Method for identification and quantification of electroactive phases in electrospun poly(vinylidene fluoride) nanofiber prepared at different electrospinning parameters

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Abstract

Poly(vinylidene fluoride), PVDF nanofibers were prepared using electrospinning method and the influence of electrospinning parameters such as PVDF concentration, DMF:Acetone ratio on the formation of different phases (α, β, and γ) and desired morphology were investigated. A simple strategy of peak assignment method for accurately identifying the peaks associated to a particular PVDF phase were employed for X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectrometer data. This method further helped in optimizing and quantifying the desired β-phase as well as in obtaining a condition for bead-free nanofibers. Interestingly, the mechanism of formation of phases are found mostly governed by the balance between surface tension and viscosity which is controlled by PVDF concentration and acetone content in the solution. A PVDF concentration of 20% (w/v) and DMF:Acetone ratio 1:1 was found suitable for maximum β-phase in a completely bead-free nanofibers. The methodology and understanding of underlying mechanism of desired phase and morphology suggest a guideline for optimization of β-phase and bead-free fibers in PVDF-based nanocomposite as well.

Keywords: Electrospinning, PVDF, Phase, Morphology
Introduction

Polyvinylidene fluoride (PVDF) is the most important electroactive (EA) fluoropolymer that have been studied in last couple of decades due to their attractive piezoelectric and ferroelectric properties, which are used in a variety of applications including sensors, actuators, and nanogenerators 1-6. More recently, PVDF nanofibers prepared by electrospinning have gained a lot of interest from the researchers as a multifunctional fiber producing method that has been used in a variety of commercial industries, including membrane and filter technology 7-11, tissue engineering and drug delivery in healthcare, solar and fuel cell in energy, as well as defense and security 12-14. Many of these applications demand presence of maximum EA-phase and the control over the fiber morphologies 12, 15, 16. Therefore, the challenge has always been to control the electrospinning parameters to obtain a maximum EA-phase and desired morphologies at the same time. In general, PVDF is a semi crystalline polymer known to exist in EA polar β-phase in all-trans (TTTT) and less polar γ-phase in tri-trans gauche (TTTG+TTTG'), and non-polar α-phase in alternate trans gauche (TG+TG') conformations 17, 18. Furthermore, the amount of EA-phase in PVDF is largely determined by the β-phase content, microstructure and degree of crystallinity, which are highly influenced by the processing conditions. Thermal, mechanical, and poling treatments, as well as solution casting method utilizing various solvents, are commonly used to obtain the most desirable β-phase from an existing α-phase 19. However, these procedures are laborious and time consuming, even not always very effective as they can produce several coexisting crystalline phases 15, 20-22. On the other hand, electrospinning provides in-situ mechanical stretching and electrical poling to obtain β-phase from polymeric solution 20, 23, 24. Despite the fact that electrospinning is a convenient and versatile method, several studies have been published that focused on optimizing electrospinning parameters such as system (viscosity 10, 25-27, conductivity, surface tension 10, 26-30, molecular weight 25, 30-33, concentration 10, 23, 33-35),
process (applied field $^{10, 32, 33, 36, 37}$, tip-collector distance $^{10, 30, 33, 38-40}$, flow rate $^{10, 27, 30, 37, 41}$, needle diameter), and ambient parameters (temperature $^{28, 30, 42}$, humidity $^{43-45}$) to enhance β-phase content and desired morphology of PVDF nanofibers, there are still many inconsistencies in some results. These discrepancies are mostly owing to the obvious fact that it has a large number of interdependent electrospinning parameters $^{46, 47}$. Second, inaccurate identification of XRD and FTIR peaks for different coexisting phases $^{15, 48}$, resulting in phase quantification inconsistencies. Most importantly, comprehensive data and understanding of how the various system, process, and ambient parameters influence the crystallinity, β-phase content and morphology, as well as a correlation among them, are still lacking.

As a result, the objective of this work is to provide a comprehensive method for elucidating the influence of some important electrospinning parameters on the mechanism of different phase formation and on morphology in PVDF nanofibers. For this, we have varied PVDF concentration and binary solvent (DMF:Acetone) ratio for the preparation of PVDF nanofibers. Different phases obtained at varied electrospinning parameters were characterized using X-ray diffractometer (XRD) and Fourier-transform infrared spectroscope (FTIR). Further, using Scanning electron microscope (SEM) and a peak assignment method, it was possible to identify and further quantify the phases present in PVDF nanofibers with the required morphology by establishing a correlation among them. The findings allowed us to find a suitable combination of PVDF concentration and DMF:Acetone ratio for obtaining a maximum β-phase in completely bead-free nanofibers. The mechanism of phase formation during electrospinning were also discussed which could provide a guideline for nanofiber preparation in pristine as well as PVDF based nanocomposites.
EXPERIMENTAL SECTION

Preparation of PVDF nanofibers

A PVDF solution of concentration 15, 20, and 25% (w/v) were prepared by dissolving PVDF powder (99.9% purity, Sigma-Aldrich, India) in a mixture of DMF/acetone (Both were purchased from Sigma Aldrich with 99% purity) taken in a ratio of 1:1, 1.5:1, and 2:1 by continuously stirring at 60 °C on a magnetic stirrer. Sample ids are assigned hereafter as \( PVDF \) concentration\_DMF:Acetone (e.g., 15\_1:1; 15\_1.5:1; 15\_2:1; 20\_1:1; 20\_1.5:1; 20\_2:1; 25\_1:1; 25\_1.5:1; 25\_2:1). For the preparation of electrospun nanofiber the solution was filled in a 10 ml plastic syringe with a blunt edge needle (22G) of outer diameter 0.8 mm. The syringe was placed in an infusion pump (NE-300, New Era, USA) to maintain a constant flow rate of 1 ml/h. A dc voltage of 18 kV was applied between the needle and the metallic stationary collector that was kept 12 cm apart. The nanofiber mat was directly collected on an Al (aluminium) foil and dried at 60 °C in oven for 6 h.

Characterization of PVDF nanofibers

The phase formation of the PVDF nanofiber mat was confirmed using an X-ray diffractometer (Bruker D8 Advance, Germany) pattern and Fourier transform infrared (FTIR) (xxxxx) spectra data. Morphology was studied using a scanning electron microscope (SEM) (Tescan MIRA 3 MUG FEG, Czech Republic). The diameter of the fibers was measured using Image J (USA) software from the SEM micrographs. For accurately identify the peak position of different phases in PVDF nanofiber, first, the peaks that obtained from XRD data for the 20 range 10-30° were deconvoluted. The deconvoluted XRD peaks were then indexed \(^{15, 49}\) and assigned the phase simultaneously comparing phases that obtained from FTIR peaks \(^{48, 50}\) using a peak assignment method that is provided in Table 1. The morphology (shape, diameter) of each PVDF nanofiber samples were also included in the Table 1 so to establish a
correlation among XRD, FTIR data and SEM micrographs. This method helps us to identify accurately and effortlessly the phases present in each nanofiber samples as well as quantifying them further. The detail analysis of identified phases and quantification based on various approach is discussed below.

Results and discussion

XRD study

XRD patterns of all the samples with varying PVDF concentrations (15, 20, 25 %w/v) and DMF:Acetone ratios (1:1, 1.5:1, 2:1) were collected for the 2θ range 10-90° as illustrated in Figure 1. As the PVDF concentration is increased from 15 to 25%, a predominating α-phase characterized by peaks from (100) plane at 2θ ≈ 18.3° and (021) at 2θ ≈ 26.6° gradually disappeared while a weak broad peak at around 40.7° from (002) plane exists for all samples. A strong and sharp peak at around 2θ ≈ 20.5° progressively appeared at higher concentrations of PVDF is attributed apparently from the dual characteristics of β from (110/200) or γ-phase from (110). Therefore, it must be clarified as this problem regarding identification of β and γ-phase persisted in the literature for long back 36, 39, 51, 52. Furthermore, two relatively weak characteristic peaks of β-phase appeared at 2θ ≈ 36.2 and 56.0° from (101) and (221) plane respectively. This result suggests that as PVDF concentration is increased α-phase gradually changed into an electroactive phase. Further, quantification of the electroactive phase, particularly individual β and γ-phases, as well as the degree of crystallinity in distinct PVDF samples, becomes critical to understanding its piezoelectric properties. This requires a peak deconvolution to identify each phase separately and their contribution in calculating the overall crystalline phase of the PVDF. The deconvoluted peak profile of all the samples for the 2θ range 10-30° with varying concentration and DMF:Acetone ratios is depicted in Figure 2. The presence of the exclusive diffraction peak from the α(100) plane at 17.7° revealed a
pre-dominating α-phase in 15_2:1 and 15_1.5:1, whereas it was absent in 15_1:1. On the other hand, α(100) still present in all 20% but rather weak compared to 15%, while it was completely absent in all 25% PVDF samples. The other exclusive diffraction peak for α-phase from α(021) at 26.6° is evident in all 15%, but gradually diminished for 20%, and disappeared in 25_1:1 and 25_1.5:1 except for extremely small peak in 25_2:1. This result suggest that, as the PVDF concentration is increased the dominating α-phase is reduced. Moreover, it was also found that, when the DMF:Acetone ratio is decreased for any particular PVDF concentration, α(100) and α(021) peak intensities are also decreased, indicating a reduction in the dominant α-phase. Furthermore, the other characteristics peaks of α-phase, α(020) at 18.3° and α(110) at 19.9° are clearly visible in 15_2:1 and 15_1.5:1. However, for 15_1:1, the diffraction peak α(020) has emerged as mixed phase with γ and appeared as α,γ(020) at slightly higher 20 value of 18.5°, while the peak α(110) is attributed to γ(110) that appeared also at little higher 20 value of 20.3°, since both exist in monoclinic phase. This is further suggesting that, as DMF:Acetone ratio is decreased, a dominant α-phase is changed to an electroactive phase. Similar result has been obtained in both 20 and 25% also, where the diffraction peak α(020) has appeared as a mixed α + γ phase at 18.5° as α,γ(020). The peak α(110), on the other hand, has appeared as mixed α + γ phase as α,γ(110) at 20.04° in 20%, while, it appeared as γ(110) at 20.3° in 25%. This is also indicating a significant reduction in α-phase in both 20 and 25% PVDF. This remained always a challenging task to many authors to identify γ(110) as it appeared in mixed phase as α,γ(110), even sometimes mistakenly reported as β(110/200). Furthermore, the only characteristics diffraction peak for β-phase, β(110/200) has appeared at 20.7° for all samples (15, 20, 25%), however becomes more sharper and stronger as PVDF concentration is increased irrespective of DMF:Acetone ratio. Thus, concluding the above results as the DMF:Acetone ratio is decreased a predominant α-phase changed into electroactive γ and β-phases for a fixed PVDF
concentration, while for a fixed DMF:Acetone ratio, as the PVDF concentration is increased more electroactive γ and β-phases are developed. However, it must also be noted that DMF:Acetone ratio has not significantly changed the peak positions in 25, and 20%, except for 15% PVDF as disappearance of α(100), α(110) and α(020) appeared at higher 2θ value as γ(110) and α,γ(020) respectively. As a result, a quantification of each phase would be critical at this stage to investigate the influence of concentration and DMF:Acetone ratio on the phases as different phases (α, γ) exhibit similar peaks in PVDF nanofibers\textsuperscript{15}. Another common way several authors have quantified relative proportion of β-phase is sum of the intensity ratio of peaks associated to β-phase to those α, β, and γ-phases and is given by\textsuperscript{54-56},

\[
\frac{I_β}{I_α+I_β+I_γ} = \frac{I_{(200/110)}+I_{(101)}+I_{(221)}}{I_{(100)}+I_{(020)}+I_{(110)}+I_{(021)}+I_{(221)}+I_{(002)}+I_{(200/110)}+I_{(101)}+I_{(221)}}
\]

Equation (1)

where, \(I_α, I_β, I_γ\) are peak intensities for α, β, and γ-phases respectively and planes (100), (110), (021), (002) associated to α-phase, (200/110), (101), (221) planes to β and (020), (110) plane to (α + γ) and γ-phase respectively. The relative proportion of β-phase are summarized in table 2. Although, XRD is a very powerful tool for identification and quantification of polycrystalline solids, quantification of each crystalline phases (α, β, γ) of PVDF is not possible from XRD data as α, and γ-phases represent similar peaks, however once each peak of α, β, γ-phase is accurately identified and indexed using deconvoluted method, the overall crystallinity can be found out. The degree of crystallinity (\(χ_c\)) was calculated from,

\[
χ_c = \frac{\Sigma A_{cr}}{\Sigma A_{cr} + \Sigma A_{amr}} \times 100\%
\]

Equation (2)

where, \(\Sigma A_{cr}\) and \(\Sigma A_{amr}\) are the sum of integral area of crystalline peaks and amorphous halo respectively\textsuperscript{57}. Table 2 listed the values of crystallinity, \(χ_c\) (%), which further confirmed from DSC data.

DSC study
FTIR Study

FTIR spectra of all the samples with varying PVDF concentrations (15, 20, 25 %w/v) and DMF:Acetone ratios (1:1, 1.5:1, 2:1) were collected for the frequency range 450-1500 cm\(^{-1}\). The peaks corresponding to vibrational bands associated to each PVDF crystalline phases (\(\alpha, \beta, \gamma\)) are labeled as shown in Figure 3. However, some of the common peaks in the range, 876-885, 1067-1075, 1171-1182, 1398-1404 cm\(^{-1}\) are not considered as they appear in mixed phases. The predominant \(\alpha\)-phase is characterized by two exclusive absorption peaks at 614, 763 cm\(^{-1}\) and other characteristics peaks at 489, 532, 796, 976 cm\(^{-1}\). These peaks are comparatively more intense in 15%, and gradually faded as PVDF concentration is increased to 20 and further to 25% indicating a conversion of \(\alpha\)-phase to other electroactive phases (\(\beta, \gamma\)). Furthermore, the presence of a significant amount of electroactive phase (mainly \(\beta\)-phase) in all electrospun PVDF samples is indicated by a strong exclusive absorption peak for \(\beta\)-phase at 1276 cm\(^{-1}\) and an undetectable, rather weak shoulder for \(\gamma\)-phase at 1234 cm\(^{-1}\) that appeared for all samples. No other characteristics absorption peaks of \(\gamma\)-phase at 776, 812 cm\(^{-1}\) were detected. Consequently, the other characteristics peaks for \(\beta\)-phase appeared at 471, 1431 cm\(^{-1}\), while absorption peaks at 512, 841 cm\(^{-1}\) are assigned to both \(\beta\) and \(\gamma\) (\(\beta + \gamma\)) phase. This is because, both \(\beta\) and \(\gamma\) phase has similar chain conformation resulting in similar absorption band peaks.\(^{58,59}\) For instance, \(\gamma\)-phase shows absorption band at 512 cm\(^{-1}\) which is very close to \(\beta\)-phase absorption peak at 510 cm\(^{-1}\)\(^{50,60}\), whereas, it is believed that the strong absorption band at 841 cm\(^{-1}\) is due to \(\beta\)-phase and the \(\gamma\)-phase appeared as a shoulder at 833 cm\(^{-1}\) as common to both polymorphs.\(^{58,61}\) To further clarify the identification of 841/512 cm\(^{-1}\) band, if both the exclusive absorption peak for \(\beta\)-phase at 1276 cm\(^{-1}\) and \(\gamma\)-phase at 1234 cm\(^{-1}\) are present, the 841/512 cm\(^{-1}\) band is assigned as (\(\beta + \gamma\)) phase. The former phase is assigned to 841/512 cm\(^{-1}\) band if one of them is present and the other is absent.\(^{48}\) Thus, as
841 cm\(^{-1}\) band represents both the electroactive β and γ phases in PVDF, the fraction of electroactive (\(F_{EA}\)) phase presents in a sample containing all α, β, and γ can be quantified from Lambert–Beer law given as \(^{19,62}\),

\[
F_{EA} = \frac{A_{EA}}{(K_{EA})A_{α} + A_{EA}} \times 100\% \quad \text{Equation (4)}
\]

where, \(A_{α}\) and \(A_{EA}\) refer to the absorbance of α- and electroactive phases (at 763 and 841 cm\(^{-1}\)), respectively. \(K_{α}\) and \(K_{EA}\) represent the absorption coefficients with values of \(6.1 \times 10^4\) and \(7.7 \times 10^4\) cm\(^2\) mol\(^{-1}\) respectively. Although equation (4) was originally used to quantify only one of the electroactive phase only (β or γ) \(^{19,63,64}\), it was later utilized for quantification of both β and γ-phases \(^{48,57}\). A peak deconvolution method has been employed for 841 cm\(^{-1}\) band to further quantify the individual β and γ phases, considering that the strong absorption band at 841 cm\(^{-1}\) is due to β-phase, while the γ-phase appeared as a shoulder at 833 cm\(^{-1}\) as common to both polymorphs \(^{58,61}\). The following equations (5a, 5b) are used to quantify relative proportion of β and γ phases in respect to the total electroactive phase (\(F_{EA}\)) present in each PVDF sample \(^{57}\).

\[
F(β) = F_{EA} \times \frac{A_{β}}{(A_{β} + A_{γ})} \times 100\% \quad \text{Equation (5a)}
\]

\[
F(γ) = F_{EA} \times \frac{A_{γ}}{(A_{β} + A_{γ})} \times 100\% \quad \text{Equation (5b)}
\]

where, \(A_{β}\) and \(A_{γ}\) are the area under the deconvoluted curve centered at 841 cm\(^{-1}\) (Shown in Fig. 4a, 4b, 4c) for β and γ phases respectively. The calculated β and γ phase fractions are summarized in table 2.

Another alternative method Cho et al. have used to calculate the relative content of a particular phase by sum of the intensity ratio of the absorption peaks associated to the phase to those α, β, and γ-phases and is given as \(^{55}\).
\[
\frac{l_{\beta \text{ or } \gamma}}{l_{\alpha} + l_{\beta} + l_{\gamma}} = \frac{(I_{471} + I_{512} + I_{841} + I_{1276} + I_{1431}) \text{ or } (I_{1234})}{(I_{489} + I_{532} + I_{614} + I_{979} + I_{978}) + (I_{471} + I_{512} + I_{841} + I_{1276} + I_{1431}) + (I_{1234})}
\]

Equation (6)

The calculated β and γ phase fractions using eq. (6) are also summarized in table 2. It should be noticed from table 2 that the β-phase fraction estimated from eq. (5) has increased from 58.3 for 15-2:1 to 64.1% for 15_1:1 as acetone content is increased (namely DMF:Acetone ratio decreased), while the γ phase fraction changed from 3.5 to 4.8% respectively. This result is in good agreement with the calculated values from eq. (6), however it differs from the result that obtained from eq. (1) calculated using XRD data. When DMF:Acetone ratio was changed from 2:1 to 1:1, the β -phase fraction has increased from 45.4 to 63.6% in 20% PVDF, while it is not changed significantly in 25%. In contrast, the γ-phase fraction obtained from eq. (5) has significantly large values (18.5-19.9%) in 20%, yielding a contradictory result as compared to the values obtained from eq. (6). This could lead to the conclusion that because eq. (5) deals with deconvoluted curve for β -phase centered at the band 841 cm\(^{-1}\) with a small shoulder of γ -phase at 833 cm\(^{-1}\), it may introduce inaccuracies because γ-phase peak at 833 cm\(^{-1}\) is not possible to fit well, as seen in Figure 4. Despite the fact that, some authors have employed this strategy, no fitting parameters were reported anywhere\(^{48,57}\).

The overall total electroactive phase calculated from eq. (5) and (6) is presented in Figure 5. From figure 5, it is clear that for any particular DMF:Acetone ratio as the PVDF concentration is increased, \(F_{EA}(\%)\) is increased. However, a maximum \(F_{EA} = 82.1\%\) is obtained for 20% when the acetone DMF:Acetone ratio is 1:1 that calculated from eq. (5). There is no significant deviation in the results obtained from eq. (5) and (6), suggesting more reliable method for calculating EA-phase. This also confirms that, PVDF concentration 20% is the critical concentration where DMF:Acetone plays important role in the nucleation and stabilization of electroactive β and γ phases.

Morphology study
A significant influence on the morphology (shape, diameter) of PVDF fiber due to variation in the concentration of PVDF and DMF:Acetone ratio can be found in the SEM micrographs of the samples. It is evident from the micrographs that low concentration of PVDF, i.e., 15% results in beaded fiber, however when the DMF:Acetone ratio is reduced from 2:1 to 1:1, the bead formation is also reduced. This is because when the concentration of PVDF is low the entanglement of the polymer macromolecular chain in the solution is not very strong \(^{27, 65}\). Furthermore, when a sufficiently large field is applied, the electrospinning process changes to electrospraying \(^{66}\). However, the SEM micrographs show that a 15% PVDF concentration is viscous enough for electrospinning, whereas different volume ratios of binary solvent have varying entanglements and evaporation rates, affecting the extensional viscosity of the jet and resulting in diverse morphologies \(^{67}\). Moreover, when acetone concentration is increased (namely by reducing DMF:Acetone ratio), consequently the surface tension of the solution is also reduced creating a stable Taylor cone and a continuous jet starts forming due to effective stretching of the solution. This leads to reduction in bead formation as evident from sample 15_1:1. It is therefore confirmed that the bead formation is mainly related to solvent evaporation rate controlled by the concentration of acetone in the solvent while viscosity of the samples (15_1:1, 15_1.5:1, and 15_2:1) does not change much as further confirmed by their fiber diameter \(^{67-69}\). In all three samples of 15%, ultrafine fibers are produced having diameter ranging from 76 to 86 nm. Further, in PVDF concentration 20%, as the PVDF concentration is increased the viscosity of the solution is increased results in larger diameter (129-134 nm) fiber with almost negligible beads. Although, a very small number of beads are still found in 20_2:1, because of low evaporation rate of the solution, there are completely bead free fibers are obtained in 20_1:1. So, it can be concluded that, if a polymer solution jet is allowed to evaporate completely before collected, a bead-free fibers are formed \(^{24}\). In PVDF concentration 25%, large diameter (230-259 nm) with almost bead-free fibers can be
seen. However, the viscosity is high enough to overshadow the influence of acetone concentration unless DMF:Acetone is 1:1 in 25_1:1. Therefore, it is speculated that, in 25_2:1 and even in 25_1.5:1, the solvent cannot be evaporated completely before collected in collector and small traces of liquid solvent still present. This results in wrinkle in the fiber due to further evaporation of the solvent. This was confirmed from the high magnification SEM micrograph shown in Fig. 6. As can be seen from Fig. 6, an almost uniform fibers with smooth surface are observed in all other samples of different PVDF concentrations 15 and 20% including 25_1:1 except 25:1.5:1, 25_2:1. Thus, it is confirmed that, acetone lower the surface tension while concentration of PVDF increase the viscosity which favors the formation of uniform and bead-free fibers which is mainly governed by the balance between viscosity and surface tension. Therefore, a suitable PVDF concentration and DMF:Acetone ratio is very much important for not only a desired morphology of the fibers but also to obtain the maximum electroactive phase. The concentration lower than 15%, results in much beaded fibers even at any DMF:Acetone ratio, while PVDF concentration 15% with DMF:Acetone of 1:1 shows minimum numbers of beads. The DMF:Acetone ratio less than 1:1 was not used as it can dry up quickly results in clogging of the needle. Therefore, the most suitable combination was found for PVDF concentration 20% with DMF:Acetone ratio 1:1. It is believed that PVDF concentration 20% is just above the critical concentration and a DMF:Acetone ratio 1:1 is much favorable for complete solvent evaporation during electrospinning to obtain bead-free fibers 70, 71. Although, a higher PVDF concentration 25% can produce bead-free fibers but solvent evaporation during electrospinning was not possible which could have a detrimental effect in EA-phase formation. It is expected that the macromolecular chain of the polymer solidifies under the high elongation rate during electrospinning to enhance the polymer crystallinity and consequently the EA-phase. If, however, fibers contain traces of solvent after collection, effective stretching in the air will
not occur and therefore, orientation of the macromolecule are allowed to relax back resulting in α-phase. As a consequence, the EA-phase in 25% is reduced as compared to 20%. So, intensive stretching of fibers leads to conversion of PVDF into β-phase, while a suitable solvent evaporation rate contributes to retain β-phase in solidified fibers.

Conclusions

The influence of electrospinning parameters such as PVDF concentration and DMF:Acetone ratio on the phase formation and morphology of PVDF nanofibers have been investigated. It is found that, viscosity and solvent evaporation rate of the solution played the most important role in obtaining the desired electroactive phase and morphology. The content of acetone lowers the surface tension while concentration of PVDF increase the viscosity which favors the formation of uniform and bead-free fibers. Accurate identification of different PVDF phases (α, β, and γ) was possible using peak assignment method of XRD and FTIR peaks and establishing a correlation with morphology. This method helps in finding a suitable PVDF concentration and DMF:Acetone ratio for obtaining maximum β-phase in bead-free nanofibers and would be useful for understanding the actual mechanism for phase formation and morphology development. This would provide a guideline for further optimization of PVDF based nanocomposite nanofiber preparation in future.

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Figure caption

**Figure 1:** XRD patterns of PVDF samples with varying concentrations (15, 20, 25 %w/v) and DMF:Acetone ratios (1:1, 1.5:1, 2:1).

**Figure 2:** The deconvoluted peaks all the PVDF samples for the 2θ range 10-30°

**Figure 3:** FTIR spectra of PVDF samples with varying concentrations (15, 20, 25 %w/v) and DMF:Acetone ratios (1:1, 1.5:1, 2:1) shown for the frequency range 450-1500 cm⁻¹.

**Figure 4:** Deconvoluted curve for the band 841 cm⁻¹: (red) for γ-phase centered at 833 cm⁻¹; (green) for β-phase centered at 841 cm⁻¹; (blue) cumulative fit for PVDF concentration (a) 15, (b) 20, and (c) 25% with DMF:Acetone ratios: 1:1, 1.5:1 and 2:1.

**Figure 5:** Fraction of total electroactive phase $F_{EA}$ (%) at different DMF:Acetone ratio of 1:1, 1.5:1 and 2:1 for PVDF concentrations 15, 20, 25%.

**Figure 6:** SEM micrographs of PVDF samples with varying concentrations (15, 20, 25 %w/v) and DMF:Acetone ratios (1:1, 1.5:1, 2:1) is shown.

**Figure 7:** High magnification SEM micrographs of PVDF samples with varying concentrations (15, 20, 25 %w/v) and DMF:Acetone ratios (1:1, 1.5:1, 2:1) is shown.
Table caption

**Table 1:** XRD and FTIR peak assignment to PVDF nanofiber sample for a particular electrospinning parameter (Concentration_DMF:Acetone) including morphology of fibers.

**Table 2:** Summary of calculated crystallinity and β and γ phase fractions for different DMF:Acetone ratio of 1:1, 1.5:1 and 2:1 for PVDF concentrations 15, 20, 25%.
FIGURE 1

A series of X-ray diffraction patterns are shown, labeled with various ratios: 15_2:1, 15_1.5:1, 15_1:1, 20_2:1, 20_1.5:1, 20_1:1, 25_2:1, 25_1.5:1, and 25_1:1. The peaks are labeled with \( \alpha \), \( \beta \), and \( \gamma \). The Intensity is measured in arbitrary units (a.u.) and the 2\( \theta \) values range from 10 to 90 degrees.
FIGURE 5

![Graph showing the relationship between DMF ratio and FEₐ (%) for different concentrations. The graph indicates that FEₐ (%) decreases as the DMF ratio increases, with different concentrations showing slight variations.](image-url)
Table 1: XRD and FTIR peak assignment to PVDF nanofiber sample for a particular electrospinning parameter (Concentration_DM:Acetone) including morphology of fibers.

| Sample id | 15_1:1 | 15_1.5:1 | 15_2:1 | 20_1:1 | 20_1.5:1 | 20_2:1 | 25_1:1 | 25_1.5:1 | 25_2:1 | Crystalline phase |
|-----------|--------|----------|--------|--------|----------|--------|--------|----------|--------|------------------|
| **XRD peak position (2θ deg)** |        |          |        |        |          |        |        |          |        |                  |
| 17.7      | A      | P        | P      | P/W    | P/W      | P/W    | A      | A        | A      | α (100)          |
| 18.3      | A      | P        | P      | A      | A        | A      | A      | A        | A      | α (020)          |
| 18.5      | P      | A        | A      | P      | P        | P      | P      | P        | P      | α, γ (020)       |
| 19.9      | A      | P        | P      | A      | A        | A      | A      | A        | A      | α (110)          |
| 20.04     | A      | A        | A      | P      | P        | A      | A      | A        | A      | α, γ (110)       |
| 20.3      | P      | A        | A      | A      | A        | P      | P      | P        | P      | γ (110)          |
| 20.7      | P      | P        | P      | P      | P        | P      | P      | P        | β      | β (110/200)      |
| 26.6      | P/W    | P        | P/S    | P/EW   | P/W      | P/W    | A      | A        | P/EW   | α (021)          |
| **FTIR peak position (cm⁻¹)** |        |          |        |        |          |        |        |          |        |                  |
| 1431      | P      | P        | P      | P      | P        | P      | P      | P        | P      | β                |
| 1276      | P      | P        | P      | P      | P      | P/S    | P/S    | P/S      | P/S    | β                |
| 1234      | P/W    | P/EW     | P/EW   | P/W    | P/EW    | P/EW   | P/W    | P/W      | P/W    | γ                |
| 976       | P      | P/S      | P/S    | P/EW   | P/W      | P/EW   | A      | A        | α      |                  |
| 841       | P/S²W⁷ | P/S²EW⁷ | P/S²EW⁷ | P/S²W⁷ | P/S²W⁷ | P/S²W⁷ | P/S²W⁷ | P/S²W⁷ | β/γ   |                  |
| 812       | A      | A        | A      | A      | A        | A      | A      | A        | γ      |                  |
| 796       | P/S    | P/S      | P/S    | P/EW   | P/W      | P/W    | P/EW   | A        | A      | α                |
| 776       | A      | A        | A      | A      | A        | A      | A      | A        | γ      |                  |
| 763       | P/S    | P/S      | P/S    | P/EW   | P      | P/S    | P/W    | A        | P      | α                |
| 614       | P/S    | P/S      | P/S    | P/EW   | P      | P/S    | P/W    | P/EW     | P      | α                |
| 532       | P/W    | P/W      | P      | A      | P/EW    | P/W    | A      | A        | P/EW   | α                |
| 512       | P/S²W⁷ | P/S²W⁷ | P/S²W⁷ | P/S²W⁷ | P/S²W⁷ | P/S²W⁷ | P/S²W⁷ | P/S²W⁷ | β/γ   |                  |
| 489       | P      | P        | P/S    | P/W    | P      | P/S    | P/W    | P/W      | P/W    | α                |
| 471       | P      | P        | P/W    | P/S    | P      | P/W    | P/S    | P/S      | P/S    | β                |
| SEM morphology | Nature of beads | Very small number, mostly spindle shape, smooth surface | Small number, spherical and spindle shape, smooth surface | Large number, spherical shape, smooth surface | No beads, smooth surface | Extremely small number, spindle shape, smooth surface | Very small number, mostly spindle shape, smooth surface | No beads, smooth surface | No beads, wrinkle in surface | No beads, wrinkle in surface |
|---------------|----------------|------------------------------------------------------|------------------------------------------------------|-------------------------------------------------|------------------------|------------------------------------------------------|------------------------------------------------------|------------------------|-----------------------------|-----------------------------|
| Diameter of fiber (nm) | 80 ± 34 | 86 ± 43 | 76 ± 25 | 134 ± 57 | 129 ± 40 | 130 ± 40 | 230 ± 73 | 259 ± 67 | 241 ± 44 |

P: Present; A: Absent; W: Weak; S: Strong; EW: Extremely Weak; Sβ: Strong β-phase; Wγ: Weak γ-phase; EWγ: Extremely Weak γ-phase
Table 2: Summary of calculated crystallinity and $\beta$ and $\gamma$ phase fractions for different DMF:Acetone ratio of 1:1, 1.5:1 and 2:1 for PVDF concentrations 15, 20, 25%.

| Sample id | Crystallinity% ($\chi_c$) From Eq. (2) | Crystallinity% ($\chi_c$) From DSC | % of $\beta$-phase | % of $\gamma$-phases |
|-----------|----------------------------------------|------------------------------------|-------------------|---------------------|
|           |                                        |                                    | From Eq. (1)      | From Eq. (3)        |
|           |                                        |                                    | From Eq. (4a)     | From Eq. (5)        |
|           |                                        |                                    | From Eq. (4b)     | From Eq. (5)        |
| 15_1:1    | 50.3                                   | 28.96                              | 38.22             | 64.1                | 55.62               | 4.8                 | 10.11               |
| 15_1.5:1  | 42.2                                   | 21.63                              | 25.96             | 60.2                | 55.37               | 3.2                 | 10.26               |
| 15_2:1    | 29.2                                   | 23.86                              | 30.05             | 58.3                | 48.48               | 3.5                 | 9.17                |
| 20_1:1    | 55.9                                   | 56.82                              | 59.21             | 63.6                | 62.01               | 18.5                | 10.99               |
| 20_1.5:1  | 41.8                                   | 43.91                              | 44.14             | 52.2                | 45.06               | 19.1                | 12.08               |
| 20_2:1    | 49.6                                   | 39.58                              | 40.98             | 45.4                | 50.97               | 19.9                | 10.14               |
| 25_1:1    | 43.0                                   | 43.23                              | 51.66             | 67.9                | 58.48               | 10.5                | 11.21               |
| 25_1.5:1  | 26.2                                   | 49.64                              | 55.22             | 70.2                | 63.64               | 7.3                 | 11.99               |
| 25_2:1    | 36.6                                   | 52.28                              | 53.73             | 69.2                | 58.05               | 7.6                 | 10.88               |