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Preparation and Characterization of flexible PVDF based polymer film for energy harvesting applications

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Abstract

In this work, Zirconium oxide based PVDF nanocomposite films are fabricated by using solution casting method with varying zirconium oxide fractions (0, 1, 5 wt%). The crystalline structure of prepared nanocomposite films is studied by X-Ray diffraction (X-RD) and FTIR methods. To check surface morphology, SEM study is carried out. From this study, it is observed that zirconium filler is well dispersed in the PVDF matrix. The piezoelectric performance of the prepared film is analyzed. From this analysis, maximum output voltage of 0.61V is observed during mechanically finger tapping and releasing condition for 5% of zirconium filler content film.

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Keywords: PVDF; Crystalline structure; Morphology; Solution casting;

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1. Introduction

To overcome the conventional energy demands, development of new technology is essential. Although, there are varieties of energy sources such as solar energy, thermal energy, chemical energy, and mechanical energy which are present abundant in the surrounding environment [1]. Mechanical energy harvesting utilizes the variety of mechanical energies such as vibrations originated from any part of machine movement or movements of parts of human body, fluid flow, movements of air etc. For portable and self -powered electronic devices, energy conversion

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by using piezoelectric materials is a promising technique [2]. Ceramic based piezoelectric material such as lead zirconate titanate (PZT), barium titanate (BaTiO3) and zinc stannate were used for fabrication of piezoelectric nanogenerators. However, ceramic-based materials have high piezoelectric coefficient, but those are toxic, and hazardous to human beings. These materials are also brittle and hence difficult to integrate into the complex surfaces. Therefore to overcome these limitations, researchers are working on polymer- ceramic based composite materials which could result in more flexible and high piezoelectric coefficient. Piezoelectric energy harvesters are getting interest for their considerable potential applications in microelectronic devices where small amount of power requirement [3,4].

Recently, self- powered piezoelectric nanogenerators made from polymer films are drawing attention because of their unique electroactive properties. Among piezoelectric materials, Poly (vinylidene fluoride) (PVDF) and its copolymers are most promising, known for its highest dielectric constant and electroactive phases such as piezoelectric, pyroelectric and ferroelectric effects.

PVDF is good semi-crystalline piezoelectric polymer, which could be used as smart material such as sensor, actuator or energy harvesting device. PVDF has five crystalline phases depending on their chain confirmation as α, β, γ, δ, and ε. Among these, most investigated phases are α, β, γ. Because of the presence of Trans gauche$^+$ Trans gauche$^-$ (TGTG) confurmation, the α phase is the most stable phase. The polar β phase exhibits superior piezoelectric properties, due to all fluoride and hydrogen atoms being perpendicular to the carbon backbone. The polar β phase has all trans-planar zigzag (TTT) confirmation. Also, it has large polarization sensitivity [5]. To obtain β phase, different ways have been identified, such as mechanical stretching, and electrical poling, annealing at high temperature, and drawing. β phase is characterized by stabilization in alignment of CH_2-/CF_2- dipoles [6].

However, the problems associated with these methods are that quantity of films and mass production in the industry are not up to the mark for device fabrication. So another approach, to enhance the piezoelectric property of PVDF is incorporation of filler or nanomaterial's such as graphene oxide, titanium dioxide, nanoclay and MoS_2into the PVDF which acts as nucleating agent and improves the β phase and piezoelectric performance [7]. Various researchers are fabricated nanogenerators by using only PVDF, PVDF co-polymers and adding filler in it. Singh et al. [8] prepared nanocomposite film synthesized zinc oxide nanorods as filler in PVDF matrix and fabricated nanogenerators and obtained maximum output voltage of 1.81V and 0.21 µW/cm2 power density. PVDF-TrFE based spin coated films are casted by Nunes-Pereira et al. [4] by varying the ceramic based $BaTiO_3$ material and obtained maximum output voltage of 0.5V.

In this work, a flexible, durable, lightweight PVDF/ Zirconium oxide nanocomposite film was synthesized for the first time by using a solution casting method. β phase in PVDF films is enhanced by adding zirconium oxide as filler without any mechanical stretching or electrical poling. Further, investigations on crystallinity, polymorphism, morphology and piezoelectric performance of PVDF/ZrO_2 nanocomposite are carried out.

2. Experimental Details

2.1 Materials

The material used in this experiment was commercially available PVDF with molecular weight 180000, density 1.77g/cc, melting point temperature 155-160 ^{0}C. The material was purchased from M/s Arkema, France. Solvent N, N-dimethyl formamide (DMF) with 97% purity were purchased from Merck India Ltd. The filler used was Zirconium oxide. All these materials were used in their original condition.

2.2 Sample preparation

For the preparation of PVDF/Zirconium oxide solution, 1.2g of PVDF material was dissolved in 10ml of DMF by stirring for 2 hours at room temperature. At the same time, Zirconium oxide powder was weighed corresponding to 0, 1, 5 wt% and dissolved separately in DMF by ultrasonication for 2 hours. In the next step, the dissolved filler 1wt% and 5wt% were added to the PVDF solution and stirred for 4 hours at 500rpm. The homogeneous mixture solution was casted on a petri dish and kept in an oven for 3h at 75^{0}C to get flexible nanocomposite film. Figure 1 shows the flowchart for preparation of the flexible nanocomposite film and Figure 2(a) shows the prepared film.

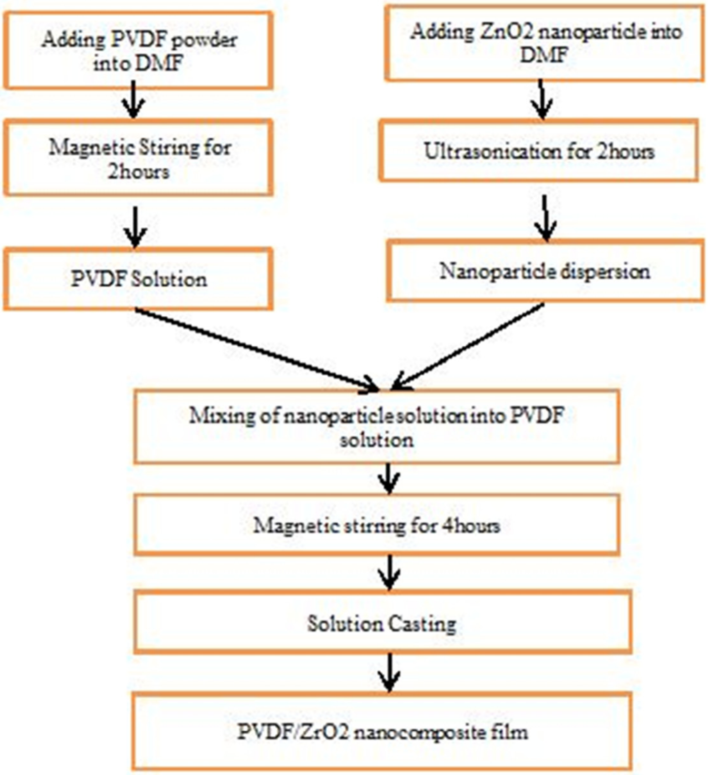

Fig. 1. Flowchart for synthesis of nanocomposite film

3. Characterization Methods

The PVDF composite thin films were characterized for % crystallinity, β-phase content, and surface morphology. The Morphology of the prepared samples was analyzed by Scanning Electron Microscopy (JEOL, JSM 6380, Japan). Fourier transformed infrared (FTIR) spectroscopy was used to provide information about PVDF structure and to distinguish between the different crystalline forms of PVDF. Analysis was carried out in the range of 1200-650 cm^{-1} with a resolution of 1 cm^{-1}. X-Ray Diffraction (XRD) was performed on prepared nanocomposite film by using Bruker D-8, advanced diffractometer instrument operated at 40kV and 40mA with Cu target Kα radiation with wavelength (λ) 1.54 Å. All the data were collected from 2θ ($20^o \leq 2\theta \leq 35^o$).

4. Results and Discussion

4.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was performed in order to evaluate the surface morphology of the composite films. This study gives information about pores, irregularity present in the surface and dispersion of the nanofiller in the PVDF matrix. Fig 2 (b) shows the morphology of the pure PVDF film, where the surface is smooth and absence of pores and irregularity. Fig 2(c) shows 1Wt% Zro2/PVDF film, where the surface is a little bit altered due to the presence of filler and Fig 2(d) shows 5% ZrO2/PVDF film, where the rough surface and pores are clearly visible.

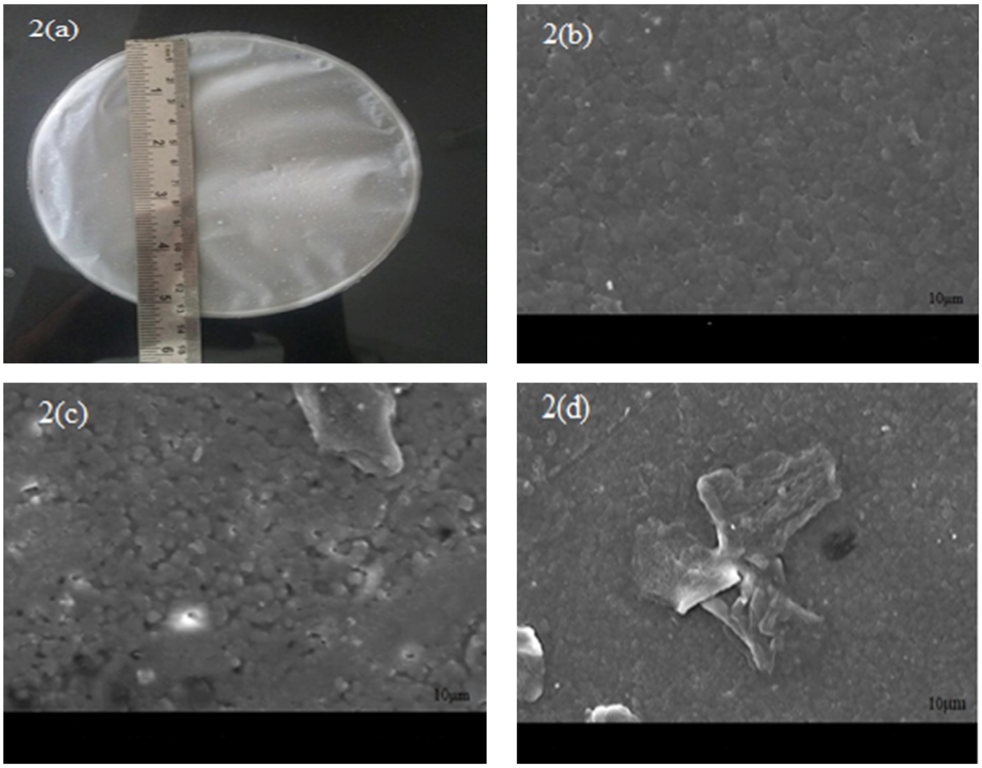

Fig. 1.SEM images of using a solution casting method, (a) Prepared flexible film (b) pure PVDF (c) PVDF/ZrO_2(1%) and (d) PVDF/ZrO_2(5%)

4.2 FTIR Analysis

Effect of zirconium oxide on the polymorphism of PVDF was investigated using FTIR spectroscopy. FTIR spectra of the composite films are show in Fig 3. FTIR spectra of pure PVDF and PVDF/ ZrO_2 composites with different weight percentages of Zirconia in the spectral range of 650 -1500 cm^{-1} was carried out, the characteristic vibrational peaks at 675, 763, and 820 are observed and corresponds to α- phase [9]. Were as peaks observed at 833, 872, 1162 and 1251 cm^{-1} corresponds to β phase [10, 11]. The additional peak at 1233 is observed because of nucleation of β- phase and semi polar γ-phase, respectively. An increase in β- phase is observed as zirconium content increased. A few vibrational frequencies below 800 cm^{-1} disappeared. This shows interaction between PVDF and Zirconia during formation of PVDF-ZrO2 nano-composite. PVDF's original structure is changed and some groups in PVDF are fixed in zirconia. As the concentration of zirconia increases, some vibrational bands of PVDF gradually decrease.

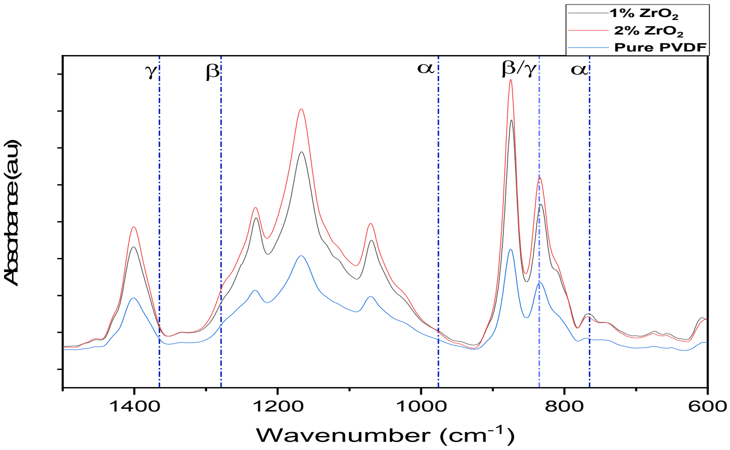

Fig 3. FTIR spectra of the composite film showing different phases.

4.3 X-ray diffraction analysis

The X-ray diffraction patterns of only 5 wt% zirconium in PVDF composite is shown in Fig 4. From FTIR study, it is concluded that β – phase in 5wt% zirconium showed high β – phase, hence X-RD is performed for 5wt% composite. Peaks observed at 17.7, 18.4, and 19.9 are characteristic of α-phase. Peaks at 17.7, 18.4, and 26.6 corresponding to (110), (020) and (110) planes of PVDF.

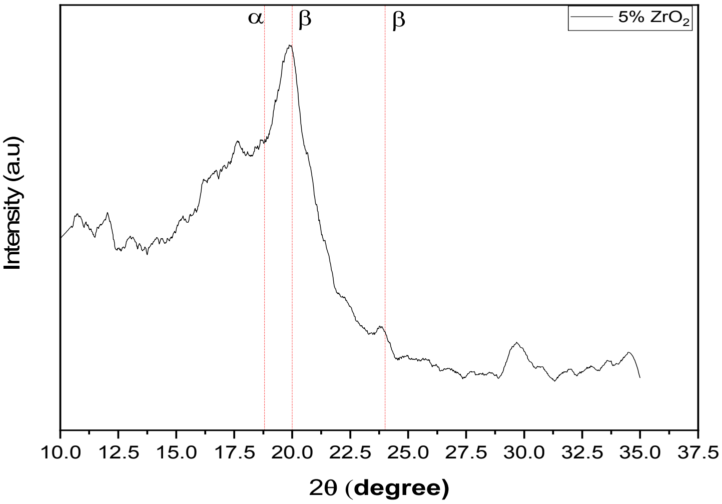

Fig 4. X-RD analysis of 5wt% ZrO_2/PVDF nanocomposite

The peak position corresponding to 21.6 and 23.3 could be indexed to β- phase of PVDF, respectively. The XRD Pattern of zirconia/PVDF film over 2θ ~ 10^0 -35^0 indexed, with increase in zirconia concentrations in PVDF matrix, we conclude that structure of zirconia remains un-affected upon blending with PVDF matrix.

4.4. Piezoelectric performance of the composite film

The piezoelectric performance of synthesized PVDF/ ZrO2 flexible composite films was subjected to micro energy harvesting studies. To demonstrate the application of synthesized PVDF/ ZrO2 composite films, we have fabricated nanogenerator by cutting the film into 2 × 2 cm^2 dimension. On the both side of the film copper paste was applied to act as electrodes, wires are connected to electrodes and whole system was laminated. The output voltage was recorded by simple finger tapping and releasing on the nanogenerator. The output voltage generated by 5 wt. % nanogenerators ware shown fig. 5. The pure PVDF flexible film generated an output voltage of 0.21 V. With increasing zirconia content in the PVDF matrix, the output voltage increases. For 5 wt% zirconia content the output voltage is 0.62V. This may be due to uniform attribution of zirconia, which increases the β- phase and improves the piezoelectric performance.

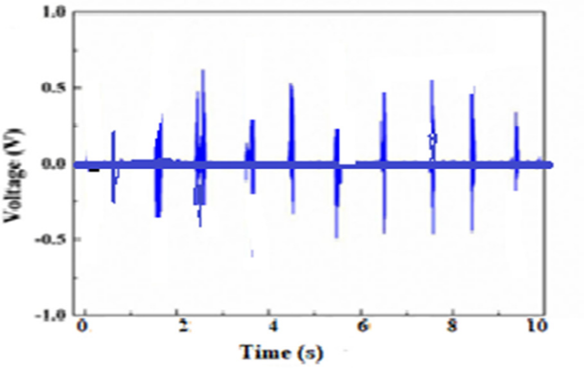

Fig 5. Piezoelectric performance of the composite film.

5 Conclusion

In summary, the PVDF/ZrO_2 nanocomposite films prepared by varying zirconium oxide percentage by using simple solution casting. The results of FTIR and X-RD studies confirmed the presence of β- phase. SEM revealed the dispersion of nanofiller in PVDF matrix. The addition of zirconium oxide, drastically enhanced the β- phase in PVDF. For 5%wt ZrO_2, the piezoelectric output voltage was maximum (0.52V). These results from our experimental investigations indicated that PVDF/ZrO_2 nanocomposite films could be suitable for energy harvesting applications such as self-powered nano devices.

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