three different temperatures viz. 70, 90 and 110 °C. Then four films viz. as cast, annealed at 70, 90 and 110 °C of each set were characterized by XRD, FTIR and UV-Vis spectroscopy. For XRD films on glass substrate were used where as self standing films were used for FTIR and UV-VIS spectroscopy.

2.2 Characterization techniques

The XRD patterns were recorded using D8 Discover diffractometer from Bruker. The XRD patterns were recorded 2θ ranging 10° to 50° with step scanning was performed at 0.05° intervals and CuK α radiation ($\lambda=1.54 \text{ \AA}$) was used as the X-ray source. The FTIR spectra in the wave number range 400-4000 cm^{-1} were recorded in transmissions mode using Vertex 70 FTIR spectrometer from Bruker. UV-Vis Spectra were recorded using Shimadzu 2450 spectrophotometer. The absorption spectra were measured in wavelength range 200-1100nm.

III. RESULT AND DISCUSSIONS

3.1 X-Ray diffraction

The XRD scans of PVDF films set-1 and set-2 are shown in Fig. 1.1 and 2.1 respectively. The general feature of the observed spectra indicates the presence of a semicrystalline structure. The XRD pattern of rapid dried as cast PVDF film showed amorphous nature of sample with signature of peak around $2\theta=20.20^\circ$. This is because of rapid drying which froze the mono-mers of PVDF in random that found no time to crystallize. Whereas XRD pattern of slowly crystallize as cast film is semicrystalline with characteristics peaks at $2\theta = 18.46^\circ, 20.45^\circ, 26.70^\circ$ and 39.20° . The peaks at 18.46° and 39.20° assigned to α -phase whereas peak at 20.45° was assigned as β -phase [3],[5],[6]. When the rapid dried and slowly crystallized films thermally annealed at 70, 90 and 110 °C for 5 hour peaks appear and assigned to different phases of PVDF which are tabulated in Table 1. The XRD patterns of rapid dried films conforms that the presence of β -phase around $2\theta = 20.23^\circ$ the peak become prominent with increase in annealing temperature up to 90°C. The β -phase is dominant in which was film rapid dried and annealed at 90°C for 5 hour. The films slowly crystallized result in dominant α phase because monomers of PVDF had enough time to settle to stable crystalline structure. The XRD patterns of these films have prominent peak at $2\theta = 18.60^\circ$ and 39.30° assigned to α -phase. There is no effect of annealing on α -phase while peaks assigned to β -phase at 20.40° got intense a bit.

3.2 Fourier Transform Infra-red Spectroscopy

Figure 1.2 and 2.2 shows the FTIR spectrums of the set-1 and set-2 pure PVDF films. According to literature, the α -phase shows the characteristic absorption bands at 975 cm^{-1} (CH₂ twisting), 796 cm^{-1} (CH₂ rocking), 763 and 616 cm^{-1} (CF₂ bending and skeletal bending), 532 cm^{-1} (CF₂ bending) and 489 cm^{-1} (CF₂ bending) while β -polymorph has peaks at 510(CF₂ bending) and 840 cm^{-1} (CH₂ rocking mode)[8][9][10]. The spectra contain clear absorption peaks characterizing both α and β -phase. The peaks at 511, 840 and 886 are figure prints of β phase and peaks at 616 cm^{-1} 763 cm^{-1} and 975 cm^{-1} are assigned to α -phase. The spectra contain

clear peaks characterizing β phase occurs most notably at 511, 839 cm^{-1} , 886 cm^{-1} and 1173 cm^{-1} and α phase at 430, 616, 796 and 975 cm^{-1} . In order to compare the content of each crystalline phase, a characteristic IR frequency bands for each phase is required. In this study infrared bands at 839 cm^{-1} and 616 cm^{-1} were used in the analysis as the characteristic bands for β and α phase respectively.

The FTIR spectra of films conforms the β and α phases exist. It is found that with increase in annealing temperature absorption intensity at 616, 763 cm^{-1} sharply decreases whereas the absorption intensity increases at 510 and 840 cm^{-1} . It advocates the increase in β phase of PVDF is observed in PVDF films of set-1. In the FTIR spectral analysis of set-2 films it become clear that shifting of band positions observed but α -phase peak height remained unaltered, however minute absorption band at 510 cm^{-1} signifies presence of β -phase. The above discussion of FTIR conform the x-ray diffraction results.

3.3 Optical absorption

The UV/VIS optical absorption was measured for the present PVDF system. The UV-visible absorption spectroscopy technique is used for the investigation of optical properties of the PVDF polymer samples in the wavelength range 190–800 nm. The UV-visible spectra of set-1 and set-2 PVDF films are shown in Fig.1.2 and 2.2 respectively. The absorption of light energy by polymeric materials in the ultra violet and visible region involves the promotion of electrons in σ , π and n-orbitals from the ground state to higher energy state [11]. The optical absorption spectrum of the as-cast film in Fig. 1.2(a) shows that the absorption decreases sharply from 190 nm to 220 nm and then decreases gradually up to 320 nm. In between 320 nm and 360 nm, two distinct characteristics peaks are observed which may be correlated with electronic transition occurring in fluorocarbon (CF). After 360 nm the optical absorption decreases linearly at higher wavelength. The fundamental absorption shows a sudden rise in absorption, known as absorption edge, which can be used to determine the optical band gap ($E_g = h c/v$). Absorption is expressed in terms of a coefficient $\alpha(v)$ (absorption coefficient), which is defined as the relative rate of decrease in light intensity. The absorption coefficient $\alpha(v)$ + was calculated from the absorbance (P). Where $\alpha(v) = 2.303P/d$ and d is the sample thickness.

Band gap analysis

In order to study the effect of structural change due to annealing time of crystallization on optical behaviour of PVDF films, optical band gap (E_g) for PVDF films has been determined using Tauc's relation equation-(1) [8].

$$(\alpha h\nu) = A [h\nu - E_g]^n \text{-----(1)}$$

where $h\nu$ is the photon energy, h is Planck's constant, α is the absorption Coefficient, E_g is the optical energy gap, A is the constant, for direct transitions $n=1/2$. We plot a graph between $(\alpha h\nu)^2$ versus $h\nu$, the linear part of each tauc curve in Fig. 1.4 indicates the presence of an optical gap E_g . The extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ axis gives E_g . Figure 1.4 and 2.4 shows the plots of $(\alpha h\nu)^2$ versus $h\nu$ for the set-1 and set -2 PVDF films respectively. The fundamental absorption edge is one of the most important features of the absorption spectrum of crystalline and amorphous materials. Is found absorption edge shifted to longer wavelength with increase in annealing temperature. The values of absorption edge and energy band gap E_g obtained for both set of films is tabulated in table 2. It is found that the band gap of PVDF films decrease with increase in annealing temperature and absorption edge shifted to longer wavelength. Further rapid dried films has lower band gap as compared to films crystallized slowly under set-2 as shown in fig 3. The decrease in band gap is a result of increase in crystallite size in PVDF films. Since band gap is inversely related to crystallite size.

IV. FIGURES AND TABLES

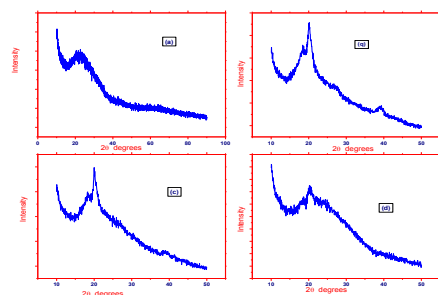


Fig.1.2 XRD pattern of PVDF set-1 films (a) as cast film, (b), (c) and (d) are films annealed at 70, 90 and 110 °C respectively
Optical spectra for set 1 PVDF films

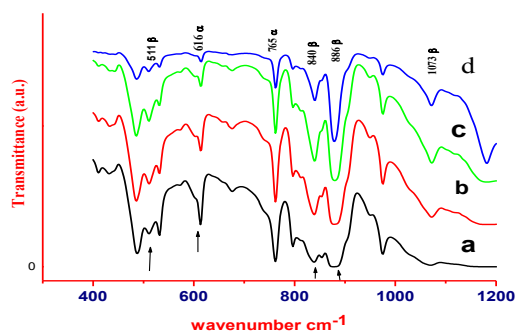


Fig.1.2 FTIR spectra of PVDF set-1 films (a) as cast film, (b), (c) and (d) are films annealed at 70, 90 and 110 °C respectively.

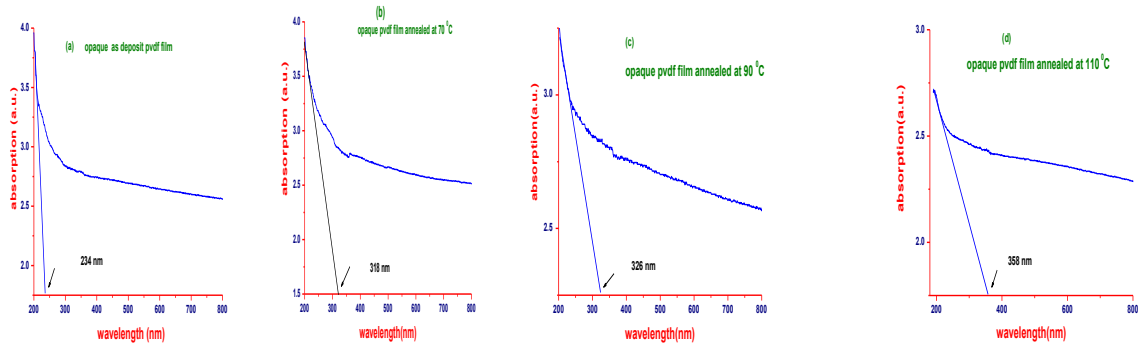


Figure 1.3 Absorption plot of PVDF set-1 films (a) as grown film, (b), (c), and (d) for samples annealed at 70, 90 and 110 °C respectively.

Taus's Plot:

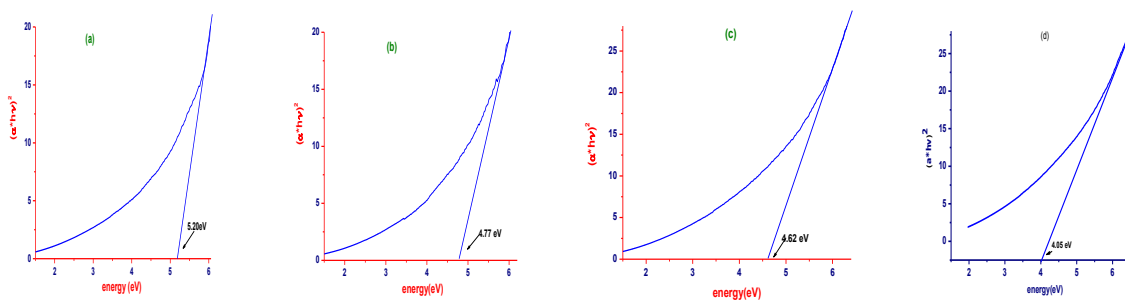


Figure 1.4 Square of $\alpha \cdot h\nu$ Vs energy plots of set-1 films (a) As cast film. (b), (c) and (d) are films annealed at 70, 90 and 110 °C.

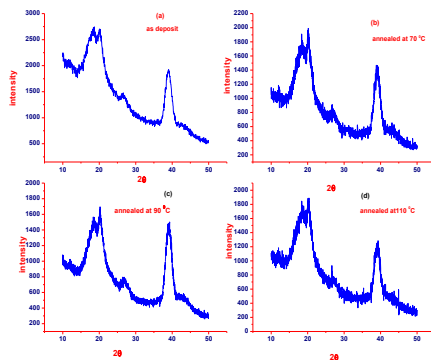


Figure 2.1 XRD patterns for set – 2 films, (a) as cast film, (b) films annealed at 70 °C, (c) films annealed at 90 °C and (d) films annealed at 110 °C.

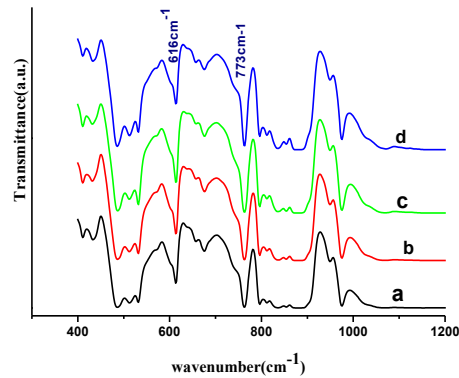


Figure 2.2 FTIR patterns for set – 2 films, (a) as cast film, (b) films annealed at 70 °C, (c) films annealed at 90 °C and (d) films annealed at 110 °C.

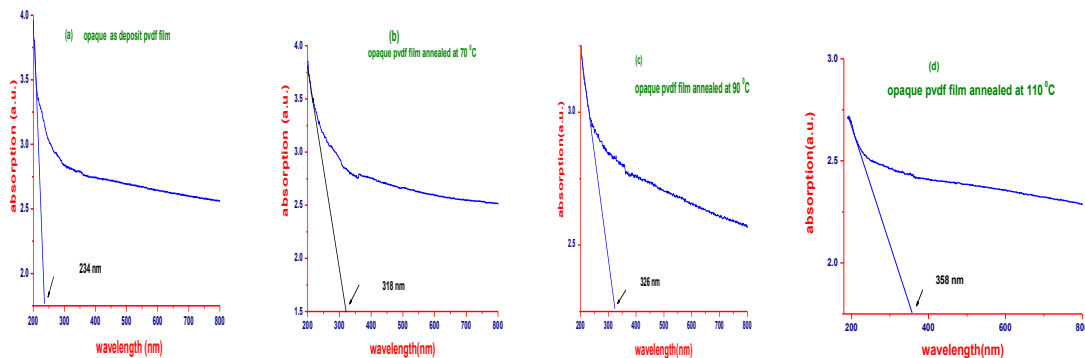


Figure 2.3 Absorption plot of PVDF set – 2 film (a) As cast film. (b), (c) and (d) are films annealed at 70, 90 and 110°C.

Tauc's plot:

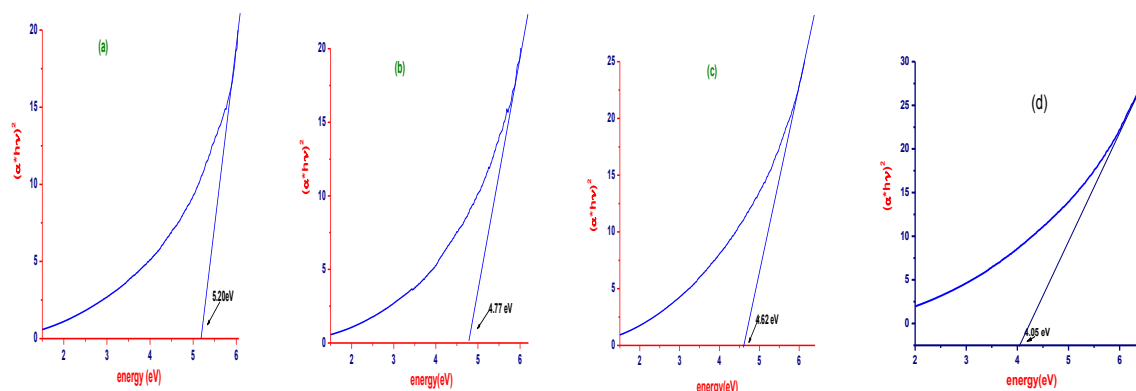


Figure 2.4 Square of alpha*energy Vs energy for PVDF set – 2 films (a) As cast film. (b), (c) and (d) are films annealed at 70, 90 and 110 °C.

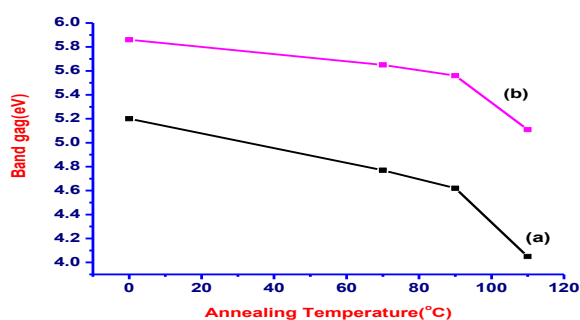


Figure 3.1 Band gap against annealing temperature (a) and (b) for samples prepared under set – 1 and set – 2 conditions respectively

TABLES

Sample	Set – 1		Set – 2	
	2θ	Assignment	2θ	Assignment
As grown film	20.6	β phase	18.46	α phase
	22.6	α phase	20.45	β phase
	42.7	α phase	26.80	α phase
			39.20	α phase
Annealed at 70 °C	18.4	α phase	18.46	α phase
	20.2	β phase	20.42	β phase
	26.7	γ phase	26.80	γ phase
	39.6	α phase	39.30	α phase
Annealed at 90 °C	18.2	α phase	18.59	α phase
	20.1	β phase	20.40	β phase
	38.4	α phase	26.80	γ phase
			39.30	α phase
Annealed at 110 °C	18.6	α phase	18.30	α phase
	20.1	β phase	20.40	β phase
	21.0	α phase	26.80	γ phase
			39.30	α phase

Table1 Peaks feature in XRD patterns of samples under study.

S. no.	Samples	Set – 1 PVDF thin films		Set – 2 PVDF films	
		Absorption Edge λ (nm)	Band gap (eV)	Absorption Edge λ (nm)	Band gap (eV)
1.	As deposit	227	5.20	238.8	5.86
2.	Annealed at 70 °C.	320	4.77	233.3	5.65
3.	Annealed at 90 °C.	326	4.62	240.6	5.56
4.	Annealed at 110 °C.	358	4.05	296	5.11

Band gap and absorption edge of PVDF samples:

Table-2 Experimental values of band gap and absorption edge for under study samples.

V. CONCLUSION

In this report it is observed that the same solvent can yield all the three phases of PVDF. By changing the time of crystallization different phases of PVDF can be obtained using less polar acetone solvent. The time of crystallization and annealing conditions decide the presence of different phases and conversion of one phase to other phase of PVDF. The β -phase which is important for ferroelectric application is obtained using less polar solvent and by suitable annealing. Maximum β -phase exists in the rapidly dried PVDF films when are annealed at 90°C for 5 h. for. The enhanced β -phase at different annealing condition has been confirmed from XRD and FTIR of PVDF film. Thus dominant β -phase films can be prepared under rapid drying of solution and annealing at 90°C for 5 hour. Films produced by slow crystallization are rich in stable α -phase and remain unaltered after annealing. UV-VIS study shows presence of absorption edge in each case. The position of absorption edge shifts to longer wavelength with annealing temperature. Energy band gap is calculated using tauc plot and it is found that annealing effect band gap. The decrease in energy band gap for each film is observed. Thus films with wholly β -phase can be produced by less polar solvents.

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