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Effect of annealing process on the phase formation in Poly(vinylidene fluoride) Thin Films

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Abstract. This work reports the initial study on the effect of annealing process on the crystalline phase of poly(vinylidene fluoride) (PVDF) thin film. PVDF powder was dissolved in N,N-dimethylformamide before spin-coated onto a glass substrate to form a film. The films were annealed at 30°C, 90°C and 110°C for 5 hrs. The crystalline phase of the powder PVDF as received was investigated by using XRD and FTIR techniques. Moreover, the crystalline phases of thin films after annealing were investigated by using the same techniques. XRD analysis showed that in powder form PVDF exists in α -phase. Each annealed PVDF thin films exhibited identical formation of three-phases material namely γ (as major phase) while α and β phases as the minor phases. The FTIR analysis showed that the powder form of PVDF exists in α and β phases. FTIR measurement further confirmed the XRD results implying that the annealing process has no significant effect on the phase formation in PVDF films.

Keywords: crystalline phase, piezoelectric, spin-coated, XRD, FTIR.

PACS: 77.55.hn, 77.90.+k

INTRODUCTION

Poly(vinylidene fluoride) PVDF, has been widely investigated during the last three decades fundamentally because of its unique properties. It can be facilely treatment, and has exceptional mechanical properties, high chemical resistance, good thermal stability as well as high pyro and piezoelectric coefficients. These properties supply a wide range of scientific as well as technological applications [1] especially in the field of sensor and actuator devices [2-3].

PVDF is a semi crystalline polymer that subsists in four polymorphs, α , β , γ and δ , based on the sort in which they were found out, the last three being polar [4-5]. The relative amount of each phase is dependent on the thermal, mechanical and electrical processing conditions used for manufacturing PVDF thin film. PVDF is composed of repeated units of fluorinated hydrocarbon connected linearly; Crystallization conditions will decide the type of constitution and in turn the crystal structure of PVDF.

PVDF in α -Phase is the most general constitution. The chain conformation of α -Phase consists of trans-gauche (TG^+TG^-) sequences, with zero net dipole moment as a result of the fluoride atoms the order of an anti-parallel mode along the chain, thus neutralizing the full structure [2]. Identical, the δ -Phase has TG^+TG^- constitution, but are differed by C-F bonds lined up in one direction around the chain direction with every other chain rotated, resulting in a net dipole [7]. PVDF in β -Phase consists of an all trans (TTT) planar zig-zag structure crowded in an orthorhombic unit cell, give rise to in a considerable dipole moment profiling to the chain axis [2,6]. The dipole moments for β -Phase have the two F-C and two C-H bonds put up in such a way that the monomer gets an effectual dipole moment in the direction perpendicular to the carbon backbone. Consequently, the β -Phase exhibits the most superior ferroelectric and piezoelectric properties because it has the largest spontaneous polarization per unit cell.⁷ Monoclinic crystal lattice γ -phase PVDF has a structure identical to those in the β -Phase, with a little different chain constitution ($TTTG^+TTTG^-$) [6].

To obtain each phase, the α -Phase is the most general constitution because it is easily created from melt re-crystallization at temperatures below 160°C [8]. The β -Phase is the mainly attractive from a technological point of view, for providing that pyro and piezoelectric are better properties. It obtained by using highly polar solvent hexamethylphosphoramide (HMPA) by drying films cast at temperature between 60 and 140°C [9]. Also, by using polar solvent dimethylsulfoxide (DMSO) and changed the solution temperature, different phases of PVDF obtained, and annealing at 90°C for 5 hrs, maximum percentage of β -Phase can be obtained [10]. Spin coating was used to obtain thin films of β -Phase [11-13]. α and β -Phase conformation were produced in PVDF thin films cast by varying solvent polarity (DMF and HMPA) respectively, evaporation rate and drying temperature 140°C [14]. By crystallization at temperatures near the melting temperature (T_m) of the α -Phase, the γ -Phase

may be outcome [8,15-16]. Also, the γ -Phase obtained in annealing at temperatures near to T_m , because of transformation from α -Phase to γ solid state phase [16-19]. Different phases of PVDF thin films were cast by using acetone solvent, which was obtained by changing the time of crystallization and annealing temperature [20].

The aim of this work is to initial study on the effect of annealing processes on the crystalline phases of poly(vinylidene fluoride) (PVDF) thin film. The thin film prepared by using spin coating method. The crystalline phases of powder and thin films can be investigated by using X-ray diffraction and Fourier transformation infrared FTIR spectroscopy with an ATR system.

Methods

PVDF powder received from (SIGMA-ALDRICH-France) was dissolved in N,N-dimethylformamide (DMF) (15wt %), by using a magnetic stirrer with angular velocity 400 rpm, heating 50°C and time 15 min to help the powder to dissolve and preventing agglomerates. The solution (0.1ml) was deposited on clean glass substrates (2.5 cm x 2.5 cm) by using spin coating (angular velocity 1000 rpm and time 30 sec). The thin films dry under ambient conditions (room temperature 30°C).

The thin film was annealed at temperature 30°C, 90°C and 110°C for time 5 hrs. The crystalline phases of the powder PVDF and PVDF thin films were determined by X-ray diffraction (XRD) and Fourier transformation infrared spectroscopy (FTIR) with an ATR system (FTIR-ATR). Both X-ray diffraction and FTIR were used to check the phase formation in the samples. Each scan was performed with x-ray diffraction with 2θ angle ranging from 10° to 60°. FTIR spectrum was obtained in the wave number range of 600-1600 cm^{-1} .

RESULTS AND DISCUSSION

XRD Analysis

FIGURE 1 shows the X-ray spectrum of the PVDF powder as received (i.e. powder may annealing at room temperature) and PVDF thin film annealed at room temperature 30°C. XRD spectrum contains sharp peaks due to the crystallites, while the amorphous regions give rise to a much broader background scattering. This figure shows the existing of α -phase peaks at $2\theta=18.123^\circ$, 19.675° , 26.93° in PVDF powder, while in the PVDF thin film annealed at 30°C the existing of three phases, γ -Phase (as major phase) at $2\theta=20.3^\circ$, α -Phase at $2\theta=18.875^\circ$, 18.4° and β -Phase at $2\theta=20.8^\circ$ as the minor phases. This is attributed to reaction between solute and solvent. The growth of these phases as a result of activation energy given to the thin film samples. The existing of α -phase only in PVDF powder means that this phase grows at the expense of other two phases as a result of environment conditions.

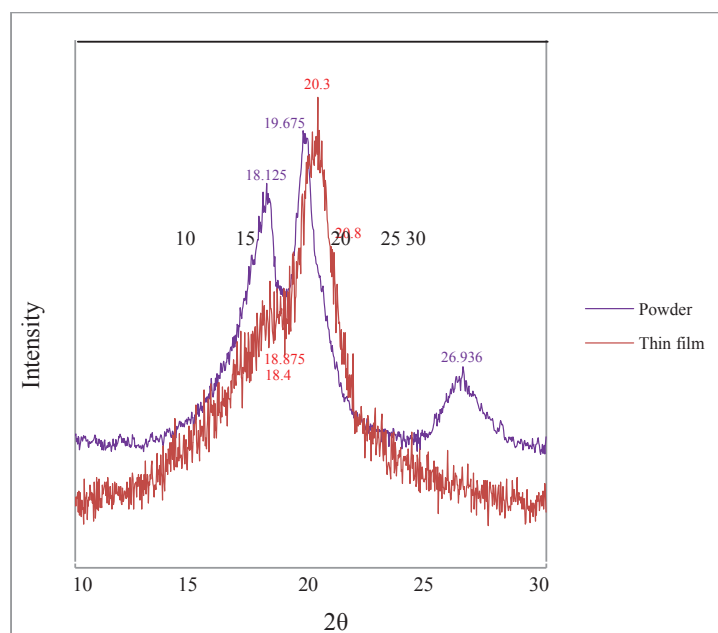


FIGURE 1. X-Ray diffraction pattern of PVDF powder as received and thin film annealed at 30°C.

FIGURE 2 shows X-ray spectrum of the annealed PVDF thin films at 30°C, 90°C and 110°C for 5 hrs. The figure shows the existing of γ , α and β -Phases for each sample. For thin film annealed at 30°C, the peak at $2\theta=20.3^\circ$ corresponded γ -Phase, $2\theta=18.875^\circ$ for α -Phase and $2\theta=20.8^\circ$ for β -Phase. In the case of annealing at 90°C, the peak at $2\theta=20.3^\circ$ coincided with γ -Phase, $2\theta=18.4^\circ$ for α -Phase and $2\theta=20.625^\circ$ for β -Phase. At 110°C the peak at $2\theta=20.3^\circ$ confirms excising γ -Phase, while the peak at $2\theta=20.25^\circ$, 20.45° and 20.7° confirms the existence β -Phase and the peaks at $2\theta=18.8^\circ$, 19.75° for α -Phase. Despite of three phases were appeared in each annealing temperature 30°C, 90°C and 110°C, the γ -Phase shows more growth at expense of other phases, i.e. the annealing temperature plays an important role of increasing γ -Phase. Satapathy [10] used dimethyl sulfoxide (DMOS) solvent, and obtained a maximum percentage of β -Phase in PVDF thin films when annealed at 90°C for 5 hrs. Imtiaz Noor Bhatti [20] got as analogous result as Satapathy by using the acetone as solvent but pointed out that $2\theta=20.3^\circ$ belong to the β -Phase. The results of this work are not agreed with previous works. So, there is no effect of annealing temperature on the crystalline phases.

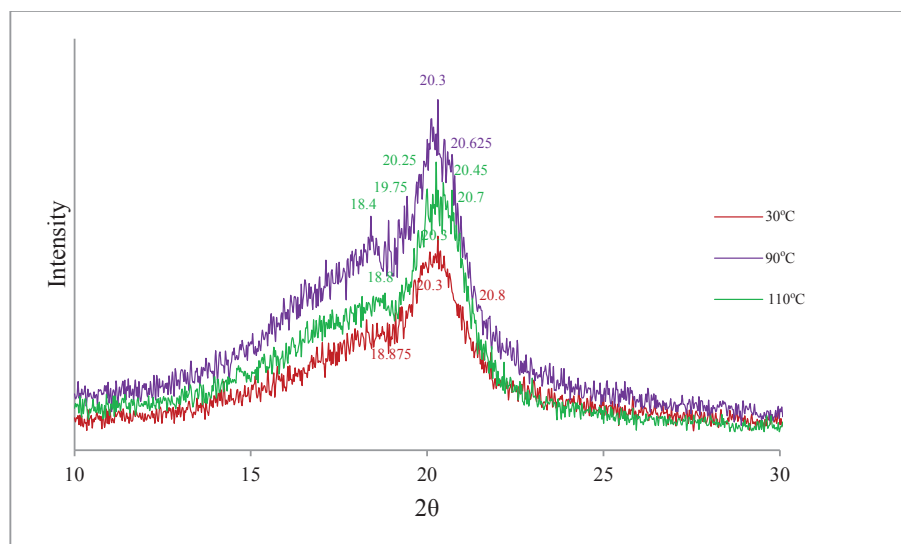


FIGURE 2. X-Ray diffraction pattern of annealed PVDF thin films.

FTIR Analysis

FIGURE 3 shows the FTIR spectrum of PVDF powder and thin film annealed at room temperature 30°C. The FTIR of PVDF powder confirms existing of α and β phases. The IR vibration modes of PVDF powder due to α -Phase are 762, 796, 877, 975 and 1402 cm^{-1} , while IR vibration modes of β -Phase are 838 and 1072 cm^{-1} . The FTIR spectra of PVDF thin film exhibited existence three phases γ , α and β . The peak at 1233 cm^{-1} conforms for γ -Phase. The peak due to the α -Phase are identified at 876, and 1402 cm^{-1} and the peak for β -Phase are 838, 1072 and 1170 cm^{-1} .

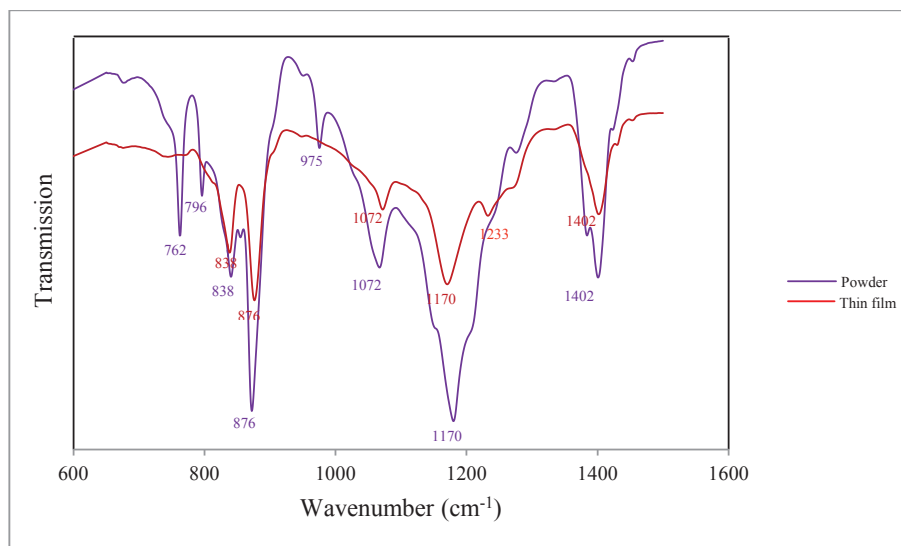


FIGURE 3. FTIR spectra of powder PVDF as received and thin film annealed at 30°C.

FIGURE 4 shows that the FTIR spectra of annealing thin films at 30°C, 90°C and at 110°C for 5 hrs. Main characterizing peaks of PVDF thin films can be discussed as follows. The IR vibration modes due to the γ -Phase are 1233 cm^{-1} and the vibration modes due to the β -Phase are 838, 1072 and 1170 cm^{-1} . The IR vibration modes due to the α -Phase are identified at 876, and 1402 cm^{-1} . The increase in intensities of the peaks at 876 and 1170 cm^{-1} indicates the increase of α -Phase in the annealed thin films. In this work, there is no difference in FTIR spectra of PVDF thin films. So that, the annealing temperature has no significant effect on the crystalline phases of PVDF thin film.

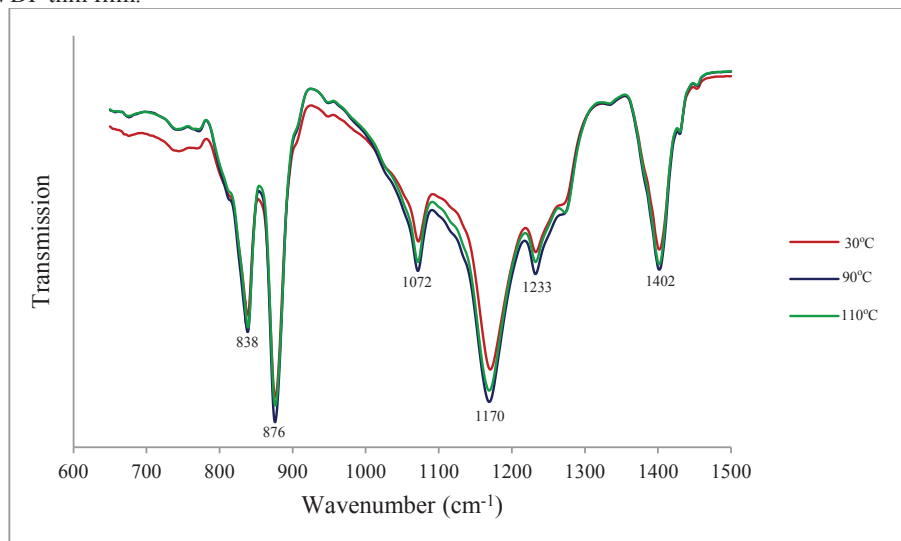


FIGURE 4. FTIR spectra of annealed PVDF thin film.

CONCLUSION

In this study, the effect of annealing process on the crystalline phases of poly(vinylidene fluoride) (PVDF) is observed. XRD analysis showed that the powder form of PVDF exists in α -phase. Each annealed PVDF thin film exhibited identical formation of material with three phases namely, γ (as major phase) while α and β phases as the minor phases. The annealing process changed a phase of substance, however, there was no effect for annealing temperatures on changing the phase of matters. The FTIR analysis showed that the powder form of PVDF exists in α and β phases, while annealed PVDF thin film shown conformable formation of α , β and γ -Phases. FTIR measurement further confirmed the XRD results implying that the annealing temperature has no significant effect on the phase formation in PVDF films.

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