Effect of Adding BaTiO3 to PVDF as Nano Generator

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Abstract. Piezoelectric nanogenerator based on a composite structure formed of Polyvinylidene Fluoride (PVDF) as the matrix and Barium Titanate BaTiO$_3$ nanospherical after dissolving them in a solvent of Dimethyl Sulfoxide DMSO/Acetone in (1/3 v/v) then spanning it’s homogeneous solution on Aluminum foil. structural and morphology analyses that of fabricated nanofibers characterized by X-ray diffraction, Scanning Electron Microscope and the electrical output of piezoelectric membrane devices was measured by using oscilloscope. The electrical output of different samples were measured for the pure powder PVDF and for composite PVDF & BaTiO$_3$. The highest PVDF composite piezoelectrically generated voltage for samples with BaTiO$_3$ (20%PVDF & 25% BT) wt. %, where improved to 6 V in general the addition of BT Nc increases the piezoelectric response of electrospun PVDFnanofibers.

Key word: Electrospinning; Nanofiber; Piezoelectric.

1. Introduction:

Piezoelectric materials are one of the greatest main materials used for harvesting energies and various studies have been performed on them. Usual piezoelectric materials, which are generally in the procedure of thin films, have low productivity in replying to offend mechanical powers. Semi-conductive nanowires, such as ZnO, InN, GaN, CdS and ZnS, are additional group of piezoelectric materials that require displayed the capability to produce mechanical energy as of body movements, acoustic/ultrasonic vibrations or hydraulic forces into electrical energy [1-12].

A number of approaches have been advanced to harvesting energy as of the environment, such as solar cells, thermoelectric cells, hydrogen fuel cells; and practical the PVDF for biomedical applications owed to its capability for transform thermal, mechanical, otherwise magnetic signals into electrical ones, as mechanical sensors, biosensors, besides actuators among others. Moreover the nanogenerator transforms mechanical energy into electric energy and is a unique energy harvest procedure since of the ubiquity of the mechanical energy [13-23].

Modification between the single nanofibers and nanofiber mats is electric potential that molded along the fiber and through the nanofiber layer thickness, respectively. Since PVDF is a polymorphic, semi-crystalline polymer which crystallizes into at least four crystallographic phases, namely the $\alpha$- $\beta$- $\gamma$- and $\delta$-phases, but most importantly the $\beta$- phase. Each phase of PVDF has a specific conformation, and it is possible to transform from one phase to the other [24-29].
To attain the required piezoelectric properties in PVDF great $\beta$ crystal must be produced. Typically, the former is achieved using mechanical stretching along by an electrical poling treatment. Here is no requisite of added poling treatment which applied for the method near field electrospun PVDF nanofibers. Therefore, the arbitrarily oriented electrospun nanofiber mats can be exactly applied to fabricate a piezoelectric power generator with no any additional poling treatment [23] [30-32].

However, produced nanofibers devices yet possesses low output productivity; several studies to develop the working of the PVDF nanofibers require effected in largely of which, the apply of nanoparticles such as, ZnO, and BaTiO$_3$ has controlled to this enhancement. As of piezoelectric properties, BaTiO$_3$ is unique of the possible option to adjusting occurrence of nanogenerators [33-36].

So a number of researches have been prepared on ceramics, especially their procedure as fillers for polymeric materials and envisaged that the size of the $\alpha$-phase spherules reduced with the adding of nanofillers. It is mostly estimated that the adding of nanofillers in PVDF produces the $\beta$-phase at the amount of the $\alpha$-phase; in this situation the microparticles did not produce the $\beta$-phase. This can happen owing to the bulk of the filler and the lack of defects. These assets show a main character in joining PVDF chains strongly to the particles in require to produce the $\beta$-phase [37-40].

BaTiO$_3$ is noble filler since it has a big surface area and various defects to advance $\beta$-phase creation. Therefor used in this paper to have better output although the addition of BaTiO$_3$ nanoparticles to the polymeric solutions might modify the best environments for the electrospinning procedure, by the adding of BaTiO$_3$ nanoparticles to polymer solution, were greatly dissolved in the polymer solution, although they created agglomerates at some times. The aim of this paper is to fabricate an uniform pure PVDF in tow percentages besides nanocomposite of (PVDF-BT) fibers in four percentages by applied four difference forces but in the same frequency for all samples.

2. Experimental Procedures:

Poly(vinylidene fluoride) (PVDF) powder (Mw=534,000), Dimethyl Sulfoxide (DMSO), Acetone and BaTiO$_3$ powder with diameter ≤ 100 nm in Cubic phase were purchased from Sigma-Aldrich with purity > 99. The solution was prepared by dissolving PVDF powder at percentages (12, 14, and 20 % wt.) in solvents mixtures of DMSO/Acetone solvent (1/3 v/v) under a magnetic stirrer for almost 2 h, then add the powder of BaTiO$_3$ with percentages (20 and 25%) respectively on 50 °C for around 2 h after that the homogeneous solution sonicated for 10 min by (Cycle 0/5with frequency 60 Hz).

Finally, white heterogeneous solution was established and putted in 6 ml syringe which was placed in a syringe pump to electrospinning the solution on a foil Aluminum at a distance (15 cm), with high voltage (18 kV) and rate flow between (0.1- 0.3ml/ h). to create homogeneous nanofiber mats at the same frequency (1.9231 Hz) illustrating of samples by various strictures and layers generated in this study is in Fig. 5.

3. Synthesis of PVDF nanofibers & nanocomposite samples:

Electrospinning of nanofibers was presented in a horizontal electrospinning operation (Pump: medifusion ms-2200 Company, Fig. 1). It consist of a syringe located horizontally through its needle, a precisely-controlled syringe pump. A cylindrical drum collector (outer diameter 4.3 cm) was wrapped with aluminum foil as the collector. A high voltage power supply able of 18 kV, and a grounded collector. When operating the high voltage, a fluid jet was ejected beginning the tip of the needle. Since the jet enhanced to a target, which was located at 15 cm from the syringe tip, the solvent evaporated and nanofibers were placid on an aluminum foil substrate. Mass flow rate of the solutions among (0.1- 0.3) mL/h to create homogeneous nanofiber mats.
Figure 1: Diagram observation of electrospinning setup used for assembly of Nanofiber.

4. Fabrication of the Generator:

Fabricating a nanofibrous power generator, consisting of a small part of PVDF nanofiber mat was worked as an active layer between two aluminum foil. Two pieces of thin aluminum tape putted at top and bottom the device which work as electrodes, in addition because the sharp edge of aluminum foil, a paper frame was put between two layers of aluminum foil to prevent surface scratching of the electrospun web. Paper surround furthermore better to prevent from environmental noises.

The entire device was later wrapped by a commercial paper strips. Fig. 2 (a) represented device layers structured while (b) appearance the photo image for the final device fabricated.

Figure 2 (a) Representation device layers structures and (b) Photo image of designed the device.
5. Results and Discussions:

XRD analysis:

XRD analysis was obtained to study the structural properties for pure powder PVDF and BT beside BT crystalline phase in the PVDF fibers, as per displayed in Fig.3 (a, b, c, d, e, f, g, and h) using the process of the electrospinning force. Since the XRD show polycrystalline phase for BT NP have six diffraction peaks 21.983° (100), 31.361° (1 10), 38.644° (111), 44.926° (200), 50.583° (210), and 55.861° (211). Moreover, the double-peak shape at 45°designates that BT NP are fine-crystallized through a tetragonal phase by matching the data with Card No (01-075-2119) [41].

Firstly Fig. 3 (a) for pure powder PVDF at 2θ=18.4° (020), 19.9° (110) and 26.4° (021) that approving the origin α phase for pure powder PVDF that agree with reference [42]. phase besides four weak peaks at (33.2, 38.8, and 41.1°) conforming of 130, 002, and 111 refe raction of the monoclinic α-phase, respectively. [43-45]. While in Fig. 3 (b) for nanofiber mat 12% PVDF The peak at 2θ = 20.7° (110) point to β-phase while the peak at 2θ = 26.7° (021) was very small and weak corresponding for α phase. Then it approves in Fig.3 (c) for electrospun 18%PVDF fiber mat with three phases -phase, α-phase and β-phase. The peak at 2θ = 18.3° (002) which approves the perfection of -phase besides a central peak at 2θ=20.14° (110) showcases attributed for α phases. While that the pea k at 2θ = 20.78° (200), as well as at 2θ=31.9° (001) which approves that by electrospunining for PVDF fiber mat perfection creation of β-phase.

Whereas for composite BT NP with PVDF are very difficult designed for XRD between the α-, - and β-phases in PVDF, since together phases have a shared peak about 20° which agree with references [46,47]. In Fig. 3 (d) for 12% PVDF&20%BT where a primary peaks at 2θ=17.4° (100) confirm for α phase and at 2θ=20.8° (110) crystalline phase to their positions where for β phase [48], continue for PVDF looked between 2θ between 22–45° alongside by the peaks for BT crystalline phase to their positions where for β phase. Also in Fig. 3(e) of 12%PVDF&25%BT the projecting peak was positioned at 2θ=20.8° (110) for PVDF β phase [48], then at 2θ looked between 22–45° alongside by the peaks for BT. In completely the diffractograms in Fig. 3 (f) for 14%PVDF&20%BT where the peak seemed as the highest peak, at 2θ=20.7° (200) for formation of a β-phase to the PVDF in the sample. As well as in Fig. 3 (g) of 20%PVDF&25%BT the bordered peak at 2θ=20.8° (110) too confirmed for PVDF β phase, and in the same position at 2θ looked between 22–45° alongside by the peaks for BT. Finally (h) in Fig. 3 the data with Card- No (01-075-2119) was for BT.

Figure 3 X-ray diffraction pattern of electrospun for (a) powder PVDF, (b) 12%PVDF, (c) 18%PVDF and composite with BT structures: (d) 12%PVDF&20%BT, (e) 12%PVDF&25%BT, (f) 14%PVDF&20%BT, (g) 20%PVDF&25%BT, and (h) powder BT.
6. Morphology:

Scanning electron microscopy (SEM) pictures was operated for describing the microstructure and the morphology of the nanofibers and the images were obtained at an acceleration voltage of 20 kV, with resolution 3.5 nm and the samples were analyzed at room temperature. Proper to the opposing piezoelectric influence, principle piezoelectric were oscillated and the so were the samples. Since a properly and stable piezoelectric property appears from homogenous nanofiber mats, enhancing the electrospinning procedure is required.

SEM images were behaved to investigate the morphology and structure of fabricated nanofiber. It is capable of imagined from the SEM images that the nanofiber are random positioned. Agreeing to the SEM image show nanofibers with different diameters ranging between (100-600 nm) and the diameter distribution histogram by using software Image J were shown in Fig. 4.

Because the ceramic constructer solution does not contain enough viscosity to create a jet through ElectroSpinining process, a polymer reagent is frequently performed in spinning solution pointed at enhancing ceramic NFs. Mohammadi et al. [49] and Zadeh et al. [50]. Therefore in this study the composites, PVDF/BT, nanoparticles BT are perfectly distributed besides instilled in the PVDF emulsion automatically beside superior designed which made a little agglomerates in the PVDF medium. But it appears a greater in the container of the (12% PVDF & 25% BT additive.)
7. Output Measurement:

The measurement of the electrical response is the greatest appropriate technique for compare between the samples about which material goods for resonance to piezoelectric, because it expose the ending inefficiency of a mechanical-to-electrical energy harvesting device. In this study to investigate the effect of BT nanoparticle on the electrical response of generated devices, six samples were measured in different conditions. Designed for certifying the stability for these calculations, therefore all samples were calculated three times by the same trying condition. Fig.5 represented the output voltage for six samples in different force with constant the frequency for all samples.

![Figure 4](image1.png)

Figure 4. Appearance the Images of Composite PVDF & BaTiO₃.

![Figure 5](image2.png)

Figure 5 Illustration the output voltage for pure PVDF and composite with BT.

Figure of the scheme which was used to measure the piezoelectric response is displayed in Fig.6 as experiential, that the increased of the addition for BT nanoparticle, due to increase the electrical response of samples.
Figure 6: Device of the considered operation for difference Sample's electrical.

The distribution chart in Fig. 7 expresses that ratio of the particles range between (0% and 25%) gm. It is moreover distinct from this chart that mechanical activation did not considerably effect the size distribution of the particles (BT) in PVDF.

Figure 7: Display the effect of add BT to PVDF.

8. Conclusion:

Pure PVDF and BaTiO$_3$–PVDF composite nanofibers were formed at different percentages then confirmed their effect enhancement as piezoelectric materials. A polymer solution of (12% wt./wt.) in normal informed conditions was created and weights of BaTiO$_3$ was additional. Procedure was modified for 25 % Wt./Wt. of BaTiO$_3$ and nanofibers were formed corresponding to the cases in different percentages. Since the BaTiO$_3$ are nanoparticles therefore doing as a nucleating agent throughout the polymer phase crystallization as a result the electrical reply of samples that as evidenced by a substantial increase in piezoelectrically generated voltage with increased amounts of BaTiO$_3$ which offer on a simple, proficient flexible methodology to self-powering of microelectronics on behalf at many applications in medicin, industry and others.
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Abbreviations: PVDF; Poly Vinylidene Fluoride, BT; BaTiO$_3$, and SEM; Scanning Electron Microscopy; XRD; X-ray diffraction

The Ourthure: Used software for drawing: Origin, Spas, Image J and EndNote for arranged the references.

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