Enhancing the β -phase of PVDF by nano piezoceramic hybrid for advanced capacitive and energy storage application

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Abstract

Present work focussed on the preparation and characterization of ferroelectric ceramic-polymer composites, specifically using Poly Vinylidene Fluoride (PVDF) as the polymer host and PbZr_{0.48}Ti_{0.52}O₃(PZT), Bi_{0.5}Na_{0.5}TiO₃ (BNT) ceramics as the filler. The composites were prepared using the solution casting technique, and various properties were examined under different experimental conditions. The composites were characterized for various properties, including structural, microstructural, vibrational (FTIR-Fourier Transform Infrared), dielectric, and ferroelectric properties. XRD (X-ray Diffraction) analysis was used to observe the electroactive β -phase fraction in the composites. The microstructure of the composites was examined to understand the arrangement of the components. FTIR analysis provided insights into the mechanism of enhancing the β -phase and the interaction between negatively surface-charged ions of the PZT/BNT (BP) filler and the CH₂ dipole of the PVDF polymer matrix. Dielectric constant variation with PZT/BNT (BP) filler concentrations was studied. The interplay between functional properties and the β -phase, likely related to ferroelectric behaviour, was discussed in detail. The electroactive β-phase fraction was observed to increase in the ternary composite PVDF/PZT/BNT (BPP). For PVDF/PZT (PP) composite concentration, β -phase fraction decreased because of percolation effect. The study explores the comprehensive characterization of ferroelectric ceramic-polymer composites, focusing on the interaction between the polymer matrix and piezoceramic (PZT/BNT) (BP) filler. The observed changes in properties, especially the electroactive β -phase fraction, provide valuable insights into the composition-structure-property relationships in these composites. The work sheds light on the potential applications and optimization of these composites for capacitive applications.

Keywords: Polymer · Capacitor · Composites · Lead free piezoceramics · Ferroelectric

1 Introduction

Polyvinylidene fluoride (PVDF) has gained significant attention as a highly promising polymer for a wide range

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of applications due to its exceptional piezoelectric properties, chemical stability, and mechanical flexibility [1, 2]. This semi-crystalline polymer features a complex molecular structure, characterized by five distinct crystalline phases. Each phase corresponds to specific chain conformations: the β -phase adopts an all-trans (TTT) planar zigzag configuration, the α - and δ -phases exhibit a trans-gauche-transgauche (TGTG) arrangement, while the γ - and ϵ -phases display a T_3GT_3G conformation [3, 4]. In capacitive applications, optimizing the β -phase is crucial due to its superior piezoelectric response [d₃₃~34 pC/N] [5, 6]. This is attributed to the all-trans conformation of parallel dipoles (the difluoro methylene group, -CF2), which creates an imbalance in the distribution of negatively charged fluorine ions, resulting in an electric dipole and, consequently, a piezoelectric effect. As a result, significant research efforts have been directed toward enhancing the β -phase content in PVDF and its copolymers for technological applications,



including sensors, actuators, energy harvesting devices, membranes, and biomaterials in the biomedical field [7, 8].

However, achieving complete β-phase formation in PVDF and its copolymers, such as polyvinylidene fluoride co-hexafluoropropylene (PVDF-HFP), remains a considerable challenge due to the thermodynamically stable non-polar α -phase [9].Researchers have explored various strategies to address this issue, including mechanical stretching to induce forced molecular conformation, electrical poling to align the crystalline polar axis, electrospinning, low-temperature polar solvent crystallization, and the addition of nucleation agents [10–12]. While these methods have shown promise, they often lead to undesirable structural deformations or microstructural defects. Additionally, scaling these techniques for industrial processing is complex, which may hinder their application in areas such as electro-optical sensors and non-volatile memories. Another approach involves embedding nanofillers, such as carbon nanotubes (CNTs) [13], BaTiO₃ [14], ZnO [15], and CoFe₂O₄, or utilizing template methods like anodized alumina membranes to provide a scaffold for controlled β-phase growth. Each method presents unique challenges and advantages, and the choice of approach depends on the specific requirements of the intended application

Despite these advancements, the piezoelectric response of PVDF remains limited for certain practical applications. To address this, recent studies have explored the incorporation of piezoceramic fillers into PVDF. PVDF/piezoceramic composites have demonstrated enhanced electrical properties, making them suitable for advanced technological applications [16]. Piezoelectric materials, such as ZnO, BaTiO₃ [17], PbZr_{0.52}Ti_{0.48}O₃(PZT), Bi_{0.5}Na_{0.5}TiO₃ (BNT), KNaNbO₃ (KNN), are known for their high dielectric and piezoelectric properties, including high piezoelectric coefficients, strong pyroelectric constants, and excellent electromechanical coupling. Among these, PZT stands out due to its exceptional piezoelectric properties and its morphotropic phase boundary at a Zr/Ti ratio of 52/48. Studies by Pradhan et al. have shown that PVDF/4%PZT polymerceramic composites exhibit a prominent β -phase, along with enhanced dielectric and ferroelectric properties [18]. Further research has demonstrated that Mg-doped PZT incorporated into a PVDF matrix increases the dielectric constant, γ and β-phase content in PVDF/PMZT composites, with no significant chemical reaction between PVDF and PMZT [19]. These findings highlight the critical role of PZT in improving the dielectric and piezoelectric properties of PVDF for device applications [20].

However, the use of PZT raises environmental and health concerns due to the toxicity of lead, a heavy metal. Lead's volatility at high temperatures during calcination, sintering, and disposal poses serious environmental risks and health hazards, particularly affecting neurological and intellectual development. Additionally, synthesizing PZT in its pure phase is challenging due to its complex structure. In response, researchers have focused on developing lead-free piezoceramics with comparable electrical properties [21, 22]. A promising alternative to PZT is BNT, which shares a similar structure and has been extensively studied for its potential in improving physical properties for commercial applications. Studies by Sugato et al. on PVDF/Ba-doped BNT composites reported an enhanced β-phase in PVDF, along with a high dielectric permittivity (~61) and low dielectric loss (~1.4) compared to pure PVDF [23]. Similarly, Anand Kurakela et al. demonstrated the enhanced energy harvesting capability of PVDF/BNT composites, achieving an efficient electric output of 19 V, 1.2 µA, and 3.5 mW/m² for a 0.5 wt% BNTloaded PVDF composition [24].

The multifunctionality of passive electronic components, particularly capacitors, underscores the importance of their ongoing development. While PZT has been the material of choice for such applications, the environmental and health risks associated with lead have necessitated the development of lead-free alternatives. Although BNT has emerged as a promising lead-free material, its piezoelectric coefficient remains inferior to that of PZT but superior to PVDF. To develop a flexible film with higher efficiency and reduced lead content, this study explores the fabrication of PVDF composites with PZT, BNT, and a combination of PZT-BNT, followed by a comparative analysis. The primary motivation behind this research is the incorporation of external fillers (PZT and BNT) into the PVDF matrix, with the expectation of enhancing the functional properties of the matrix while stabilizing the polymer phase. This stabilization is crucial for improving the physical properties of PVDF-based piezoceramic composites.

In this work, we investigate the structural properties of PVDF, PVDF/PZT (PP), PVDF/BNT (BP), and PVDF/ BNT/PZT (BPP) composites with a polymer-to-ceramic weight ratio of 10:1. Additionally, we report on the enhancement of dielectric and ferroelectric properties in PVDF polymer matrices with piezoceramic composites. This systematic investigation aims to advance the performance and capabilities of capacitors in electronic applications, contributing to the development of more efficient and environmentally friendly materials.

2 Experimental procedure

For this study we opted Wet chemical methods for synthesis of PZT and BNT. The PZT have been synthesized by hydrothermal route while for BNT we used hydrothermal route followed by combustion method.

The precursors chosen for PZT synthesis were, lead (II) acetate trihydrate, Pb(CH₃COO)₂.3H₂O (Merck>99), titanium iso-propoxide, Ti(OiPr)₄ (Across, 98%) and zirconium propoxide, Zr(OPr)₄ (Aldrich, 70 wt% in 1-propanol) and KOH used as mineralizer while propan-2-ol has used as a solvent [25]. While for BNT Bismuth nitrate (Aldrich, 98%), sodium nitrate (Merck, 99%), titanium iso-propoxide, Ti(OiPr)₄ (Across, 98%), were used as precursors while nitric acid has been taken as a solvent and citric acid has been taken as a fuel. Liquor ammonia have been used to adjust the pH of the solution to 6 (optimize conditions) [26]. The detail procedure is mentioned in our earlier published report. To get the crystalline structure we calcined the as synthesized powered of PZT at 850°C for 3 h whereas the calcination temperature of BNT was taken as 700°C for 3 h. PVDF and composite thin films were fabricated by the solution casting method. The appropriate amount of PVDF was mixed with DMAc (Dimethylacetamide) (1:10 ratio) in a beaker and stirred at 60°C. After forming a homogeneous solution, the solution was poured into a petri dish to make a film. In order to make ceramic polymer composites, PZT, BNT, and PZT-BNT were mixed with DMAc in different beakers and stirred at 60°C, followed by ultrasonification. The ceramic powder to PVDF ratio was taken as 1:10 (vol), in PZT-BNT-PVDF the ratio was taken 0.5:0.5:10. After mixing the solution with the PVDF solution, the final solution was kept at 60°C for stirring until it became homogeneous. After that, the solution was poured into a petri dish and dried overnight in a vacuum oven set to 60°C. Figure 1

represents the Flowchart for the preparation of pure polymer, ceramic and polymer composite films. In this study we made four thin films PVDF pure, PZT-PVDF (PP), BNT-PVDF (BP) and PZT-BNT-PVDF (BPP) and compared its properties with bulk PZT and BNT.

Structural confirmation of calcined PZT (bulk), BNT (bulk), PVDF, PP, BP, and BPP thin films was carried out by X-ray diffractometry Philips PW 1710 equipped with a copper target (CuK_a \approx 1.5406Å) in the scanning range 10-90°. Fourier Transform Infrared spectroscopy (FTIR, Bruker Alpha) was used to observe the functional group in the wavenumber range 400 cm⁻¹ to 4500 cm⁻¹. The measurements of dielectric constant were carried out using computer-controlled dielectric measurement system consists of an LCR-meter (Wayne *Kerr* 4100), a temperature chamber, and a computer system. Electric field dependent polarization (P-E curve) studies were performed using the MARINE PE LOOP Tracer system. A scanning electron microscope (JEOL: JSM-6380 Analytical SEM) fitted with an electronic probe analyzer system (Accelerating voltage 5 kV) was used to study the surface morphology of pristine PVDF PP, BP and BPP film.

3 Results and discussions

3.1 Structural study



Fig. 1 Synthesis method of PVDF-BNT/PZT/BNT-PZT

The crystalline structure of PVDF and changes in the phases of PVDF with different piezoceramic filler composition



Fig. 2 (a) X-ray diffraction of pure-PZT, BNT, PVDF and nano films of different composite PP, BP, BPP (b) X-ray diffraction between 17° to 24° of Pristine PVDF and PVDF piezoceramics (c) Changes in the relative intensity of β - phase peak of PVDF at 20.22 with different piezoceramic composites

were revealed by X-ray diffraction pattern shown in Fig. 2. The X-ray pattern of PZT and BNT shows the crystalline phases with tetragonal and rhombohedral structure respectively without formation of pronounced impurity phase. The diffraction peak of the PZT and BNT were indexed with the space group P4mm and R3c respectively using JCPDS card number 33-0784 and 36-0340 respectively. The obtained XRD data were refined by using the Rietveld refinement method with the Fullprof software. The Rietveld refinement as shown in Fig. 3 clearly reveals the good agreement between the experimental and observed data with a goodness of fit parameter $\gamma = 1.46 \& 1.68$ for PZT & BNT respectively. However, high chi value and the zigzag blue line suggest that further refinement is needed. From Fig. 2(a) the XRD pattern of pristine PVDF shows the predominant characteristics peaks of α and β two crystalline phase of PVDF were clearly obtained. The broad XRD peaks of pristine PVDF shows the semi-crystalline nature of the polymer matrix.

The X-ray diffraction of PP, BP, and BPP shows that ceramic was well mixed in the polymer matrix. It shows the combination of α and β -phases of polymer and tetragonal phase of ceramic in PVDF-PZT composites. The α and β -phases of polymer and rhombohedral phase of BNT ceramic in BP composites and the β -phases of PVDF/tetragonal phase of PZT/rhombohedral phase of BPP composites.

The XRD pattern of all composites shows decrease in intensity of α -phase and increase intensity of β -phase in PVDF matrix with ceramic addition. The low angle measurement between the 17° to 24° versus normalized relative intensity as shown in Fig. 2(b). respectively. From the graph it is observed that, the intensity of the characteristic peaks at 17.2° representing the β -phase enhance with piezoceramic fillers in PVDF. The changes in the intensity are attributed to the piezoceramic addition in a polymer matrix led to the creation of specific electrostatic interaction near the polymer ceramic interface which is responsible for the nucleation of β -phase. As it is also reported that introduction of nucleating agent, such as ceramic nanoparticles, which promote the polar phases due to electrostatic interaction between the filler surface and the polymer chain [27, 28]. It is observed that the intensity is maximum for tri-composite BPP and minimum for bi-composite PP composites.

3.2 Fourier transform inferred spectroscopy (FTIR)

FTIR is used to provide the quantitative information about the PVDF and PVDF-piezoceramics composites structure allowing distinguishing and quantifying the different crystalline forms as well as the interaction of piezoceramics with polymer matrix. The Fig. 4(a) shows the FTIR spectrum of pristine PVDT, PP, BP, and BPP composite ceramic in the wavenumber range 500–4000 cm⁻¹. From the Figure the band at ~766 (CH₂ rocking vibration) and ~840 cm⁻¹(CF₃ stretching vibration) corresponding to α and β phase of PVDF respectively were found in all spectra with varying transmission intensity [29]. Figure 4(b) shows the variation of the relative fraction of the β -phase with nanocomposites fillers in the wave number range 600 to 1200 cm⁻¹. A strong absorption band observed around 618 & 645 cm⁻¹ is attributed to the Ti-O octahedra of the



Fig. 3 Rietveld analysis of BNT and PZT filler



Fig. 4 (a) FTIR of PZT, BNT, PVDF, PP, BP, BPP, (b) FTIR 1400–600 cm⁻¹ (c) FTIR spectroscopy within the 3100–2900 cm⁻¹ range and (d) Asymmetric shift in PVDF, PP, PB and BPP samples

PZT and BNT ceramic system respectively. The intensified and broadening of 840 cm⁻¹ band with the piezoceramic filler addition is the characteristics of both β- and γ-phases of PVDF. The appearance of band at 840 cm⁻¹ indicate that the nano-ceramic successfully nucleate the β-phase of the polymer [30]. Therefore, the FTIR results reveal that BP filler can control the crystalline polymorph in PVDF and subsequently improves the electroactive phase content.

To investigate the development of the electroactive phase in the polymer nanocomposites we conducted FTIR spectroscopy within the 3100–2900 cm⁻¹ range, and the corresponding spectra are depicted in Fig. 4(b) This spectral region predominantly originates from the asymmetric stretching vibration (ν_{as}) and symmetric stretching

vibration (ν_s) of the (-CH₂-) functional group. Notably these vibrational bands remain unalloyed with any other vibrational modes. The examination of this spectral band proves highly advantageous for assessing potential interfacial interaction between the CH₂ dipoles and the nanoceramics [31]. The position of the asymmetric stretching vibration (ν_{as}) and symmetric stretching vibration (ν_s) bands associated with (-CH₂) moieties exhibit a discernible shift towards higher energies ($\overline{\nu}$) in the polymer nanocomposites in contrast to the pristine PVDF reference ($\overline{\nu}$). This illustrated by the arrows in Figure, demonstrating the presence of interfacial interaction between PVDF and BP piezoceramics.



Fig. 5 The molecular structure of (a) α -phase and (b) β -phase of PVDF. (c) The representation of electrostatic interaction on the Polymer-Ceramic

The observed shifts in the mentioned vibrational characteristics exhibit a progressive increase with the maximum for BPP ceramics. The lower shift for PZT may be attributed to the percolation effect of PZT ceramics with PP loading within PVDF matrix. This result shows the same behaviours of relative intensity of XRD with β -phase as shown in Fig. 4(d). This pattern suggests a direct correlation between the formation of the electroactive phase in PVDF and the interfacial interaction of the CH₂ dipoles with the surface charges of PZT, BNT, BP nano-ceramics. The schematic Fig. 4(b, c) represent of semi-polar β -phase formation attributed to the interaction between PVDF and piezoceramics surface leads to the attraction of certain segments of the PVDF chain, while others are repelled ultimately contributing to the formation of the β -phase (see Fig. 5).

3.3 Scanning electron microscope

Figure 6 shows the Scanning Electron Microscopy (SEM) of PVDF, PP, BP, and BPP composites involves using a focused electron beam to scan the surface of the material. In the context of PVDF and PVDF-piezoceramics composites, SEM can reveal information about distribution of piezoceramics particles within the PVDF matrix and the overall structure of the material, aiding in understanding its mechanical and physical properties. It provides insights into the composite's surface features, such as particle agglomeration, size distribution, and any potential interfaces between PVDF and the piezoceramic materials. The microstructural analysis indicates that in the PVDF-piezoceramic composites membrane, the PZT, BNT, BP piezoceramics are well-dispersed without any agglomeration, and the solution casting method proves effective.

3.4 Dielectric property

A dielectric investigation of the polymer nanoceramic film was conducted varying the end piezoceramics within the PVDF polymer matrix. The frequency dependent behaviour of dielectric constant and loss tangent are depicted in Fig. 7 (a) respectively. Notably the dielectric constant of the piezoceramics films exhibits on overall decreases across the entire frequency range (20 Hz-200 kHz) in comparison to the pristine PVDF-film.

Furthermore, it is noteworthy that, the dielectric constant of the synthesized samples decreases rapidly with increasing frequencies and becomes nearly constant at higher frequencies, which can be attributed



Fig. 6 SEM of (a)PVDF(e), (b) PP(f), (c) BP(g), and (d) BPP(h)

to space-charge polarization and the material's inhomogeneous structure. The composites exhibit a significantly higher dielectric constant compared to pure PVDF, though still lower than BP ceramic. At low ceramic filler content, the dielectric constant is primarily determined by the polymer matrix, which has low permittivity. However, as the filler content increases, enhanced connectivity among the filler particles leads to stronger dipole-dipole interactions, resulting in a higher dielectric constant. The relative dielectric constant and loss factor are graphically represented against the piezo nanoceramic within the PVDF matrix at 1 kHz frequencies [Fig. 7. (b)]. Notably in the BPP the dielectric constant achieves a value of ~443 with remarkably loss. Furthermore, it has been obtained that the dielectric constant of polymer nanoceramic films in the higher frequency range 1 kHz is significantly higher compared to pristine PVDF. This observation underscores the potential applicability of these films as energy storage material across a wide frequency spectrum.



Fig. 8 (a) P-E of PVDF, PP, BP, BPP (b) Saturation polarization, Remanent polarization and coercivity (KV/cm of PVDF, PP, BP, **BPP** composites

Fig. 7 Dielectric constant and

PP at different frequencies

3.5 Ferroelectric property

The graph (Fig. 8) shows hysteresis loops of polarization versus electric field for the pristine PVDF, BNT, PZT, and PP, BP, PP, BPP polymer piezoceramic composite film at frequency 10 kHz. Hysteresis refers to the lag in response exhibited by a system. In this context, it likely refers to the delayed response of polarization to changes in the electric field. Polarizing PVDF typically requires a high electric field of approximately 2 MV/cm, which may explain the unsaturated hysteresis loops observed in pure PVDF and its composites [32, 33]. The addition of PZT, BNT, or their combination in the composites enhances remnant polarization and coercivity. Although the polarization values in this study are lower than those found in pure ferroelectric materials, these measurements highlight the ferroelectriclike behavior of the composites, particularly due to the electroactive β -phase in PVDF. The electric-field-induced dipoles in the polymer contribute to polarization; however, at lower BP concentrations, smaller crystallite sizes increase macrostrain, leading to more grain boundaries and polymer chain interfaces. These interfaces initially polarize the polymer chains and subsequently polarize the BP particles. The reduced particle size results in an increased number of grain boundaries and domains, with the domains orienting in various directions relative to the electric field, ultimately causing a lower polarization response. Additionally, in the composite structure, ferroelectric particles embedded in the

polymer matrix form an equilibrium domain configuration to minimize electrostatic and elastostatic energies. This configuration eliminates charge accumulation at particle interfaces, reducing the internal depolarization field and leading to "head-to-tail" closed-circuit polarization domains, as previously reported. While these local polarization domains can respond to an external electric field, the resulting interfacial charges amplify the depolarization field and electrostatic energy, thereby weakening the overall polarization response [34–36]. From the graph it is observed that as the electric field increases, the polarization of the material increases and reaches a maximum value (P_{max}). When the electric field decreases, the polarization also decreases, but there is still some residual polarization at zero electric field, known as remnant polarization (P_r). The presence of remnant polarization at zero fields indicates that the material retains a certain level of polarization even when the electric field is removed. The large value of remnant polarization makes the material suitable for memory applications. The remnant polarization increases with an increase in the concentration of piezoceramic in the polymer matrix. This could be attributed to the increase in polar domains representing the β -phase in the sample, as observed by XRD and FTIR spectroscopy. Also, the lattice strain due to the stretching and bending of chemical bonds is identified as a factor contributing to the enhancement of ferroelectric properties in the PVDF/piezoceramic composite films [37, 38]. Figure 8 (b) provides a visual representation of the relationship between coercive field, remnant polarization, and the applied electric field for different PVDF piezoceramics composites, highlighting the optimal composite BPP for minimum remnant polarization and coercivity with maximum saturation polarization. This information is valuable for understanding and optimizing the material for specific applications in ferroelectric devices.

4 Conclusion

In this study, we developed a straightforward and effective method to synthesize β -PVDF films by incorporating PZT and BNT piezoceramics. Our systematic investigation used XRD and FTIR analyses to explore the impact of these nanostructures on the nucleation and enhancement of the polar β -phase of PVDF, which is critical for improved ferroelectric performance. XRD revealed that the presence of PVD//BNT (BP) particles promoted β -phase crystallization, while FTIR demonstrated their role in inducing a self-poling process. The inherent piezoelectricity of BP generated surface polarization, which interacted with the dipoles of PVDF chains, aligning them into the polar β -phase. This synergistic interaction significantly enhanced the ferroelectric response of the composite material. Our findings offer valuable insights into the structural dynamics of PVDF/ PZT/BNT (BPP) composites and provide a foundation for designing advanced materials with superior capacitive properties and related applications.

Author contributions Writing - Original Draft: SKS Synthesis and Characterization: SA, SS Data Compilation: TQ& ND Conceptualization (Origin of Work): SA Writing - Review & Editing: SA.

Data availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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