Designing and synthesis of a polymer matrix piezoelectric composite for energy harvesting

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Abstract. Now a day, a large variety of electronic and network devices require small yet steady power supply for operation. Traditionally, these devices are battery operated and the batteries are periodically charged for continuous operation. Often, the devices are so located that supply of power to recharge the batteries becomes challenging. Electrical energy harvesting by means of principle of piezoelectricity could be a viable solution to the above problem by means of providing a permanent power source. In this regard, piezoelectric lead zirconium titanate (PZT) was found to be a potential material. However, poor mechanical properties (brittleness) of bulk ceramic materials have been a concern for energy harvesting by means of mechanical motion (footsteps). In the present work, \( Pb(Zr_{0.52}Ti_{0.48})_1-xNb_xO_3 \) at \( x=0.05 \) was prepared by conventional solid state synthesis route. XRD and SEM analyses were performed for structural characterization. PZT powders were found to be in single phase with tetragonal symmetry without any trace of a second phase. To render the required mechanical properties (flexibility), in the present work, we designed a polymer matrix ceramic composite without much compromising the piezoelectric properties. We prepared composite thick films of lead zirconium titanate (PZT) ceramic in poly vinylidene fluoride (PVDF) polymer matrix with varied composition of PZT from 10-50 vol %. The study of surface morphology by scanning electron microscope (SEM) shows good degree of dispersion of PZT in PVDF matrix. Ferroelectric characteristics of the composite films were studied by measuring the polarization-electric field hysteresis loops. Generated output voltage and current from the composite films are found to be approximately 0.35 volt and 4 nA, respectively.

1. Introduction

Over the past decades, piezoelectric materials have been considered due to their favorable physical properties such as high dielectric constant, low dielectric loss and high energy storage density which have been considered for possible energy harvesting applications such as transducers, actuators, capacitors, energy storage devices.[1] Nevertheless, the ceramic piezoelectric materials are brittle, often with low dielectric breakdown strength and thus poses difficulties in practical applications though they are associated with high dielectric constant which can provide good energy conversion efficiency. [2] On the other hand, polymer piezoelectrics owns high breakdown strength, good flexibility and mechanical strength as well as they are easy to process at low temperature, albeit having very low dielectric constant.[3]
Thus, to get optimum properties, a blend of properties of both piezoelectric ceramic and the polymer is needed to make a composite where polymer act as the matrix and ceramic particle as the reinforcement. Currently, polymer matrix ceramic composites are being used in a number of applications such as embedded capacitors, sensors and gate dielectrics.[1, 2]

A Piezoelectric lead zirconium titanate (PZT) was found to be a potential material owing to its impressive piezo as well as ferroelectric properties.[4] Recently, piezoelectric polymer, polyvinylidene fluoride (PVDF) has also been paid increased attention due to its high breakdown strength, easy processing, good thermal stability and most importantly nontoxic in nature.[3] PVDF is a semi-crystalline polymer having different phases (α,β,γ,δ) depending on the process parameter such as solvent, melt temperature, annealing temperature, method of casting, starching of the film and pressure on film.[5] Among the four phases β phase is known for its ferroelectric nature.[6-8] Table 1 depicts the important physical properties of PVDF.

Table 1  The physical Properties of PVDF [reference]

| PVDF (Sigma Aldrich) | Density (gm/ml) | Melting point (°C) | Crystallizing (°C) | Glass transition (°C) | Thermal stability (°C) |
|----------------------|-----------------|--------------------|-------------------|----------------------|-----------------------|
| CAS 79-9 Number 24937-79-9 | 1.74 | 171 | 138 | -38 | >400 |

2. Experimental Details

2.1 Synthesis of PZT Powder

The starting materials for making lead zirconium titanate (PZT) with composition Pb(Zr0.52Ti0.48)1 – xNbx03 where x=0.05 are PbO (sigma Aldrich, >99.0% purity, granular form), ZrO2 (sigma Aldrich,99% purity,5µm powered), TiO2 (Himedia,99% purity, powered) and Nb2O5 (sigma Aldrich,>99.9% purity, -325 mesh powered). This composition is near to the morphotropic phase boundary (MPB) to achieve better electromechanical properties due to coexistence of ferroelectric tetragonal PbTiO3 (Tc=490°C) and ferroelectric rhombohedral PbZrO3 (Tc=230°C) at room temperature [9, 10] precursors with stoichiometric ratio were taken to achieve the aimed composition with 2% extra PbO to compensate for vaporized lead during calcinations and sintering at high temperature due to its high partial vapor pressure.[10] Precursors were mixed in a ball mill with isopropyl alcohol with zircon balls (ZrO2) as grinding media for 24 Hrs. to achieve homogenization throughout the bulk sample and after that dried in an oven until all alcohol is removed from the prepared sample at a temperature around 80°C.[9] Calcination was done at 900°C for 2 Hrs. The conditions of temperature rate and soaking time are 5°C/min and 2 Hrs. respectively. Calcined powder was subsequently ground for 48 Hrs. in isopropyl alcohol with zirconia ball (ZrO2) as grinding media to break down the agglomerated particles. The dried powdered were mixed with polyvinyl alcohol as binder solution for making green pellet of 10 mm diameter in a hydraulic pressure about 12 kg/cm². Afterwards sintering was done in a closed alumina crucible with PZT powdered bed to compensate PbO vapor pressure at high temperature around 1250°C for 4 Hrs.[11-13]
2.2 Synthesis of PZT-PVDF Composite

For making thin film composite, the materials are Poly vinylidene fluoride (PVDF) (Sigma Aldrich) and sintered lead zirconium titanate (PZT). Initially PZT powder of 600 nm size was stirred around 30 minutes at 80°C in water and ethanol in order to achieve OH order on the surface of PZT powder.[2] Surfactant, Span 80 (CDH, chemical name Sorbitane monoooleate) is added to the OH order PZT powder and stirred for 10Hrs at room temperature. After that, solvent acetone was removed from it PVDF and DMF (dimethyl formamide) solution was added. PVDF was mixed with dimethyl formamide (DMF) and stirred until a transparent solution is achieved. When the transparent solution is achieved that shows all PVDF is well mixed with the solvent, then add the pre-prepared PZT powered in it. Mixed and stirred at around 70°C for 30 minutes. After that it is probe-sonicated for 1 minute. The sonicated solution contains air bubble, which was removed in an evacuated desiccator for 10 minutes. Next, the solution was poured it into a petri dish and heated to around 110°C for 30 min to remove all residual solvent present. The process is called solvent casting method.[2]. Different volume fraction from 10 to 50% PZT were made successfully by the above described process.

2.3 Characterization

Room temperature XRD was performed on both bulk ceramic and PZT-PVDF composites of different composition by a Bruker D8 Advanced A25 X-Ray diffractometer using Cu Kα radiation of wavelength $\lambda = 1.5418\text{Å}$. This was done over a wide range of 20 ($20^\circ \leq 2\theta \leq 80^\circ$). The morphology study were examined with an environmental scanning electron microscope (EVSEM). Silver electrode was applied on both side of the sample to study the V-I characteristics and ferroelectric behaviour by using Kiethly 6517B high resistance electrometer and Radiant ferroelectric tester.

3. Results and discussion

3.1 XRD and SEM Study of Both PZT and PZT-PVDF Composite

Powder XRD patterns of PZT powder is depicted in Fig. 1 which was matched with JCPDS card no 00-050-0346. It was observed that pure tetragonal phase of PZT without any trace of any secondary phase was formed upon sintering.

![Fig. 1 XRD patterns of PZT powder](image-url)
Powder diffraction patterns of PZT-PVDF composite films having different PZT contents of 10-50 vol. % were studied as shown in Fig. 2. Phase evolution of PVDF depends on processing conditions. The first peak at 20 corresponding to 18.5 was allotted to α-phase, at 20 = 20 corresponding to β-phase and broad peak corresponding to γ-phase.[2] With the increase in the PZT content into the PVDF matrix, the diffraction peaks of PVDF gradually reduced in intensity and PZT peaks became sharper. No other peaks are visible other than the matrix and reinforcement suggesting lack of significant phase evolution due to PZT-PVDF interaction. After 40 volume fraction of PZT, PVDF peaks are completely vanished because of the strong and intense diffraction peaks of the PZT ceramic particle overshadowing the PVDF peaks.

![XRD pattern of PZT-PVDF composite thin film](image)

Fig. 2 XRD pattern of PZT-PVDF composite thin film

Fig. 3(a) shows the SEM images of pure PVDF while Fig. 3(b) and 3(c) show SEM images PZT-PVDF composites with two different volume fractions of PZT. Fig. 3(d) shows a photograph of as processed PZT-PVDF composite. Fig. 3(b) and (c) clearly indicate that PZT powders are well compatible in the matrix phase. When volume fraction increases particles are being denser in the matrix. Thus, from the above morphology study it could be concluded that PZT particles are uniformly dispersed throughout the matrix phase. Fig. 3(d) depicts a 50% PZT composite film with good flexibility.

### 3.2 Electrical measurements

Fig. 4 depicts the polarization-electric field (P-E) hysteresis loops for the 30% and 050% PZT-PVDF composites. While a saturated hysteresis loop of the composite could not be found in our study, the shape of the loops suggests ferroelectric nature where in applied electric field induces rearranged domains towards the direction of electric field. The non-linear behaviour
clearly indicates that different rates at which domain walls and electric field changes which causes a phase difference between electric field and polarisation.[2] Table 2 shows a summary of P-E study for different composition of PZT-PVDF composite.

Fig. 3 (a) SEM images of pure PVDF, (b) 30% PZT composite, (c) 50% PZT composite and (d) composite film.

Fig. 4 Polarization Electric field hysteresis loop (PE Loop) of 30 vol. % and 50 vol. %.
Table 2 Remnant polarization and Coercive Field of different volume fraction composite.

| Vol. Fraction | Remnant Polarization (Pr) [µC/cm²] | Coercive Field (Ec) [KV/cm] |
|---------------|-----------------------------------|-----------------------------|
| 0.1           | 0.01                              | 0.3                         |
| 0.2           | 0.02                              | 0.4                         |
| 0.3           | 0.26                              | 0.5                         |
| 0.4           | 0.03                              | 0.4                         |
| 0.5           | 0.24                              | 0.7                         |

V-I characteristics depicts that maximum voltage and current output generated by the 0.5 PZT volume fraction. Maximum voltage was d 0.35 V and current of ~4 nA. Fig. 5 shows the data for a 50 vol. % composites, wherein output current profile is shown on left panel and right panel depicts bout the output voltage.

![V-I Characteristics](image)

Fig. 5 depicts the V-I characteristics of 0.5 PZT volume fraction composite.

4. Conclusion

Solid state synthesis process was used successfully to produce PZT powder. Solvent casting method produced well dispersed PZT-PVDF thick film composite. XRD and SEM analysis showed pure single phase of PZT was synthesized in our study which was uniformly dispersed in PVDF matrix. P-E loops indicate the signature of ferroelectric character and remnant polarization of about 0.24 µC/cm² for 50% PZT- PVDF film. Maximum output voltage of 0.35V and current of 4nA were obtained.
5. References

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