CHAPTER 5

STRUCTURAL, DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF 0-3 PZT/PVDF COMPOSITES

5.1 Introduction

As already discussed, lead based perovskites such as lead zirconate titanate PZT and its solid solutions are the most exploited ferroelectric materials known for their applications in sensors and actuators. These materials exhibit excellent dielectric and piezoelectric properties at the morphotropic phase boundary (MPB) \([18,20,132-139]\). However, these piezoceramics are brittle in nature and are difficult to conform to the desired shapes and structures. These disadvantages limit their use in applications where flexibility is desired. Polymers such as PVDF are known for their flexibility, mechanical strength, piezoelectric properties and can easily conform to different shapes and structures \([155]\). However, the piezoelectric responses of the polymers are poor as compared to the piezoceramics. The search for the new materials which can combine the complementary features of a polymer and a ceramic has led to the significant research in the field of composite materials \([60,65,178,186,187]\).

The composite materials constitute a new class of materials which combine the properties possessed by their constituent phases. The electroactive composites made up of ferroelectric ceramic and polymer has been extensively studied for their excellent properties and their possible applications in various fields are being explored. These composite films combine the interesting features of both the phases which includes high dielectric and piezoelectric properties of the ceramic and the flexibility and mechanical tolerance of the polymer. There are various parameters which control the electrical and mechanical behavior of these composites. Newnham et al. established that the connectivity of the constituent phases plays an important role in determining the material properties of these composites. The composite consisting of embedded rods of a piezoelectric ceramic in a polymer matrix exhibited superior properties than the composites made up of ceramic particles dispersed in the polymeric host. However, the composites with ferroelectric ceramic in the polymer matrix or so called composites with 0-3 connectivity have been of significant research interest owing to their mass production and their ease in the fabrication into various complex shapes and
structures. Hence, large and thin composite films are being developed and investigated for their potential use in ultrasonic and infrared detection. The properties of the composite materials can thus, be engineered for specific requirements depending on the volume fraction, connectivity and properties of the constituent phases [70-74,188].

There have been extensive studies on PZT based polymer composites with 0-3 connectivity [65,70-82]. Most of the studies dealt with the material properties of the films synthesized under the conditions which resulted in α rich PVDF phase. The basic intention of the present study is to synthesize PZT/PVDF composites in the 0-3 connectivity phase with β rich phase in PVDF under optimized processing conditions and to investigate the structural and material properties of these films as a function of volume fractions of PZT in PVDF matrix. This information is necessary for the designing of the composites with optimum properties for specific applications.

PZT ceramic particles were prepared in the MPB region with Zr/Ti = 50/50 so as to obtain better dielectric and piezoelectric properties in the system. PZT ceramic powders were synthesized by adopting low temperature calcination route which yields a pure perovskite phase via stabilization of $A_3B_4O_{13}$ pyrochlore phase as discussed in Chapter 1 [6,42,43,94,143,154,189]. Further, it was found in our previous study (Chapter 4) that the thermal processing conditions play an important role in deciding the crystalline phase and hence in turn the material properties of PVDF films [60]. Therefore, the optimized processing conditions obtained in our previous studies were employed to synthesize PZT based PVDF films aimed to incorporate the advantages of PZT ceramic and PVDF polymer [43,60,94,143,154,189].

5.2 Materials and methods

Since, the material characteristics of the composites are also governed by the composition of the constituent phases, crystallinity and their crystal structure, hence, the composite films were prepared using PZT ceramic powders in the vicinity of MPB under optimized solution cast technique.

PbZr$_{0.5}$Ti$_{0.5}$O$_3$ ceramic powders were synthesized by adopting low temperature calcination route. The raw materials of analytical grade such as PbO, ZrO$_2$ and TiO$_2$ were mixed in ethanol in stoichiometric ratio and were calcined at 700°C for an hour. These powders were
kept at 1280°C in a lead rich atmosphere for 2 hours [43,143]. 15 wt% of PVDF granules were dissolved in 20 ml of dimethylsulfoxide (DMSO) and 80 ml of acetone by stirring in a magnetic stirrer at 40°C for 30 min. The volume fraction of synthesized PZT ceramic powders was calculated by the following relation [123]

\[ v_f = \frac{w_f}{w_f + w_m(\rho_f + \rho_m)} \]  

(5.1)

where, \( v_f \) is the volume fraction of the PZT particles, \( W_f \) and \( \rho_f \) are the weight fractions and the density of PZT ceramic particles while \( W_m \) and \( \rho_m \) are the weight fraction and density of the PVDF polymer matrix respectively.

The different volume fractions of PZT particles were added to the PVDF solution and the solution was further stirred for 30 min. The solutions with different volume fractions of PZT viz. 0%, 10%, 20% and 30% PZT particles were cast over petri dish by solution cast technique and kept at 60°C for 4 days. The obtained films were treated at 80°C for 5 hrs and later quenched at 20°C [60].

The FTIR spectra of these composite films were recorded by a Perkin Elmer Spectrometer for structural investigation. The structural characterization of these films was also carried by X-ray diffraction using CuKα radiation on an XRD-6000 from Shimadzu Analytical, Japan. The dielectric measurements were carried using LCR meter, Hioki, Japan for 1 kHz. The area of the [PZT]_x/[PVDF]_1-x films used for dielectric study are 83.67 mm². The thickness of these films are found to be 0.950, 0.925 and 1.050 mm for x=0.1, 0.2 and 0.3 respectively. These films were poled in silicone oil bath at 80°C with an electric field of 10kV/mm. The samples were aged for 24 hours. The piezoelectric coefficients, \( d_{33} \) were obtained using Berlincourt Piezo \( d_{33} \) meter.

### 5.3 Results and Discussion

#### 5.3.1 Structural Analysis

**XRD**

The XRD patterns of the sintered ceramic PZT powders, pure PVDF film and the composite films of PZT/PVDF with different concentration of the ceramic powders were recorded and analyzed for the identification and quantification of the phases present in the synthesized sample. The XRD pattern of the PZT ceramic showed the formation of pure perovskite phase
within the detection limit of x-ray diffraction. A typical XRD pattern of the sintered PZT ceramic powders (Zr/Ti =50/50) in the 2θ range of 10° to 90° is shown in figure 3.2 (Chapter 3). The triplet splitting of (200) pseudocubic reflection confirmed the phase coexistence in the synthesized ceramic powders.

Figure 5.1 shows the XRD patterns of the pure PVDF and PVDF-PZT films with different concentrations of the ceramic content in the polymer matrix synthesized under the optimized processing conditions [43, 60]. The XRD pattern of the pure synthesized PVDF film revealed a mixture of α, β and γ phases. All the XRD peaks of the composite films with different volume fraction of PZT ceramics in the PVDF matrix have been indexed as those of PZT perovskite structure and of α, β and γ phases of PVDF polymer and have been labeled in the figure. The peaks corresponding to the perovskite phase of PZT ceramic and α, β and γ phases of PVDF have been denoted by various symbols. The characteristic peaks around 21.9°, 31°, 38°, 44.5°, 49° and 55° are signatures of perovskite phase while the peaks corresponding to 2θ values around 19.9°, 20.3° and 20.9° are ascribed to α, γ and β phases respectively of PVDF polymer [60].

It can be seen from the figure that the perovskite phase increased with the volume content of PZT ceramic in the PVDF as expected. The crystallinity of the films is expected to increase with the concentration of ceramic powders in the polymer matrix. The quantification of the different phases present and the estimation of the degree of the crystallinity are done to understand the structure and property correlation in these composite films.

The deconvolution of the XRD peaks corresponding to the various crystalline phases of PVDF and the perovskite phase of PZT was done for the composite films with different volume content of PZT in the PVDF matrix. Figure 5.2 shows the typical deconvoluted XRD peak profiles of PVDF and [PVDF]1-x[PZT]x. It can be seen from the figure that as-synthesized pure PVDF and PZT/PVDF composite films under optimized thermal processing condition revealed β enrich phase and the total crystalline content in the film is also fairly large as is depicted by sharp characteristic peaks. Hence, in order to quantify the crystalline content in these films, the integrated peak intensities of the various phases were considered.
Figure 5.1: The X-ray diffraction profile patterns of [PZT]_x/[PVDF]_{1-x} system (a) x = 0 (b) x = 0.1 (c)x = 0.2 (d) x = 0.3.
Figure 5.2: A typical deconvoluted XRD pattern for the quantification of α, β and γ phases and PZT perovksite phase present in the [PZT]$_x$/[PVDF]$_{1-x}$ composites with x = 0.1.

The total crystalline content of the composite film, \( \chi_{CT} \), is calculated by the relation,

\[
\chi_{CT} = \frac{A(\alpha + \beta + \gamma + c)}{A(\alpha + \beta + \gamma + c) + A(\text{amorphous phase})} \tag{5.2}
\]

The total crystalline content in the PVDF matrix, \( \chi_c \) or \( \chi_T \), can be evaluated using the expression described as,

\[
\chi_T = \frac{A(\alpha + \beta + \gamma)}{A(\alpha + \beta + \gamma + c) + A(\text{amorphous phase})} \tag{5.3}
\]
Where $A(\alpha+\beta+\gamma)$ is the area under curve corresponding to all the crystalline peaks associated with PVDF, $A(\alpha+\beta+\gamma+c)$ is the total area corresponding to the crystalline phase of PVDF and PZT phases and $A(\text{amorphous phase})$ represents the area related to the amorphous PVDF content.

Further, the quantification of the crystalline phases of $\alpha$, $\beta$ and $\gamma$ phases in PVDF polymer is done by considering the integrated intensity of the deconvoluted peaks of the same and is already described by equation 4.2.

The variation in the total crystalline content of the composite films and the amount of $\alpha$, $\beta$ and $\gamma$ phases in the PVDF matrix with the volume content of PZT ceramic have been shown in figure 5.3.

![Graph showing variation in crystalline content of different phases with PZT content](image)

**Figure 5.3:** The variation in the crystalline content of $\alpha$, $\beta$, $\gamma$ phases of PVDF along with the total crystallinity with the volume % of PZT ceramic in the PZT/PVDF composite.

It can be seen from the figure that the crystalline content is enhanced with the increase in the volume content of PZT ceramic in the composite. Further, it can also be seen that the $\beta$ phase content enhances with the volume content of PZT in the PVDF matrix while $\alpha$ and $\gamma$ phases are suppressed. However, the total crystalline content in the PVDF matrix for all the studied composites is found to be within 50-55%. Hence, the increase in $\beta$ phase is a result of the transformation from $\alpha$ and $\gamma$ phases as is evident from the figure. Since, $\beta$ phase is
responsible for the piezoelectric behavior in the PVDF, hence, the relative phase fraction is calculated as described before in Chapter 4 (equation 4.6).

The variation in the relative phase fraction of β phase in the composite films with the volume content of PZT is plotted in figure 5.4. It can be seen from the figure that the β phase content in the composite increases with the increase in volume content of PZT.

![Figure 5.4: The variation in the F(β) % of PVDF with the volume % of PZT ceramic in the composite.](image)

**FTIR**

Figure 5.5 shows the FTIR spectra of PVDF and PZT/PVDF composites. The different vibration modes at 604, 657 and 774 cm\(^{-1}\) have been attributed to the perovskite phase of PZT. The α phase is characterized by the vibration bands at 764, 795, 855 cm\(^{-1}\) while 778, 795 and 834 cm\(^{-1}\) are considered to be signatures of γ phase and 840 cm\(^{-1}\) corresponds to the β phase of PVDF films. All the characteristic vibration bands associated with α, β and γ phases of PVDF are seen in case of pure films but only the intense peaks of PVDF phase associated with vibration bands at 855, 840 and 834 cm\(^{-1}\) could be observed for the composite films due to relative intense peaks of PZT perovskite phase. The mixed α, β and γ phases of PVDF along with the characteristic vibration bands of perovskite phase of PZT is found in all the composite films.
Figure 5.5: The FTIR spectra of [PZT]/[PVDF]$_x$ system (a) $x = 0$ (b) $x = 0.1$ (c) $x = 0.2$ (d) $x = 0.3$. 
The phase content of the crystalline phases of the PVDF in the composite films was evaluated by the method given elsewhere [60]. The results obtained from the FTIR spectra were found to be in close agreement with the XRD data. The relative phase content of $\beta$ phase is found to be enhanced with the PZT inclusion in the composite as also revealed by XRD patterns.

5.3.2 Functional analysis

Dielectric properties

Figure 5.6 shows the variation in the dielectric constant with temperature for PVDF and PVDF/PZT composite films synthesized under optimized processing conditions.

A dispersive anomaly in the dielectric behavior is seen around 80°C for pure PVDF film which is attributed to the wide angle oscillations of dipoles of the polymer followed by their rotation with the main chain co-operation in the crystalline phase. The addition of the ceramic content to the polymer is seen to shift this anomaly in the dielectric constant to a higher temperature region. The addition of ceramics in the PVDF matrix results in the hindrance of
the movement of parts of the polymer chain and hence, the thermal event is shifted towards higher temperature [95,96,123,190]. The transition temperature $T_c$ in the composites associated with the transformation from all trans to a disordered mixture of $TGTG'$ and $TTTGTTT'G$ in PVDF is found to shift to a higher temperature with the addition of ceramic content. It can be seen from the figure that this transition temperature from ferroelectric to paraelectric phase is 102°C for pure PVDF films, while it is found to be 138°C for 30% volume content of PZT in the composite. The dielectric permittivity is found to increase from 60 to 72 with the increase in volume content from 0 to 30 volume % of PZT in the composite. This increase in the dielectric permittivity is observed with the increase in the ceramic content of the polymer as expected due to the increasing contribution of the PZT ceramic and due to the $\beta$ enriched PVDF in the composite. It is also found that the dielectric permittivity obtained in the present study is also higher than reported in the literature which may be due to the optimized processing conditions adopted for the synthesis of these composites [60].

Piezoelectric properties

Table 5.1 shows the variation of piezoelectric coupling coefficient $d_{33}$ with different volume percentage of ceramic in the composites.

<table>
<thead>
<tr>
<th>System $[\text{PZT}]<em>x/\text{PVDF}</em>{1-x}$</th>
<th>Piezoelectric coupling coefficient, $d_{33}$, pC/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>-32</td>
</tr>
<tr>
<td>$x = 0.1$</td>
<td>60</td>
</tr>
<tr>
<td>$x = 0.2$</td>
<td>71</td>
</tr>
<tr>
<td>$x = 0.3$</td>
<td>84</td>
</tr>
</tbody>
</table>

The neat PVDF synthesized film showed $d_{33}$ value as -32pC/N whereas with the increase in the volume content of PZT ceramic from 0.1 to 0.3 in the polymer matrix, it is observed to increase from 60 pC/N to 84 pC/N. This increase in the piezoelectric response with the increase in the volume content of ceramic may be attributed to the increasing contribution of PZT and $\beta$ enrich phase of PVDF in the composite films [98,191].
5.4 Conclusions

The thin composite films of PZT/PVDF with different compositions were synthesized under optimized processing conditions. These films were highly flexible and contained PZT ceramic particles uniformly distributed over the film. The structural characterization revealed the ceramic is in the MPB region for pure PZT powders. The pure films of PVDF and PZT/PVDF are found to be mixture of α,β,γ and perovskite phases along with the amorphous phase. The crystalline content is found to increase with the addition of PZT ceramic in the composite films. The increase in volume content of ceramic particles in the films contributed to the increase in dielectric and piezoelectric properties. It is also observed that the addition of PZT ceramic in the PVDF matrix led to an increase in β phase which further enhanced the dielectric and piezoelectric properties of the composite films.