Synthesis and characterization of spin-coated clay/PVDF thin films

T S ROOPA, H N NARASIMHA MURTHY*, H S SWATHI, GANGADHAR ANGADI
and D V N HARISH

Department of Mechanical Engineering, R V College of Engineering, Bangalore 560059, Karnataka, India

*Author for correspondence (hnmmdatta@yahoo.com)

MS received 31 July 2017; accepted 27 March 2018; published online 18 January 2019

Abstract. This paper reports the fabrication of Cloisite-15A (C-15A)-dispersed polyvinylidene fluoride (PVDF) nanocomposite thin films by spin coating and their characterization for sensor applications. The effects of nanoclay, duration of ultrasonication and spinning speed on the morphology and properties of thin films were studied. The influence of these parameters on the amount of β -phase was analysed using Fourier transform infrared (FTIR) and X-ray diffraction (XRD) techniques. The influence of C-15A on the morphology and surface quality of thin films was analysed by scanning electron microscopy (SEM). Piezoelectric coefficient was measured at 110 Hz and 0.25 N. Contact angle was measured to assess the hydrophobicity of thin films. The β -phase of 82.97% was obtained in the specimens with 5 wt% C-15A, processed at 500 rpm and spun for 35 min. The piezoelectricity of the specimens increased from -18 to -25 pC N $^{-1}$. Experiments were conducted as per L $_{16}$ orthogonal array.

Keywords. PVDF/clay thin films; Cloisite-15A; spin coating; β -crystals; piezoelectricity.

1. Introduction

Polyvinylidene fluoride (PVDF) has high piezoelectric and pyroelectric properties and hence it is widely studied as a thin film polymeric sensor material. It is highly flexible, lightweight, stable and non-depolarizing even under high alternating fields. It can exhibit polymorphs such as α , β , γ , δ and ϵ , amongst which mainly α , β and γ are studied for piezoelectric properties. PVDF in the β -phase acts as a piezoelectric material. β -Crystals are polar in nature and are in an electroactive phase [1]. PVDF consists of long chains of a repeating monomer $[-CH_2-CF_2-]$, where hydrogen atoms are positively charged and fluorine atoms are negatively charged which leaves each monomer unit with an inherent dipole moment [2]. In PVDF thin films, the α -phase can be obtained directly from the melt. But for obtaining higher β -phase, the film has to be stretched or subjected to high pressure or an electrical field. Piezoelectric thin film devices are in great demand in many applications [3]. Piezoceramics and piezopolymers are the two largest groups of materials used in thin film fabrication. Piezopolymer thin films have many advantages such as lightweight and durability over piezoceramics. They are superior to ceramics because of greater stress constant, feasibility of forming electrode patterns on their surface and selective poling [4]. Many polymers such as semicrystalline polyamides, polypropylene, polymethylmethacrylate, polystyrene and amorphous polymers such as vinyl

acetate exhibit piezoelectric properties. But in these materials, the piezoelectric effect is weak and unstable [5]. A strong and stable effect can be observed in PVDF and in its copolymer-based thin films [6].

Experimental studies on PVDF for increasing its β -phase are reported [7–12]. Stretching, use of polar solvents and application of an electric field are adopted for increasing the β -phase. Recent studies have been focused on addition of nucleating fillers to enhance the electroactive phase of PVDF. The molecular chains of PVDF interact with the surface of the nanofiller to form β -phase and improve its properties such as tensile strength and conductivity [13]. Nanoclay, carbon nanotubes (CNT) and metallic nanopowders are explored as nanofillers for PVDF. In specific studies, dispersion of Cloisite-6A (C-6A), C-20A and C-Na $^{+}$ in PVDF increased the rate of crystallization. Uniform dispersion of nanoclay in PVDF, improvement in mechanical properties and thermal stability against shrinkage along with membrane porosity of 75% are reported [14–16].

Incorporation of C-15A and C-25A into PVDF using solution casting and co-precipitation methods revealed that the phases of PVDF are dependent on the type of the fabrication process and the solvent used [17]. Improvement in mechanical properties, reduction in coefficient of thermal expansion and 78% β -phase are reported using melt compounding and solution cast halloysite- and kaolinite-dispersed PVDF thin films [7,18,19]. The effect of addition of more than one nanofiller to PVDF is studied by dispersing CNT with C-30B and C-15A.

Addition of C-15A showed an improvement in β -crystals and melting temperature up to 11°C and reduction in thermal stability. Addition of CNT improved mechanical properties and electrical conductivity [20,21].

Spin coating for fabricating thin films has several advantages over other techniques. It can be operated under atmospheric conditions, it is more economical, easy to operate and capable of inducing the stretching effect when operated at higher rpm. Hence, it is considered to be one of the best methods for development of thin films for initial studies. Several authors reported fabrication of PVDF thin films by spin coating, effect of parameters such as annealing temperature and time [22–24], multilayer deposition [10] and stretching [25–33] along with the β -phase between 75 and 80%.

A review of the literature [1–33] indicates that so far research studies on PVDF thin films/composites/membranes have been focused on processing techniques and the characterization of films. Global focus of research is to achieve higher β -phase by process optimization, addition of nanomaterials such as ceramic fillers, metallic powders, nanoclays and carbon nanotubes. Comprehensive studies on the spin coating parameters for achieving higher β -properties in PVDF thin films are scarce. The main objective of this study was to investigate the effects of C-15A, ultrasonication duration, spinning speed and duration on the morphology of C-15A/PVDF thin films, β -phase, mechanical properties, wettability and piezoelectric coefficient based on L_{16} orthogonal array experimental design. The thin films were characterized by using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM) and water contact angle techniques.

2. Experimental

2.1 Materials and processing

PVDF powder Kynar 761 grade (Arkema), *N*-dimethyl formamide (DMF) solvent (Bangalore Fine Chemicals) and C-15A (Southern Clay Products, USA) with a bulk density of 1.66 g cc⁻¹ and a platelet size of 150–250 nm were used in this study. A quantity of 25.12 wt% of PVDF/DMF solution was prepared by dissolving 7 g PVDF powder in DMF and the mixture was stirred using a magnetic stirrer at 50°C. C-15A (0, 3, 5 and 7 wt%) was added to the mixture solution and ultrasonicated for 20, 25, 30 and 35 min. The solution was spin coated at 400, 500, 600 and 700 rpm and dried at 70°C by placing in a hot air oven for four hours. Thin films of thickness of 20–30 μ m were obtained. The procedure was repeated for all the treatment combinations as per the L_{16} orthogonal array layout of table 1. Each combination was repeated 4 trials and the average values were considered. A range of spinning speed and duration of ultrasonication were selected based on initial experiments. Below 400 rpm, the films yielded low values for the β -phase and above 700 rpm, the porosity of the films increased and the β -phase decreased. Thus, the experiments were confined to 400–700 rpm. The optimum values of the β -phase based on detailed experimentation correspond to 500 rpm with not much influence of duration of ultrasonication, leaving no scope for further experiments with change of speed and duration.

Poling of thin films was performed by using silver paint to form the electrodes on both sides of the thin films to ensure better contact and homogeneous charge transfer and were dried at 60°C for 15 min in a hot air oven.

Table 1. L_{16} orthogonal array with the β -phase content and thickness of thin films.

Sample code	Nanoclay wt%	Ultrasonication duration, min	Spinning speed, rpm	Thickness, μ m	$F(\beta)^a$
S1	0	20	400	24	49.80
S2	0	25	500	22	51.97
S3	0	30	600	22	52.18
S4	0	35	700	23	53.70
S5	3	20	500	28	71.67
S6	3	25	400	22	73.52
S7	3	30	700	25	70.9
S8	3	35	600	24	77.85
S9	5	20	600	28	80.26
S10	5	25	700	25	80.75
S11	5	30	400	26	81.55
S12	5	35	500	25	82.97
S13	7	20	700	23	82.15
S14	7	25	600	23	82.64
S15	7	30	500	22	77.01
S16	7	35	400	24	74.07

^a $F(\beta)$ = average value of the amount of the β -phase in %.

The films were poled at $80 \text{ V } (\mu\text{m})^{-1}$ for 45 min and cooled to room temperature retaining the field applied. This effect reorients the dipoles in the direction of the applied electrical field and makes the dipole orientation to be effectively locked in.

2.2 Characterization of thin films

The same spin-coated films were used for both FTIR and XRD analysis. Infrared spectra were obtained by using an FTIR (Cary 600 series FTIR spectrometer) in the $600\text{--}2000 \text{ cm}^{-1}$ wavenumber range. The thickness of the samples used was in the range of $22\text{--}28 \mu\text{m}$. The literature study suggests that the samples containing α - and β -phases follow the Lambert–Beer law to calculate the relative fraction of the β -phase present in

a film as given in equation (1):

$$F(\beta) = \frac{A_\beta}{\left(\frac{K_\beta}{K_\alpha}\right) A_\alpha + A_\beta} \quad (1)$$

where K_α and K_β are absorption coefficients at the wavenumbers 763 and 840 cm^{-1} whose values are 6.1×10^4 and $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$, respectively. $F(\beta)$ represents the β -phase content, A_α and A_β are the absorbances at the wavenumbers 763 and 840 cm^{-1} , respectively [1,27].

An X-ray diffractometer with copper $K\alpha$ ($\lambda = 1.54 \text{ \AA}$) at 2° min^{-1} and scan range of $3\text{--}60^\circ$ was used to characterize the crystalline structures of the thin films. A piezoelectric coefficient d_{33} was measured using a Piezotest PM300 model with the frequency of 110 Hz and force of 0.25 N . For morphology observations, a JEOL JSM-5600LV scanning

Figure 1. FTIR spectra of thin films: (a) pure PVDF (S1–S4), (b) 3% C-15/PVDF (S5–S8), (c) 5% C-15/PVDF (S9–S12) and (d) 7% C-15/PVDF (S13–S16).

electron microscope was utilized. Water contact angle was measured using a Dataphysics Goniometer SA20 model with a drop size of 2 μl .

3. Results and discussion

3.1 FTIR analysis

FTIR peaks at 765 and 796 cm^{-1} corresponding to α -phase conformations and peaks at 837 and 840 cm^{-1} corresponding to the β -phase for spin-coated samples are illustrated in figure 1. In 5 wt% C-15A/PVDF thin films (figure 1c), the peaks at 837 and 840 cm^{-1} corresponding to the β -phase increased and those at 764 and 796 cm^{-1} corresponding to the α -phase decreased. The β -phase was 82.97% at 5 wt% nanoclay addition, 35 min of ultrasonication and 500 rpm coating speed. However, the 7 wt% C-15A addition decreased the amount of β -phase [4,12,18,21].

3.2 XRD

A combination of XRD and FTIR of spin-coated samples shows clear distinction among the different phases in thin

films. The peaks of PVDF α -crystals at $2\theta = 17.66, 18.30, 19.90$ and 26.56° correspond to the Millar indices (100), (020), (110) and (021) planes, those of β -crystals at $2\theta = 20.7^\circ$ correspond to the (110) and (220) planes and those of γ -phase at $2\theta = 18.5, 19.2$ and 20.04° correspond to the (020), (002) and (110) planes [1,10,27].

Crystallization behaviour of PVDF and C-15A/PVDF thin films was studied based on XRD patterns of figure 2. In PVDF samples, a peak at $2\theta = 18.2^\circ$ and a sharp peak at $2\theta = 19.8^\circ$ represent the α -phase. A peak at $2\theta = 20.1^\circ$ corresponded to the β -phase and (110) and (200) planes. In C-15A/PVDF, the α -peaks almost disappeared and a sharp peak at $2\theta = 20.3^\circ$ corresponding to β -crystals was observed. This clearly evidenced the enhancement of β -crystal formation due to nanofiller addition.

3.3 Morphology of thin films

Morphology of C-15A/PVDF thin films was studied using SEM (figure 3). The specimens were dried at a uniform temperature of 70°C for 4 h to study the effect of nanoclay loading. Figure 3a shows the morphology of a bare PVDF thin

Figure 2. XRD patterns of thin films: (a) pure PVDF (S1–S4), (b) 3% C-15/PVDF (S5–S8), (c) 5% C-15/PVDF (S9–S12) and (d) 7% C-15/PVDF (S13–S16).

Figure 3. SEM micrographs of thin films: (a) pure PVDF (S4), (b) 3% C-15/PVDF (S8), (c) 5% C-15/PVDF (S12) and (d) 7% C-15/PVDF (S14).

film, which shows the homogeneous surface with minimum number of pores. The porosity was nearly the same in PVDF and 3 wt% C-15A/PVDF (figure 3b). Figure 3c and d shows the morphology of 5 and 7 wt% of C-15A composite thin films, which shows a spherulitic structure with increased porosity. Along with nanoclay loading, the evaporation rate and film thickness also influences the porosity. The presence of pores hampers the deposition of electrodes, hinders the poling process and hence reduces the electrical response of thin films [11,13,16,17,34–37].

3.4 Water contact angle

Contact angle was measured to examine the hydrophobicity of the films. C-15A has higher surface energy than PVDF. Figure 4 shows increase in hydrophilicity of PVDF due to the addition of C-15A. The contact angle 127° for PVDF decreased to 92° with an increase in C-15A, indicating an increase in wettability [30–33].

3.5 Piezoelectric coefficient

PVDF polymer chains pack the unit cell in two different ways. They are either additive, having a net dipole moment

or in the opposite direction, without a net dipole moment. Only polar conformations can impart piezoelectricity. The β -phase has a net dipole moment and best piezoelectric coefficient after the poling process. The presence of β -crystals is important for piezoelectric and pyroelectric properties. The interaction between the surface of nanofillers and PVDF molecular chains is responsible for formation of the electroactive β -phase in PVDF. In the β -phase, dipoles are randomly oriented and are not piezoelectrically active until the crystals became preferentially oriented. It can be achieved by two processes such as stretching and the application of an electrical field. The phenomenon of applying an electric field is termed as poling. Spin coating induces the stretching effect in films there by results in phase transformation from α to β which is one of the methods for inducing a piezoelectric effect in thin films. The poling of spin-coated films further improves phase transformation and helps to increase the piezoelectric coefficient by locking the dipole reorientation.

Before poling, the electrodes were connected to thin films. Silver paint was utilized to form electrodes on both sides of the sample to ensure better contact and homogenous charge transfer. The films were dried at 60°C for 15 min in a hot air oven. Thin films were heated to 100°C and a large field of

Figure 4. Water contact angle measurements on thin film surfaces: (a) pure PVDF (S4), (b) 3% C-15/PVDF (S8), (c) 5% C-15/PVDF (S12) and (d) 7% C-15/PVDF (S14).

Table 2. Piezoelectric coefficients of thin films.

Sample details	$-d_{33}$ (pC N ⁻¹)
S4	18
S8	25
S12	20
S14	19

d_{33} = piezoelectric coefficient.

80 V(μm)⁻¹ was applied for 45 min and then cooled down to room temperature with the electric field still applied. This effect reorients the dipoles in the direction of the applied electrical field and makes the dipole orientation effectively locked in.

After polarization, the specimens were clamped between two probes and subjected to a low-frequency force of 110 Hz and 0.25 N. In response to the applied force, the specimens produced electrical signals. These signals were compared with those of the reference material and direct values of d_{33} were generated. It represents the charge per unit force in the direction of polarization. Table 2 presents the piezoelectric coefficient of the thin films, showing the maximum d_{33} value

of -25 pC N⁻¹ for the specimens with 3 wt% nanoclay. While the β -phase increased with an increase in nanoclay content from 3 to 5 wt%, d_{33} decreased in the films with greater than 3 wt% nanoclay which is due to increased porosity [38,39].

3.6 Analysis of variance (ANOVA)

Table 3 presents the ANOVA of the responses of the experiments as per the L₁₆ layout with three measurements of the β -phase for each experiment. Degrees of freedom, sum of squares, mean square and F values were calculated as per the standard procedure. Calculated F values were compared with standard F values for significance. Corresponding to degree of freedom 3 for each of the factors and that of error 6, the tabulated value of F is 1.78. Hence, nanoclay loading has more significance on β -phase percentage.

A range of spinning speed and duration of ultrasonication were selected based on initial experiments. Below 400 rpm, the films yielded low values of the β -phase and above 700 rpm, the porosity of the films increased and the β -phase decreased. Thus, the experiments were confined to 400–700 rpm. The optimum values of the β -phase based on detailed experimentation correspond to 500 rpm with not much influence

Table 3. ANOVA for % of the β -phase.

Source	DOF ^a	Sum of squares	Mean squares	F_{cal}	F_{tab}	$P\%$
Nanoclay loading, wt%	3	1377.05	459.02	46.79	1.78	94.0
Ultrasonication duration, min	3	9.91	3.30	0.34	1.78	0.0067
Spinning speed, rpm	3	18.98	6.33	0.64	1.78	1.29
Error	6	58.86	9.81			
Total	15	1464.80				

^aDOF = degrees of freedom; F = Fischer ratio; $P\%$ = percentage contribution.

Figure 5. (a) Normal probability plot for % of β -phase and (b) main effect plot for % of β -phase.

of duration of ultrasonication, leaving no scope for further experiments with change of speed and duration.

3.7 Normal probability and main effect plot for the β -phase

Figure 5a shows the normal probability plot of the means of the β -phase corresponding to the 16 experimental combinations. The normal probability plot indicates whether the experiments are carried out with the influence of random causes.

Figure 5b shows the effects of nanoclay loading, spinning speed and ultrasonication duration on the experimental responses. The mean plot of S/N ratio for β percentage considers ‘the larger the better’ was plotted and the highest S/N ratio of each input parameter gives the optimum configuration for obtaining the maximum β percentage. The

plot indicates an increase in the β percentage with an increase in nanoclay loading from 0 to 5 wt% and decreases with a further increase in nanoclay loading. Increasing the spinning speed from 400 to 600 rpm increases the β percentage and shows reduction at 700 rpm. Ultrasonication duration showed no significant effect on the β percentage as the values were close to mean line. Hence, the optimum configuration to obtain the maximum β percentage was chosen to be 5 wt% of nanoclay loading and 600 rpm spinning speed.

4. Conclusion

The influence of nanoclay addition to PVDF and spin coating parameters on the β -phase content in thin films was investigated. FTIR spectra revealed 82.97% transformation of α - to β -crystals in the specimen with 5 wt% C-15A, 35 min of

ultrasonication and 500 rpm spinning speed. The formation of the β -phase was confirmed by the XRD results. The porosity in the films was studied by SEM micrographs. While the highest β -phase of 82.97% was observed in 5 wt% nanoclay/PVDF thin films, the highest piezoelectric coefficient of -25 pC N^{-1} was obtained in 3 wt% nanoclay/PVDF films as the porosity increased with an increase in nanoclay addition. Water contact angle decreased from 127° to 92° with an increase in C-15A, indicating an increase in wettability.

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