



Study of β -phase development in spin-coated PVDF thick films

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Abstract. A study was conducted to ascertain the effect of variation in spin speed and baking temperature on β -phase content in the spin-coated poly(vinylidene fluoride) (PVDF) thick films (~ 4 – $25\ \mu\text{m}$). Development of β -phase is dependent on film stretching and crystallization temperature. Therefore, to study the development of β -phase in films, stretching is achieved by spinning and crystallization temperature is adjusted by means of baking. PVDF films are characterized using Fourier transform infrared spectroscopy, X-ray diffraction, differential scanning calorimetry, and scanning electron microscopy. It is observed that crystallization temperature lower than 60°C and increase in spin speed increases the β -phase content in PVDF films. Crystallization temperature above 60°C reduces β -phase content and increases α -phase content. It was also observed that viscosity of the PVDF solution affects the β -phase development in films at a particular spin speed.

Keywords. Poly(vinylidene fluoride); β -phase; spin coating; crystallization temperature.

1. Introduction

Poly(vinylidene fluoride) (PVDF) is a popular polymer among researchers due to its piezo and pyroelectric properties. In addition, PVDF films have properties like flexibility, biocompatibility, low acoustic impedance etc., which are extensively used in the field of sensors and actuators [1–8].

PVDF is a semi-crystalline polymer, which exists in five phases, namely α , β , γ , δ and ϵ . In the α -phase, molecular dipoles are anti-parallel to each other and therefore, there is zero net dipole moment. The remaining β , γ , δ and ϵ phases have molecular dipoles that are parallel one to the other; and they exhibit net non-zero dipole moment [8,9]. There are some methods to achieve these polar phases in PVDF such as mechanical deformation or stretching [8–11] and quenching from the melt, which develops β form [12,13]. PVDF composites with materials, such as, gold nanoparticles [14], carbon nanotubes [15] and nanoclay [16,17] showed the development of β -phase. Poling under large electric fields forms δ and β phases [18,19]. Annealing at higher temperatures gives rise to γ and ϵ phases [20,21]. The piezoelectricity of PVDF primarily depends on the β -phase content [8–10,22–26] and hence development and enhancement of the β -phase PVDF films is a subject of interest in the fabrication of piezoelectric sensors.

Spin coating is a very easy and affordable method to get uniform PVDF films of various thicknesses with an increase in β -phase content due to the stretching effect caused by centrifugal force [24–27]. It has advantages over conventional mechanical stretching, in which excess stretching may lead to damage or introduce defects in the PVDF films [20]. Researchers prepared spin-coated PVDF films and studied

the effect of spinning speed on the development of β -phase [24–27]. However, most of the scientists studied β -phase development in the spin-coated PVDF thin films (thickness $< 4\ \mu\text{m}$ or in nanometers). In many cases, there is requirement of thick PVDF films containing β -phase. However, the systematic study of the influence of spin speed and baking temperature on spin-coated thick films is yet to be done. Therefore, in the present work, attempts have been made to study β -phase development in spin-coated PVDF thick films of the order of ~ 4 – $25\ \mu\text{m}$.

2. Materials and methods

PVDF solutions of different viscosity were prepared by dissolving PVDF powder ($M_w = 534,000\ \text{g mol}^{-1}$ from Aldrich) in N,N-dimethylformamide (DMF, 99.8% from Sigma Aldrich). The solution was heated at 50°C and stirred for 60 min for complete dissolution of PVDF. Films were casted by spin coating the solution at room temperature (RT) ($\sim 28^\circ\text{C}$) on cleaned glass substrates. Films are prepared at different spin speeds and crystallized by baking at different temperatures for 2 h. Baking is carried out on a temperature-controlled hot plate (accuracy $\pm 2^\circ\text{C}$). Spin Coater from Laurell Technologies Corporation (WS-400E-6NPP-LITE) was used for spin coating. Humidity at the time of preparation was typically in the range of 40–45%. PVDF films were characterized using Fourier transform infrared spectroscopy (FTIR) (Jasco FTIR 6100), X-ray diffraction (XRD) (Bruker AXS), differential scanning calorimetry (DSC) (Shimadzu

DSC 60) and scanning electron microscopy (SEM) (JEOL JSM 6360A). Thickness of the films is measured using INSIZ digital micrometer (Model 3109-25).

3. Results and discussion

3.1 Effect of baking temperature on β -phase formation

Baking temperature (crystallization temperature) affects the phase formation in the PVDF films [22–25]. To study the effect of temperature on the β -phase formation, a large number of films are prepared by spin coating the PVDF solution in DMF with 16, 20 and 24 wt% concentration at constant speed of 2000 rpm for 1 min on cleaned glass substrates. Films are then dried at RT ($\sim 28^\circ\text{C}$) and baked at a temperature ranging from 50 to 90°C for 2 h. The temperature range was selected considering previously reported parameters [23,25], as baking of PVDF films above 60°C gives rise to α -phase and that of dominant β -phase below 60°C . Moreover, films at baked temperature below 50°C show almost same β -phase content.

Almost same thickness is observed for a particular wt% solution irrespective of baking temperature. Thicknesses of the films baked at a temperature from 50 to 90°C are found to be 4, 9 and $15\ \mu\text{m}$ for 16, 20 and 24 wt%, respectively. Films dried at RT are found to be very brittle and with uneven thickness, which may be due to very high porosity resulting from very slow and incomplete solvent evaporation.

FTIR spectra of PVDF films baked at different temperatures were taken. Representative FTIR spectra for PVDF films prepared using 16 wt% solution are shown in figure 1. Dominant FTIR peaks at 839 and $511\ \text{cm}^{-1}$ are attributed to TTTT (all trans) conformation of molecular dipoles, i.e., β -phase and peaks at 615 , 763 , 795 , 855 and $975\ \text{cm}^{-1}$ indicate the presence of TGTG (T = trans, G = gauche) conformation of molecular dipoles, i.e., α -phase in the films [24,25]. Very small peaks at 812 and $434\ \text{cm}^{-1}$ are attributed to TTG conformation of molecular dipoles, i.e., γ -phase [24,25]. It is clearly seen from figure 1 that the samples baked at RT, 50 and 60°C have dominant peaks of β -phase (peaks at 839 and $511\ \text{cm}^{-1}$) with very small peaks of γ -phase ($812\ \text{cm}^{-1}$). The samples baked at temperatures higher than 60°C show decrement in intensity of β -phase peak, whereas rise in intensity of the α -phase peak is observed. α -Phase is dominant at 90°C . Increase in α -phase and decrease in β -phase content above 60°C temperature is because of increase in the evaporation rate, which increases the crystallization rate of the PVDF molecules, leading to α -phase formation [12–25]. Lower crystallization rate favours β -phase formation [22–25]. Owing to lower crystallization rate at lower temperature ($<60^\circ\text{C}$), there is ample time for nucleation of the crystal molecules; whereas when the crystallization rate is higher at higher temperature, there is less time for nucleation, which leads to α -phase formation [22].

The β -phase content in terms of β -phase fraction is calculated as reported in [10,23,25]. FTIR absorption peaks at

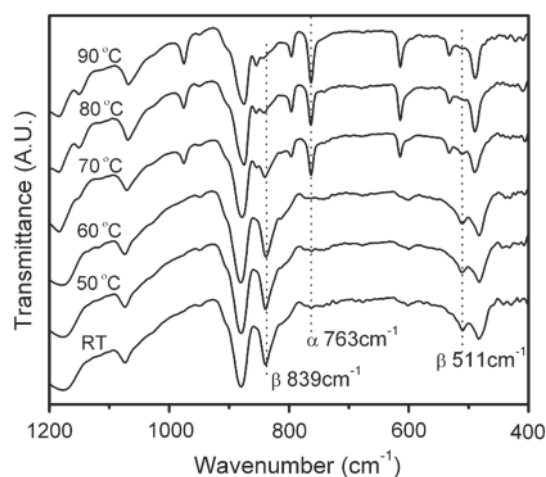


Figure 1. Fourier transform infrared spectroscopy spectra of PVDF films spin coated from 16 wt% solution at 2000 rpm and baked at different temperatures.

839 and $763\ \text{cm}^{-1}$ corresponding to β and α phases, respectively, are considered for the β -phase fraction calculation. It is assumed that IR absorption follows Lambert-Beer law. The absorbencies of A_α and A_β are at 763 and $839\ \text{cm}^{-1}$, respectively, and are explained in Eq. 1 given below

$$A_n = \log \frac{I_n^0}{I} = C \cdot K_n \cdot X_n \cdot t, \quad n = \alpha, \beta \quad (1)$$

where t is the thickness of the film, C is the average monomer concentration, α and β subscripts correspond to the crystalline phases, I^0 and I are the incident and transmitted intensities of the IR waves, respectively, K is the absorption coefficient at a particular wavenumber and X is the degree of crystallinity of every phase. The values of K_α and K_β are $6.1 \times 10^4\ \text{cm}^2\ \text{mol}^{-1}$ and $7.7 \times 10^4\ \text{cm}^2\ \text{mol}^{-1}$, respectively [10,23]. A_α and A_β values are calculated using I^0 and I at 763 and $839\ \text{cm}^{-1}$, respectively. The relative fraction $F(\beta)$ of the β -phase in PVDF films are spin coated from different wt% solutions at 2000 rpm and baked at different temperatures is calculated using Eq. 2.

$$F(\beta) = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{(K_\beta/K_\alpha)A_\alpha + A_\beta} = \frac{A_\beta}{1.26A_\alpha + A_\beta} \quad (2)$$

Variations of $F(\beta)$ for PVDF films prepared from PVDF solutions with different wt% and baked at different temperatures is calculated and plotted, which is shown in figure 2.

As seen in figure 2, $F(\beta)$ (β -phase fraction) decreases as baking temperature increases. There is a sharp decrease in β -phase fraction above 60°C in films prepared from different wt% solutions. However, the decrease in β -phase fraction is slower in case of films prepared using 24 wt% solution.

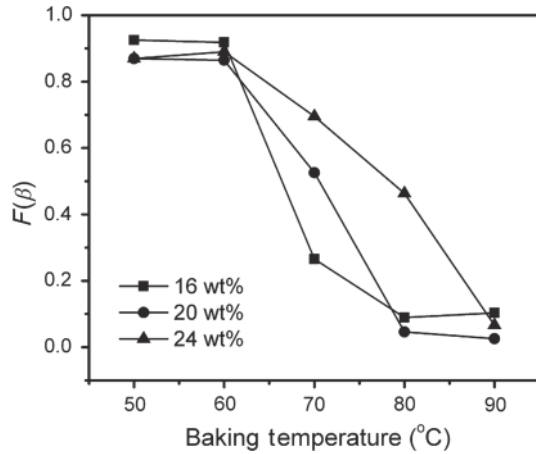


Figure 2. β -Phase fraction with respect to baking temperature spun from different wt% solutions at 2000 rpm.

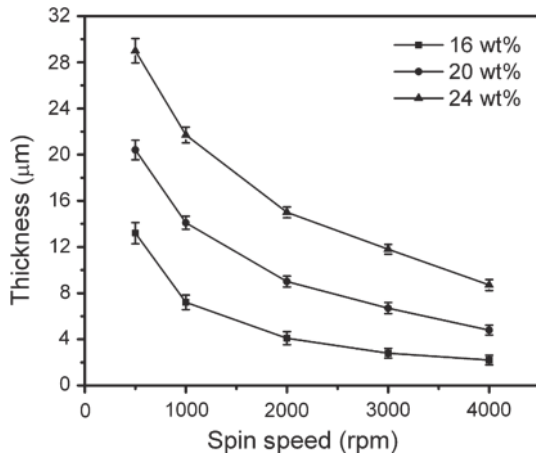


Figure 3. Thickness variation of PVDF films with respect to spin speed.

It may be attributed to the larger thickness of the films, which leads to relatively slower evaporation of the solvent and in turn relatively slower crystallization.

3.2 Effect of spin speed

To see the effect of spin speed on the β -phase formation, the films are prepared by spin coating the solution in DMF with 16, 20 and 24 wt% concentration at different spin speeds ranging from 1000 to 4000 rpm for 1 min on cleaned glass substrates. Films are then baked at 60°C and the β -phase is dominant at this stage, as discussed in the previous section. Figure 3 shows the thickness variation of the spin-coated PVDF films with respect to spin speed and solution wt% concentration. As shown in figure 3 the thicknesses of the films increase with increasing wt% concentration at a particular spin speed and the thickness decreases with increase in

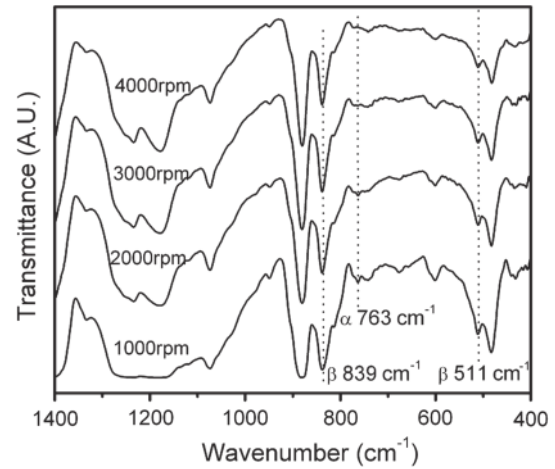


Figure 4. Fourier transform infrared spectroscopy spectra of PVDF films spin coated at different spin speeds from 16 wt% solution.

spin speed at particular wt%. In the process, PVDF films of thicknesses ranging from 2 to 28 μm are obtained.

Figure 4 shows FTIR spectra of PVDF films spin coated from 16 wt% solutions at different spin speeds. It can be clearly seen from figure 4 that upto 3000 rpm, as spin speed increases there is small increment in the intensity of the β -phase peak at 839 cm^{-1} and small decrement in the β -phase peak intensity in films spun at 4000 rpm. β -phase increment with increase in spin speed is attributed to stretching of molecular chains due to centrifugal force exerted by the spin-coating mechanism [24–27]. Gregorio *et al* [23] pointed out one more possibility that during mechanical stretching the existing crystalline order is destroyed and gets reorganized in β -phase when baked at a lower temperature. The results obtained are in agreement with the ones reported in the literature [23–25].

Furthermore, the observed decrement in β -phase in the films spin coated at 4000 rpm is attributed to the possible permanent destruction of some molecular chains because of the large centrifugal force experienced by the film. It may not be possible for such chains to reorganize again. β -Phase fraction, calculated using Eqs. 1 and 2, is a function of spin speed for PVDF films prepared using different wt% solutions and baked at 60°C as shown in figure 5.

It can be seen from figure 5 that β -phase fraction increases with spin speed up to 3000 rpm for PVDF films spin coated with different viscosities (16, 20 and 24 wt%). Similar results are reported by Cardoso *et al* [25]. Spin-coated films using 16 wt% PVDF solution show larger β -phase fraction, whereas spin-coated films using 24 wt% PVDF solution show lower β -phase fraction at a particular spin speed. This may be because at lower viscosities PVDF molecules are relatively sparsely packaged than that of higher wt% solution and therefore more centrifugal force is experienced by the molecular chain. It is also observed that there is increasing trend of β -phase fraction in spin-coated films using 16 and 20 wt% solution upto 3000 rpm. Above 3000 rpm, there is decrement in the β -phase

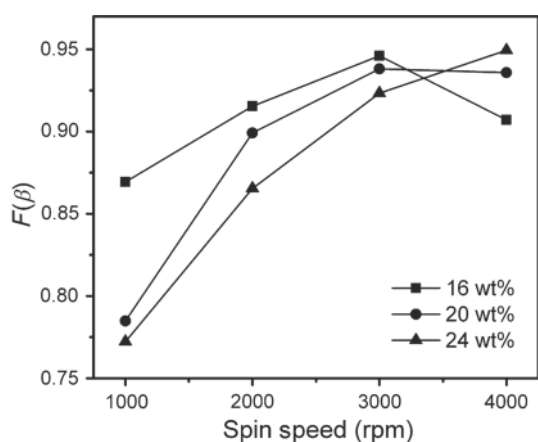


Figure 5. β -Phase fraction of films baked at 60°C as a function of spin speed.

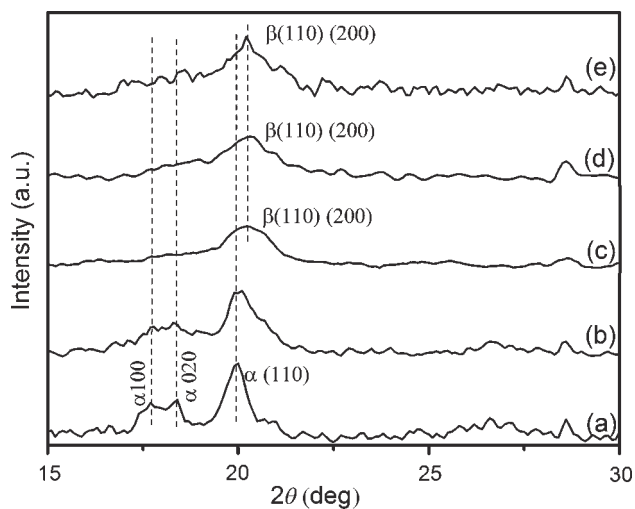


Figure 6. X-ray diffraction of films prepared using 16 wt% solution, spun and baked at (a) 2000 rpm and 90°C, (b) 2000 rpm and 70°C, (c) 1000 rpm and 60°C, (d) 2000 rpm and 60°C, (e) 3000 rpm and 60°C.

content. This is attributed to high rotational speed because of which there may be permanent destruction of some molecular chains in the films that could not be reorganized when spin coating was stopped. Films prepared using 24 wt% solution, however, show increment in β -phase even after 3000 rpm. It is attributed to higher wt% and in turn higher density of the molecular chains, which may not cause permanent damage to the molecular chains at higher spin speeds and therefore, reorganization is possible leading to β -phase formation.

3.3 XRD characterization

The FTIR results are confirmed to a greater extent by taking XRD of the films. Figure 6 shows the XRD patterns of PVDF films prepared using 16 wt% solution; spun and baked at (a)

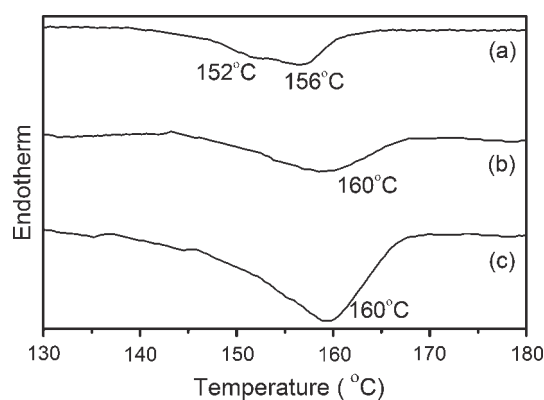


Figure 7. Differential scanning calorimetry of PVDF films prepared using 16 wt% solution, spun and baked at (a) 2000 rpm and 90°C, (b) 2000 rpm and 60°C, (c) 1000 rpm and 60°C.

2000 rpm and 90°C, (b) 2000 rpm and 70°C, (c) 1000 rpm and 60°C, (d) 2000 rpm and 60°C and (e) 3000 rpm and 60°C.

The XRD pattern of samples (a) and (b) shows dominant peaks at $2\theta = 17.7^\circ$, 18.3° and 19.9° , representing the diffraction planes in 100, 020 and 110 respectively, are attributed to α -phase [28]. In sample (b) α -phase peak intensity at $2\theta = 17.7^\circ$, 18.3° and 19.9° decreased and peak at $2\theta = 19.9^\circ$ is slightly shifted towards the right, indicating the presence of a small amount of β -phase, which is also seen from FTIR. In XRD of samples (c), (d) and (e), the peaks representing α -phase are suppressed and the peak at 20.26° is observed, which represents the summation of diffraction planes in 110 and 200 indicating the dominance of β -phase. One can notice a very small increment in the intensity of β -phase peak in case of XRD of samples (d) and (e) than (c). This is because of higher β -phase fraction occurring due to increased spin speed as seen from FTIR. Results obtained agree well with the ones reported in the literature [28].

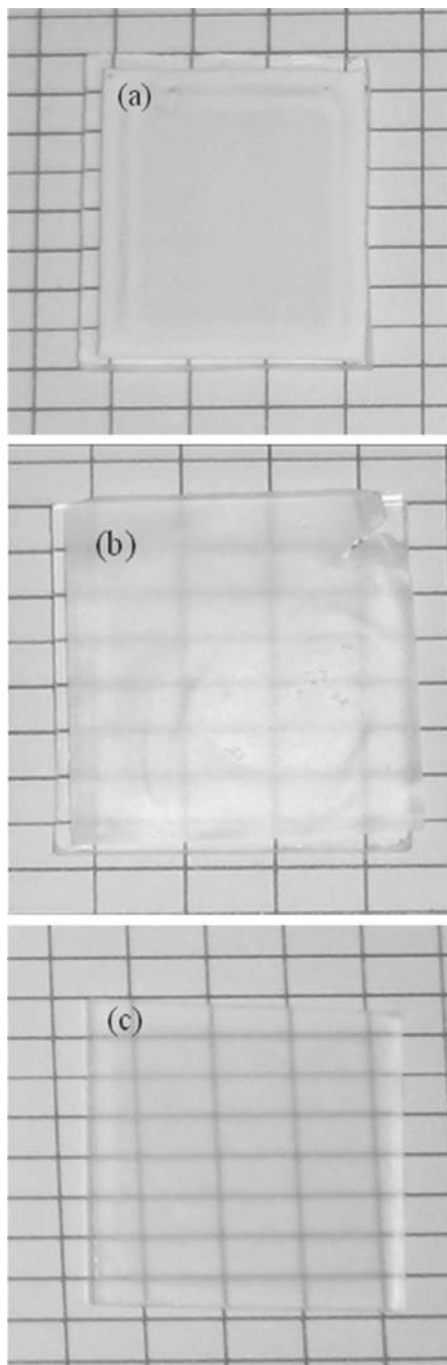
3.4 DSC thermograms

The DSC thermograms of three samples prepared using 16 wt% solution; spun and baked at (a) 2000 rpm and 90°C (b) 2000 rpm and 60°C and (c) 1000 rpm at 60°C are taken and plotted as shown in figure 7. Among the samples (a), (b) and (c); sample (a) shows the two endothermic peaks (152 and 156°C) representing melting temperature of two crystalline phases α and β . The peak at higher temperature represents β -phase and the one at lower temperature represents α -phase. The density of β -phase is highest among the other phases like α , γ and δ ; due to its all trans planar zigzag conformation, which provides more compact packing and higher melting temperature [29]. DSC of samples (b) and (c) shows the single endothermic peak (160°C) with a melting temperature higher than that of sample (a), which may be due to the dominance of β -phase content.

The intensity change in the DSC graphs is attributed to the change in degree of crystallinity of the films subject to the

Table 1. Melting enthalpy and crystallinity measured using differential scanning calorimetry.

Film spun at (rpm)	ΔH (J g ⁻¹)	Crystallinity (%)
1000	43.9	42.0
2000	19.6	18.7
3000	17.1	16.3

**Figure 8.** Photograph of the PVDF films spin coated at 2000 rpm and baked at (a) room temperature, (b) 60°C and (c) 90°C.

stretching effect [30]. Using DSC, change in degree of crystallinity in the films with increased spin speed is investigated. Enthalpy (ΔH) for melting of PVDF obtained from DSC was used to calculate the degree of crystallinity, which is the ratio of ΔH and ΔH_0 (melting enthalpy of totally crystalline material). For pure PVDF $\Delta H_0 = 104.5 \text{ J g}^{-1}$ [10]. The decrease in degree of crystallinity was observed in the film spin coated at different rpm with constant baking temperature of 60°C (see table 1). It is observed that crystallinity gets decreased with stretching, which is attributed to partial destruction of the crystalline lamellae [30].

3.5 Morphology of PVDF films

The films are observed visually and under the SEM. Optical photographs of films baked at RT, 60 and 90°C and placed on the mesh are shown in figure 8. Films crystallized at RT, when observed visually, are seen to be whitish and opaque (see figure 8a). Films prepared and baked at RT are observed to be very brittle in nature when tried to peel off from the glass substrate. SEM of these films is shown in figure 9a. Figure 9(a1) is a magnified view of figure 9a. The films are seen to be porous in nature with spherulites of size $\sim 4\text{--}7 \mu\text{m}$. The surface of the film is also seen to be uneven. Films baked at 60°C are less white (see figure 8b) as seen visually and are also porous in nature as shown in figure 9b. Figure 9(b1) shows a magnified view of figure 9b. Spherulites of size $\sim 4\text{--}7 \mu\text{m}$ are observed in the films crystallized at 60°C. These films have shown better strength than that of films baked at RT when just tested by peeling the film from substrate. Films baked at 90°C are more transparent (see figure 8c), as seen visually, than that of films baked at 60°C. Figure 9c shows the SEM of PVDF films baked at 90°C. It is clearly seen from the image that the spherulite size has increased ($\sim 12\text{--}18 \mu\text{m}$) and the porosity of the films is decreased. Figure 9(c1) shows the magnified image.

High porosity seen at lower baking temperature is attributed to lower evaporation rate of the solvent in the films. Higher evaporation rate at higher baking temperature increases the spherulite size and reduces the porosity. At higher baking temperature there is lesser time for nucleation due to higher evaporation rate of the solvent results in increased growth rate of the spherulites [23,25,27]. Gregorio [28] reported the whitish nature of the PVDF films baked at 60°C. According to them whitish nature of the films is because of refraction and reflection of light from the porous surface of the films. Cavities in the air–solid interfaces tend to reflect and refract light. In this way high porosity of the films baked at RT resulted in opaque nature.

SEM images of the PVDF films spin coated at different spin speeds are shown in figure 10. Figure 10a, b shows SEM images of films baked at 60°C and spin coated at 1000 and 3000 rpm, respectively. Microscopic pores and oriented fibrils between spherulites can be seen in image (b), which is because of higher spin speed.

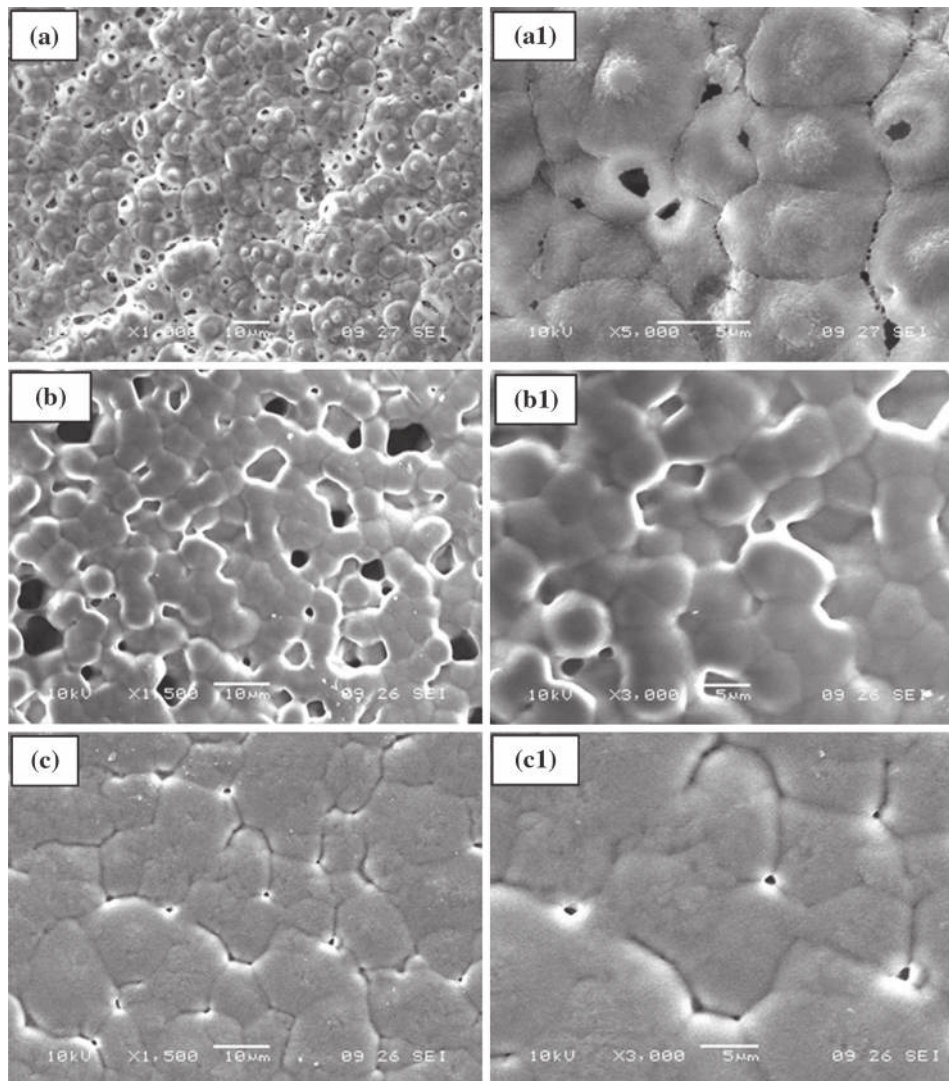


Figure 9. PVDF films crystallized at: (a, a1) room temperature, (b, b1) 60°C and (c, c1) 90°C.

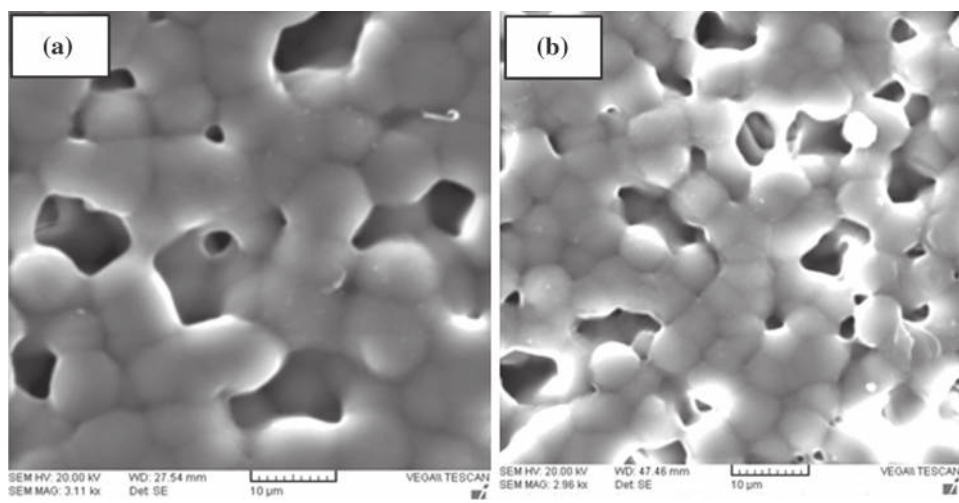


Figure 10. Scanning electron microscopy images of films baked at 60°C and spun at: (a) 1000 rpm and (b) 3000 rpm.

4. Conclusion

PVDF solution is spin coated at different spin speeds and baked at different temperatures causing changes in the β -phase content in PVDF thick films. β -Phase is dominant upto baking temperature of 60°C but for temperature beyond 60°C, β -phase decreases and α -phase increases. α -Phase is dominant at 90°C. Porosity decreases with increase in baking temperature. Increase in the spin speed initially increases β -phase content in the films upto certain limit, which is dependent on viscosity of the PVDF solution; beyond that the films are found to get molecular damage and therefore less β -phase content is observed. However, the crystallinity of films decreases with increase in the spin speed. The results obtained are consistent with previously reported literature [22–25]. Spin coating method is the easiest procedure to develop β -phase content in the PVDF films, which can be further exploited to achieve good quality films for various applications in the field of sensors and actuators.

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