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DEVELOPMENT OF PVDF THIN FILMS

Venkata Reddy[1], Somashekhar.K.Hulloli[2], H. N. Narasimha Murthy[3]

[1] *Asst. Professor, Department of Mechanical Engineering,*
PESIT, Bangalore, Karnataka, (India)
[2] *Asst. Professor, Department of Mechanical Engineering,*
Dhananjay Mahadik Group of Institute, Kagal-Kolhapur, Maharashtra, (India)
[3] *Professor, Department of Mechanical Engineering,*
R.V.College of Engineering, Bangalore, Karnataka, (India)

ABSTRACT

Coating of PVDF thin films on float glass substrates was carried out by sol-gel spin coating. PVDF films were prepared using PVDF granules and N-N, Dimethyl formamide solvent. PVDF films were characterized for β-phase by FTIR spectroscopy, roughness and thickness by Atomic force microscopy, structural characterization was carried out using X-ray diffraction and thermal behavior, melting point, heat of fusion was studied by Differential scanning calorimeter (DSC).Analysis of variance showed that β-phase was influenced by PVDF wt % (P= 82.20 %) and Spinning speed (P = 16.10 %), thickness was influenced by PVDF wt % (P= 65.71 %) and Spinning speed (P = 28.41%) 65.71 % and Roughness of PVDF films was influenced by Spinning speed (P = 65.22 %) and PVDF wt % (P= 30.98%). Regression model R^2 value indicated 94.07 % for β-phase, 92.06% for roughness and 96.24% for thickness. Comparison of initial process parameters with Grey theory prediction showed that β-phase increased from 93% to 94% roughness decreased from 4 nm to 3 nm, thickness decreased from 2.5 µm to 2.25 µm.

Keywords: PVDF thin films, sol-gel spin coating, structural properties.

I. INTRODUCTION

Polyvinylidene fluoride (PVDF) is a highly nonreactive semicryastalline polymer produced by the polymerization of vinylidene fluoride. This has some very attractive mechanical, electrical and chemical properties. It is chemically inert and has reasonably high mechanical strength and flexibility. It has been used for the parts and applications which require high purity, great mechanical strength, and good chemical properties such as resistance to solvents, bases and acids and good resistivity to heat [1-8]. PVDF is relatively inexpensive in comparison to other polymers, it has low density (1.78) compared to other polymers, low melting point of 172°C [9] and reasonable melting viscosity suitable for melt processing without the need for stabilizers, processing aids or additives, The polymer can be solution processed due to its solubility in polar solvents (NMP, DMF for example), PVDF is synthesized by addition polymerization of the CH2=CF2 monomer. When produced as the homopolymer (i.e. from 100% CH2=CF2 monomer), the majority of the PVDF chains have a regular structure of alternating CH2 and CF2 groups [10].

II. EXPERIMENTAL

2.1 Materials

Material	Specification	Suppliers
Polyvinylidene fluoride (PVDF)	Pellets form, Colourless white.	Sigma Aldrich
N,N-Dimethyl Formamide	Boiling Range 152-154°C, Density 0.948-0.950, Refractive Index 1.429-1.430	Spectrochem Pvt Ltd , Mumbai

2.2 Synthesis of PVDF thin films

2.2.1 Substrate Preparation: The glass substrates were initially cleaned in Chromic Acid to remove the impurities from its surface, then the substrates are taken into a bowl containing Acetone & the bowl is placed in Ultrasonicator for a period of 10 min. Later the substrates are rinsed in De-ionized water to remove the remaining impurities & then the substrates are dried in hot air oven for removing the water contents [11-14].

2.2.2 Thin film fabrication: PVDF Granules (Sigma-Aldrich co.) are used to fabricate thin films. Polar solvent N, N-Dimethyl formamide (DMF) (Mayora Scientific Co) was used to dissolve the PVDF. A solution of varying wt % of PVDF i.e., 10 %, 15 % and 20 % PVDF in DMF was prepared by mixing the different wt % PVDF Granules in N, N-DMF solvent and heated at 60°C with continuous stirring in a magnetic stirrer to completely dissolve all of the Granules in the solvent. The solution was then suitable for spin coating, Stretched PVDF film was prepared by spin coating the completely dissolved PVDF at 1000, 2000 and 3000 rpm for 10, 20, and 30 seconds on the glass substrates. Finally spin coated films were annealed using high temperature furnace. In order to study the effect of annealing treatment the samples were annealed at different temperatures of at 30°C, 40°C and 50°C for 1 hour to evaporate the solution and thereby curing the film. Annealing temperature higher than 70°C reduces the β- phase content in the film hence temperature was kept below it [15-19].

2.3 Characterization Techniques

The PVDF thin films were characterized for β-phase content, surface roughness, and the thickness of coated layer, surface morphology, and thermal analysis. To observe maximum % of β-phase content, % crystallinity and uniformity of coating, the above said characteristic studies were carried out by using many instruments like FTIR, X Ray Diffraction (XRD), DSC and Atomic Force Microscopy (AFM).

2.3.1 Fourier transformed infra-red (FTIR) spectroscopy

FTIR of films were carried out to provide the information about PVDF structure and to distinguish between the different crystalline forms of PVDF. FTIR results are also used to quantify the phase content of PVDF. In many literatures it is assumed that FTIR absorption follows the Lambert-Beer law [20], calculated the absorption coefficients K_α and K_β at their respective wave number of 766 and 840 cm^{-1}.In this way the relative fraction of the β-phase in a sample containing just α and β-PVDF is given by:

$$F(\beta) = \frac{A\beta}{\left(\frac{K\beta}{K\alpha}\right) A\alpha + A\beta}$$

Where F(β), represent the β -phase content; A_α and A_β the absorbance at 766 and 840 cm^{-1}; K_α and K_β are the absorption coefficients at 766 and 840 cm^{-1}, which values are 6.1×10^4 and $7.7 \times 10^4 cm^2\ mol^{-1}$, respectively.

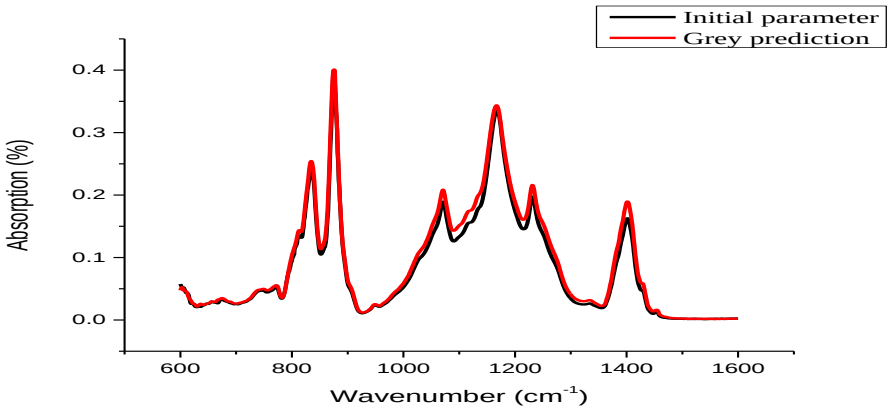

Fig. 1 FTIR images of PVDF thin films

Spin coated films at initial and grey prediction parameters were characterized to found the β -phase content, and it was found out that the β-phase was highest in the film produced by grey prediction parameters. In Fig.1 the peak values at 840 cm^{-1} are attributed to the β-phase in the PVDF material. It can be clearly seen from Fig.1 that the film spun at grey prediction parameters shows increased intensity of β-phase peaks. The increase in β-phase content is because of stretching of the film during spin coating of the solution at higher speed.

2.3.2 X – RAY DIFFRACTION (XRD)

XRD of films were carried out to determine different phases of PVDF thin films (mainly α, β and γ) and also used to find the crystalline phase of the PVDF thin films. The peak positions and their relative intensities indicate different phases of PVDF thin films and the crystalline phase of the samples and hence can be easily identified. The intensities of the peak positions allow enumerating the phases, to detect orientation of the crystals and to determine the atomic arrangement of the crystal [22-23].

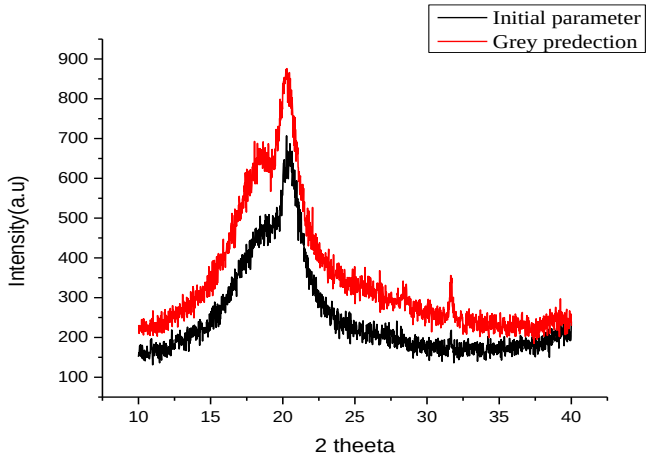

Fig. 2 XRD images of PVDF thin films

Figure 2 shows the XRD pattern of PVDF thin films. The diffraction peaks at 2θ =20.3º correspond to β-phase phase of PVDF, diffraction peaks at 2θ = 17.66º, 18.30º, 19.90º 26.56º correspond to α-phase and the peak at 2θ =18.5º, 19.2º, 20.04º corresponds to γ-phase of PVDF.

Fig.2 represents XRD pattern for initial and grey prediction parameters respectively. It can be clearly seen from Fig.2 that the film spun at grey prediction parameters shows increased intensity of β-phase peaks. The increase in β-phase content is because of stretching of the film during spin coating of the solution at higher speed, the same was observed during FTIR spectroscopy.

2.3.3 Atomic Force Microscopy (AFM)

The equipment used to measure the roughness and thickness of the film is Nanosurf A G with a scan speed up to 60ms/line at 128 data point/line and scan image rotation upto 0-360º with a maximum approach speed of 0.1mm/s [24].

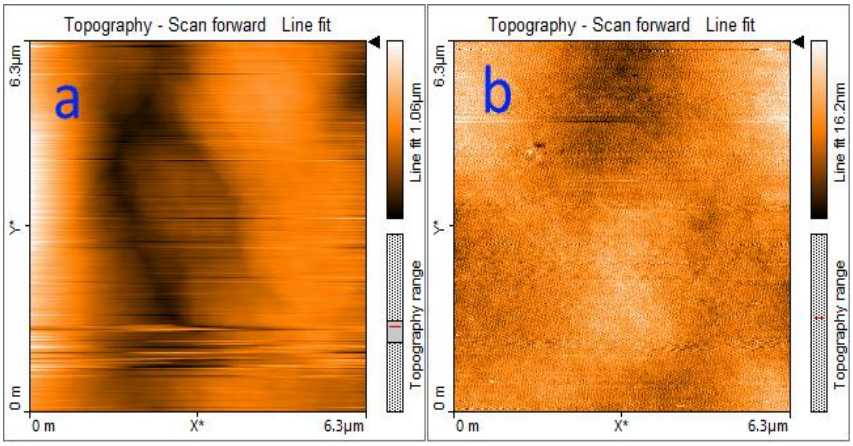

Fig. 3 a, b AFM images of PVDF thin films

Roughness and thickness were measured by AFM which shown in 2-Dimensional Fig 3 (a) shows initial process parameter where as Fig 3 (b) shows grey prediction parametric image. For initial process parameter the PVDF film had a thickness of 2.5 µm and roughness of 4nm and when experiment were conducted according to grey prediction the thickness of 2.25 µm and 3 nm roughness respectively.

2.3.4 Differential Scanning Calorimeter

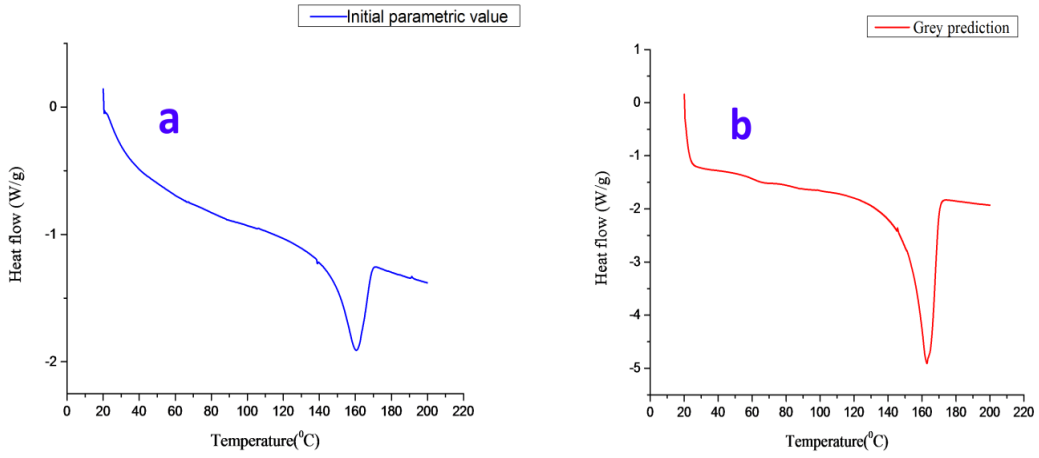

Fig. 4 a, b DSC images of PVDF thin films

Fig 4 (a, b) shows that the melting temperature with grey prediction was found to be 164 ^{0}C in that of the film having parameters such as $A_1B_3C_3$. It was noted that with increase in the spinning speed and decrease in the PVDF wt% the melting temperature of film increased, it was also know that annealing temperature and spin duration have a considerable effect on melting temperature. The initial parameter $A_3B_3C_3$ had a melting temperature of 161^{0}C.

III. RESULT AND DISCUSSION

3.1 Design of experiments and measurement of responses

3.1.1 Selection of process parameters and their variability levels

Literature review and the investigation from the past have noted the effect of various parameters on PVDF films. Four parameters are considered for the experimental studies with three levels, the parameter assigned are PVDF wt%, Spinning speed, Spin duration and Annealing temperature as shown in Table 1.

Table-1 Parameters and their corresponding levels

Symbols	Process Parameter	Level 1	Level 2	Level 3
A	PVDF wt (%)	10	15	20
B	Spinning speed (rpm)	1000	2000	3000
C	Spin duration (sec)	10	20	30
D	Annealing temperature (^{0}C)	30	40	50

3.1.2 Assigning number of levels for each factor

For the research work L_9 Taguchi's orthogonal array was considered for PVDF thin films response. From this orthogonal array study, by considering the influence of parameters to determine which parameter influence the most and which the least. Two trials of experiment were done to ensure the repeatability. Table 2 shows the Taguchi L_9 array for experimental trails.

Table-2 L_9 array for experimental Parameters

No of Experiments	PVDF wt (%)	Spinning speed (rpm)	Spin duration (sec)	Annealing temp (^{0}C)
1	10	1000	10	30
2	10	2000	20	40
3	10	3000	30	50
4	15	1000	20	50
5	15	2000	30	30
6	15	3000	10	40
7	20	1000	30	40
8	20	2000	10	50
9	20	3000	20	30

3.2 Experimental results

3.2.1 Probability plot for β-phase content, Thickness and Roughness of PVDF films

Normal probability plots for S/N ratios of β-phase, Thickness and Roughness are shown in Fig. 5 from experimental response result were found to be equally distributed along the trend line of a normal probability plot. Hence the process is said to be stable.

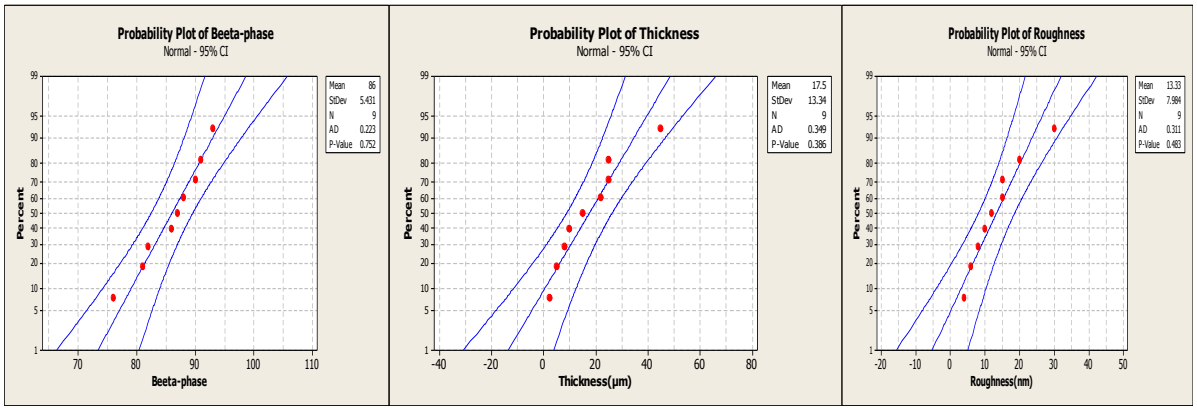

Fig. 5 S/N ratio plot for β-phase content, Thickness and Roughness of PVDF films

3.3 Optimization based on S/N ratio

3.3.1 Effect of input parameters on β-phase content

The effect of input parameters on β-phase content was estimated by using MINITAB software. Fig 6 shows the effect of wt%, spinning speed, spin duration, and annealing temperature on β-phase content thin film coatings. The parameters wt% and spinning speed have greater influence on β-phase content of the PVDF thin films as shown. Other two parameters have less significant on the β-phase content. The β-phase content increases with decreasing in wt% and with increase spinning speed. The optimum values for larger response are 10% wt, 3000 rpm speed; 30sec spin duration and 50 ^{0}C annealing temperature.

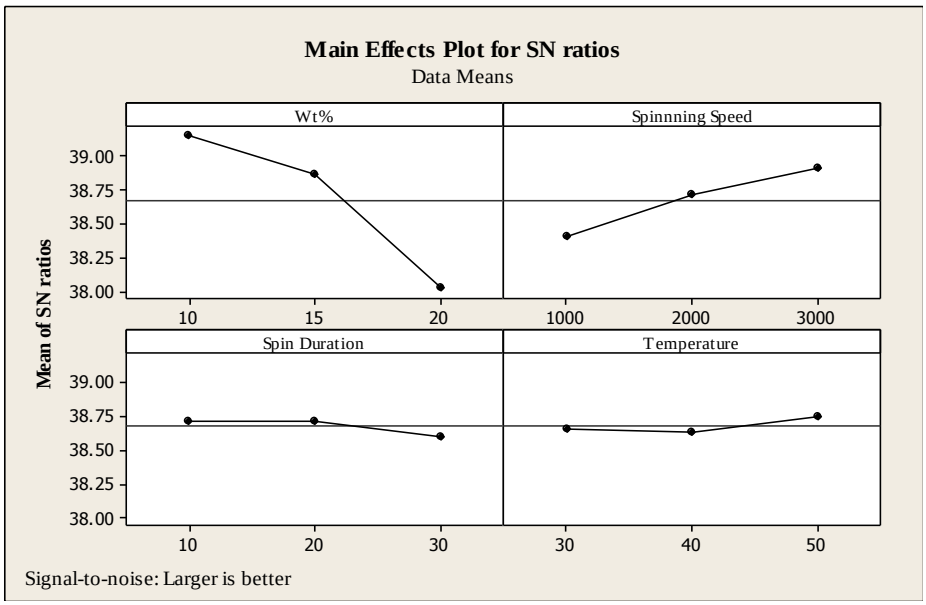

Fig. 6 S/N response for the β-phase of PVDF films

3.3.2 Effect of input parameters on Surface roughness

The effect of input parameters on surface roughness was estimated by using MINITAB software. Fig 7 shows the effect of wt%, spinning speed, spin duration, and annealing temperature on surface roughness of thin films. The parameters wt% and spinning speed have greater influence on surface roughness of the PVDF thin films as shown. Other two parameters have less significant on the surface roughness. The surface roughness decreases with decreasing in wt% and with increase spinning speed. The optimum values for smaller response are 10% wt, 3000 rpm speed; 30sec spin duration and 50 ^{0}C annealing temperature.

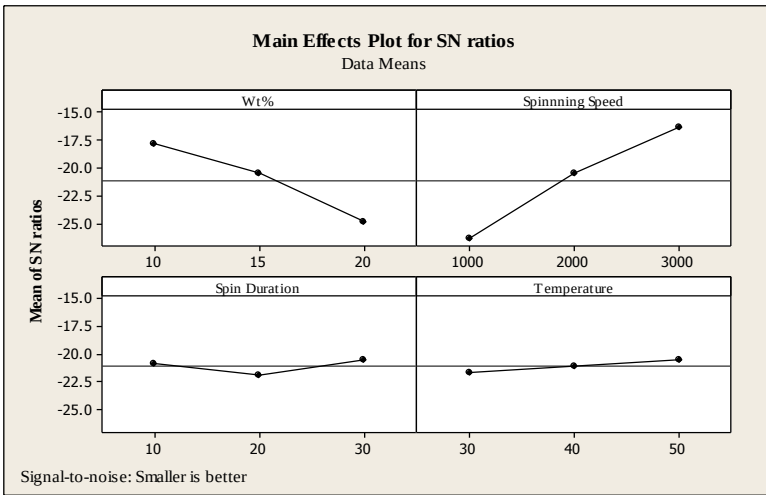

Fig. 7 S/N response for the roughness of PVDF films

3.3.3 Effect of input parameters on thickness

The effect of input parameters on thickness was estimated by using MINITAB software. Fig 8 shows the effect of wt%, spinning speed, spin duration, and annealing temperature on thickness of thin film. The parameters wt% and spinning speed have greater influence on thickness of the PVDF thin films as shown. Other two parameters have less significant on the thickness of film. The thickness of film decreases with decreasing in wt% and with increase spinning speed. The optimum values for smaller response are 10% wt, 3000 rpm speed; 30sec spin duration and 50 ^{0}C annealing temperature.

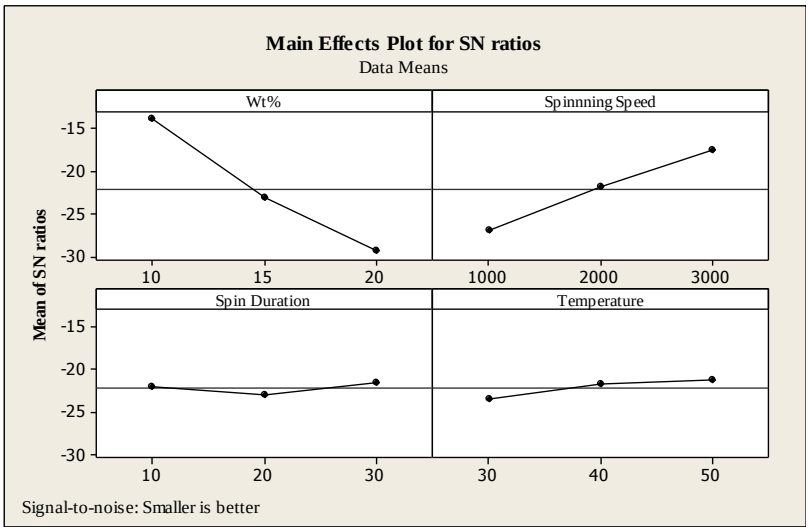

Fig. 8 S/N response for the thickness of PVDF films

3.4. GRA of Surface Roughness, thickness and Conductivity Results

3.4.1 Data normalization

In grey relational analysis data processing is first performed in order to normalize the raw data for analysis. In this work, linear normalization of experimental results is performed in the range between zero and unity. Usually, there are three categories of performance. Characteristics in the analysis of normalized value, i.e. the 'Lower the better', 'Higher the better' and the 'Nominal the better'. 'Lower the better' and 'Higher the better' were considered for the percentage parameter response.

Grey relation analysis can be used to solve complicated interrelationships between multiple performance characteristics. The Grey relational grading equation for smaller the better is given by [25]

$$X_{i(S)}(K) = \frac{\max y_i(k) - y_i(k)}{\max y_i(k) - \min y_i(k)}$$

The grey relation grading equation for larger the better is given by equation [26]

$$X_{i(L)}(K) = \frac{y_i(K) - \min x_i(K)}{\max y_i(K) - \min y_i(K)}$$

Where $y_i(k)$ is the value after the grey relational generation, $y_i(k)$ = is the k^{th} experimental results in i^{th} experiment, max $y_i(k)$ and min $y_i(k)$ were the maximum and minimum value of $n_i(k)$, respectively. The Grey relational co efficient $_i(k)$ is given by equation

$\xi i(k) = (\Delta \min + \zeta \Delta \max) / (\Delta_{oi}(k) + \zeta \Delta \max))$

Where Δ_{oi} is the deviation sequence of reference (x_0) and comparability sequence (x_i), i.e.

$\Delta_{oi} = \| x_0(k) - x_i(k) \|$, ζ is distinguishing coefficient and $\zeta \varepsilon [0,1]$. The value of ζ can be adjusted according to system requirement. The coating parameters are equally weighed in this work and therefore $\zeta \iota\sigma 0.5$. $\Delta \max = \forall^{\max}_j \varepsilon i \forall k^{\max} \| x_0(k) - x_i(k) \|$ is the largest value Δ_{oI} and $\Delta \min = \forall^{\min}_j \varepsilon i \forall k^{\min} \| x_0(k) - x_i(k) \|$ is the smallest value of Δ_{oi}

Grey relational grade is a weighting- sum of the Grey relational coefficient it is given by equation

$$\xi(x_0, x_i) = \frac{1}{n} \sum_{k=1}^{n} 1\, \xi i(k))$$

Where n is the number of performance characteristic. The grey relational grade shows the correlation between the reference sequence and comparability sequence to be compared to. The evaluated grey relational grade fluctuates from 0 to 1 and equals one if these two sequences are identically coincident [27-28].

The Grey relational grading and its ranking in each experiment using L_9 Orthogonal array for deposition is shown in Table 3.

Table-3 Grey relational co-efficient, grey relational grade and their order

Expt. No	Grey relation co-efficient			Grade	Order
	β-phase	Thickness	Roughness		
1	0.6295	0.7390	0.5416	0.458	4
2	0.8094	0.8946	0.4814	0.680	3
3	1	1	1	0.472	1
4	0.5483	0.4856	0.4482	0.533	7
5	0.5861	0.6295	0.6841	0.520	5
6	0.7390	0.8010	0.8665	0.642	2
7	0.3333	0.3333	0.3333	0.535	9
8	0.4046	0.4856	0.5416	0.425	8
9	0.4358	0.5214	0.6190	0.654	6

The highest grade of Grey relational grading shows that the results obtained experimentally are closer to ideal optimum value. In other words, the larger the Grey relational grading, the better will be the multiple performance characteristics. Therefore, experiment 3 in the Table 3 shows the highest Grey relational grading indicating the parameter of $A_3B_3C_3$ in the Orthogonal Array has the best multi performance characteristics among nine experiments.

Table-4 Grey Relational grade and its order for each level

Factors	Grey relation grade	Order
A_1	2.364	1
A_2	1.929	2
A_3	1.338	3
B_1	1.463	3
B_2	1.841	2
B_3	2.327	1
C_1	1.918	2
C_2	1.747	3
C_3	1.966	1

The Grey relational grading for the mean is summarized in Table 4 which shows the predicted optimal process parameter based on the Grey theory is $A_1B_3C_3$ since the optimal process parameter is the combination of the levels with highest Grey relational grading.

3.5 Confirmation Tests

Optimal design parameter level is selected for final step to verify the quality improvement using parametric level. Table 5 shows the initial process parameter $A_3B_3C_3$ experimental result for multiple performance characteristics of PVDF films and comparison of the Grey theory prediction design $A_1B_3C_3$ is shown in table 6

Results shows β-phase increase from 93% to 94%, Roughness decreases from 4 to 3 nm, thickness decreased from 2.5 to 2.25 µm respectively.

Table-5 Results of Initial process parameters of PVDF films

Initial parameter	β-phase (%)	Roughness (nm)	Thickness (µm)
$A_3B_3C_3$	93	4	2.5

Table-6 Result for grey theory prediction of PVDF films

Grey prediction	β-phase (%)	Roughness (nm)	Thickness (µm)
$A_1B_3C_3$	94	3	2.25

IV. CONCLUSIONS

In this study, spin coating manufacturing process especially for thin film manufacturing were explained. Definitely spinning is one of the good options for fabrication of the PVDF thin film polymers. This method would be even more beneficial with incorporation of a heating system within the spin coater which produces thinner films. In this work, it is also shown that FTIR and XRD are one of the proper investigation methods for quantifying and assessing β-phase content in the film. It was observed that the higher spin coating speed will result in thinner and uniform films. Annealing temperatures and their times are important factors for fabricating good quality PVDF films.

In this work experimental studies of β-phase content, surface roughness and thickness were undertaken for PVDF thin films. L_9 Experimental array was designed considering PVDF wt%, spinning speed, spin duration and annealing temperature.

Based on the experimental results the following conclusions were arrived at:

The following conclusions also can be drawn:

- The Responses of PVDF films were optimum when in PVDF wt% is decreased and spinning speed, duration and annealing temperature were increased.
- ANOVA results showed that the PVDF wt% was the most influencing factor with 82.20% for β-phase, 65.71% for thickness. In roughness it was found that spinning speed influence the most with that of 65.22%.
- The optimal regression analysis R^2 was obtained for β-phase of 94.07%, roughness of 92.06% and thickness of 96.24% for PVDF films.
- The GRA obtained Initial process parameter was found to be 93% for β-phase, 4nm for roughness, 2.5µm for thickness of PVDF films.
- The grey prediction obtained was 94% for β-phase, 3nm for roughness, 2.25µm for thickness of PVDF films.
- Different PVDF wt% granules and solvents with different ratio and with different parameters have been tried and several films have been made. The best film which gave highest β-phase content was for wt% 10, speed 3000, duration 10sec and temperature 50^0C.

- The range of factors such as PVDF wt% (10%-20%), spinning speed (1000rpm-3000 rpm), spin duration(10-30sec) and annealing temperature (30º C-50º C) was explored by all factor at a time approach.

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