



## Research article

# Piezoelectricity performance and $\beta$ -phase analysis of PVDF composite fibers with BaTiO<sub>3</sub> and PZT reinforcement

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## ABSTRACT

Piezoelectric composite fibers have various applications such as energy harvesting and human body monitor devices. Therefore, the construction of fibers that have the highest piezoelectric efficiency while using materials with the least toxicity is of great importance for health. Consequently, in the research a head PZT/PVDF (Lead Zirconate Titanate/Polyvinylidene fluoride) and Lead free BaTiO<sub>3</sub>/PVDF (Barium Titanate/Polyvinylidene fluoride) 0–3 connection type composites nanofibers were fabricated by Electrospinning method. Dielectric constant with Impedance analyzer, sensitivity with handmade device and their crystalline properties by using FTIR and XRD, were compared. The results showed, adding BaTiO<sub>3</sub> will increase the percentage of  $\beta$ -Phase crystal formation more than adding PZT which subsequently leads to a higher dielectric constant.

## 1. Introduction

There is a growing tendency on efficient highly portable and continuous energy sources over the last decades, therefore energy harvesting from environment received considerable heed as an alternative power source. The more appealing method among other techniques to harvest energy from ambient is piezoelectric materials on account of their capability to produce the voltage straightly from the applied mechanical stress. These materials have diversity of application such as sensors and health monitoring, transducers and actuator devices [1–4].

Piezo-ceramics have a wide spectrum of application due to their superior piezoelectric properties (high dielectric and piezoelectric values). However, brittleness, stiff mechanical properties and additional mass restrict their usage [5]. In contrast, Piezo-polymers are flexible and resistant to damage but they also have low electromechanical coupling coefficients and high dielectric losses [5,6]. Consequently, ceramic-polymer piezoelectric composites received growing attention over the last few years due to the combination properties of ceramic and polymer. They seem not only to have the mechanical strength, flexibility and formability of the polymer they also possess ceramic superior properties and ease manufacture process [3,7,8].

Numerous researches have been conducted to fabricate Piezoelectric fibers because of their unique structure and properties, such as high aspect ratio, flexibility in surface functionalities, great mechanical stiffness and tensile strength and chemical stability [9–11]. Previously several attempts had been done to synthesized ceramic fibers with in variety of methods such as solution method, laser ablation and chemical vapor deposition. Requiring multiple process steps is the main drawback of these methods [12,13]. Moreover,

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Extrusion had been used in order to produce PZT (Lead Zirconate Titanate) fibers but as far as the fiber diameters are restricted around 100  $\mu\text{m}$  and the fabrication of fine grain, high density and fibers with cross sectional dimension under critical flaw sizes is difficult, this technique is not appropriate either. Also, recently several other processing techniques have been used to prepare polymer nanofibers for instance, drawing, template synthesis, phase separation self-assembly and etc. Every each of these methods have their own downturns which can be found elsewhere. Among all diverse method which have been used, the most ease and convenient technique for mass production of one-by-one continuous fibers with diameter range from hundreds of nanometers up to few micrometers is Electrospinning [14–18]. PZT and BaTiO<sub>3</sub> (Barium Titanate) are the most widely used Piezo-ceramics due to their magnificent piezo characteristics such as high electromechanical coupling coefficient, high dielectric constant and high piezoelectric constant. Moreover, PVDF<sup>1</sup> has been heeded the most among other piezo-polymer materials on account of their excellent piezoelectric and ferroelectric properties, good mechanical characteristics and also chemical resistance [19–21]. Table 1 show some of their pizeoelectrical properties [22].

There has been several conducted research on fabricating PZT/PVDF and BaTiO<sub>3</sub>/PVDF composites as a thin film and fibers with different methods such as, Sol-Gel, Sodium alginate, Viscous suspension spinning process, natural adsorption, tape casting and hot press, spin coating onto glass substrate and Electrospinning [16,18,23–25]. the advantage of manufacturing and using piezoelectric composite fiber through electrospinning method compared to other proposed methods is that, in addition to producing flexible composite samples, it doesn't require the need for polarization process. During the electrospinning process, polarization occurs, which gives a relative advantage in the production of flexible piezoelectric composite compared to other methods [26]. PZT and BaTiO<sub>3</sub> have Perovskite structure and analogous piezoelectric properties but sintering of PZT at high temperature and the evaporation of toxic lead brings about environmental pollution and it is harmful for health.

Therefore, this study aims to fabricate PZT-PVDF and BaTiO<sub>3</sub>-PVDF with 0–3 connection type composites fibers which is lead free, with 5, 10 and 15 wt percentage of ceramic particles by Electrospinning method and compare their characteristics and piezo electrical properties in a fixed condition.

## 2. Experimental method

### 2.1. Materials and method

To prepare a solution for Electrospinning, pure PVDF (Solef1010, Solvay, France) was solved in a DMF (Dimethylformamide) (codek39524634, Merck, Germany)/Acetone (code67641, Merck, Germany) (60:40-wt/wt.) with the ratio of 1:1 for 3 h at the 70 °C temperature on Hitter stirrer (IKA, Germany). The system was securely sealed with industrial Paraffin in order to prevent the evaporation of the solvent (Solution A). Then, Ceramic powders, PZT (code5A, Morgan Electro Ceramic, USA) and BaTiO<sub>3</sub> (code12048, Merck, Germany) separately were dispersed in DMF in 5, 10 and 15 wt percentage with ultrasonic probe for 20 min with 150 w. Table 2. Shows the weight values and weight percentage of solid powders and PVDF added into the solvent.

This will be referred as sample B. A certain volume of Sample B was added to sample A, the final suspension magnetically stirred for 10 h at the 35 °C temperature and it remained stationary for 1 h and then then it dispersed by ultrasonic probe (400UPS, KTG group, IRAN) 10 min and finally The suspension was electrospun (Electroris, FNM, Iran) at following optimized conditions: The applied voltage was varied between 10 and 15 V, the distance between needle tip and collector was 15 cm and the feed rate was 3 ml/h. The Fig. 1a illustrates the process of fiber production, Fig. 1b and c shows images of samples during dispersion with ultrasonic probe and solution samples after dispersion of BaTiO<sub>3</sub> and PZT particles.

### 2.2. Characterization

Amount of  $\beta$ -crystal phase were analyzed by FTIR<sup>2</sup> (PerkinElmer, USA) and X-ray diffraction (Phillips PW 3710, Netherland, by CuK $\alpha$  radiation with  $\lambda = 1.54 \text{ \AA}$ ) and the microstructure and the morphology of samples were characterized by SEM<sup>3</sup> (VEGA, Tescan, Czech Republic). Moreover, Dielectric constant was calculated with Impedance Analyzer (4194A, HP, USA) and Sensitivity with hand-made device was analyzed.

## 3. Result and discussion

### 3.1. SEM analysis

SEM images in Fig. 2 shows the PZT/PVDF and BaTiO<sub>3</sub>/PVDF morphologies of fibers in different amount of BaTiO<sub>3</sub> and PZT (5 wt% and 15 wt%), it can be seen that the smooth surface fibers and has no beads, the average diameter of 5 wt% (a) and 15 wt% (b) BaTiO<sub>3</sub> fibers was 181.338 nm and 160.626 nm respectively and for 5 wt% (c) and 15 wt%(d) PZT fibers was 227.666 nm and 211.032. this shows that the average diameter of electrospun fibers decreases with the increase of BaTiO<sub>3</sub> or PZT particles. some researcher believes that a decrease in average diameter was accompanied by an increase in the  $\beta$ -phase (F( $\beta$ )) [27]. In some articles, it was observed that

<sup>1</sup> Polyvinylidene fluoride.

<sup>2</sup> Fourier Transform Infrared Spectroscopy.

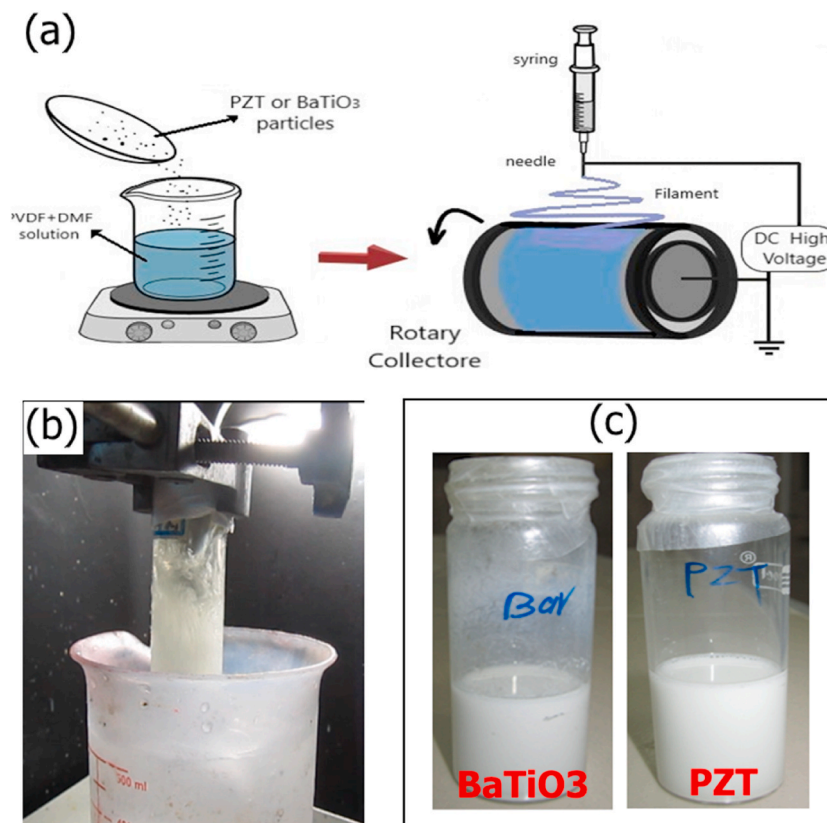
<sup>3</sup> Scanning Electron Microscopy.

**Table 1**  
Comparison of Piezoelectric properties of PZT, BaTiO<sub>3</sub> and PVDF.

Piezoelectric material	Piezoelectric constant (pC/N)		Relative permittivity ( $\epsilon/\epsilon_0$ )
	$d_{33}$	$d_{31}$	
BaTiO <sub>3</sub>	190	-78	0.21
PZT	60–130	-120	
PVDF	30	-20	12

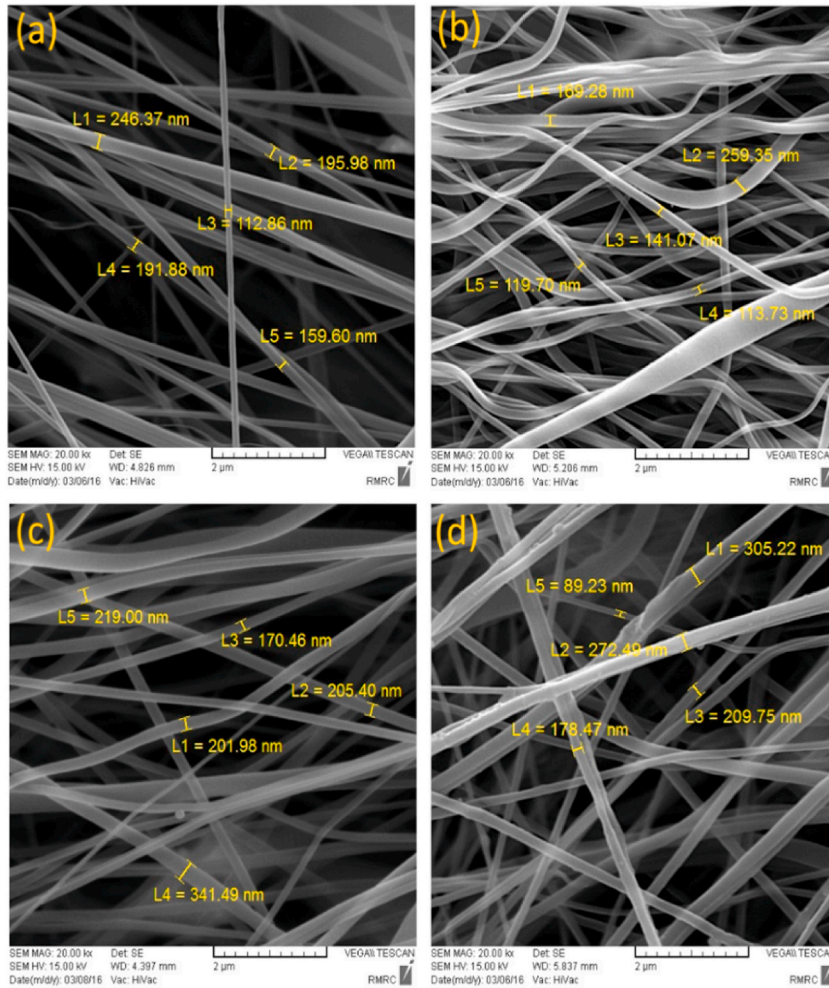
**Table 2**  
Amount of ceramic and PVDF particles in composite fibers.

Sample No.	PZT/BaTiO <sub>3</sub> (wt.%)	PVDF (gr)	PZT or BaTiO <sub>3</sub> (gr)
1	15 %	0.85	0.15
2	10 %	0.9	0.1
3	5 %	0.95	0.05



**Fig. 1.** (a) schematic of BaTiO<sub>3</sub>/PVDF or PZT/PVDF fiber process, (b) Dispersion of Nano particles in DMF with ultrasonic probe. (c) Mixture of particles after dispersion.

the reduction of fibers leads to an increase in piezoelectric properties, so that the voltage output from the fibers increased with the reduction of the fiber diameter [28,29]. In research, Shirazi et al. [30] mentioned that the fiber diameter is inversely related to the  $d_{33}$  piezoelectric coefficient, and individual crystallites of 25 nm in diameter exhibited the highest piezoelectric response. This suggests that smaller fiber diameter may lead to better piezoelectric properties. The reduction of the diameter of piezoelectric fibers made by adding ceramic particles has been observed in the studies of other researchers [31–33]. of course, not all researchers have a definite consensus on how to reduce the fiber diameter, but they consider several possibilities more effective than others. When ceramic particles are added to the polymer solution, they affect the dispersion and viscosity of the solution, so it is possible that the viscosity of the solution will increase with the increase in the amount of ceramic particles, and finally, the fibers made by electrospinning will be thinner [31]. the addition of electrospinning ceramic particles and the behavior of the polymer solution during the formation of the



**Fig. 2.** SEM images for piezoelectric composite fibers: (a) 5 wt% BaTiO<sub>3</sub>, (b) 15 wt% BaTiO<sub>3</sub>, (c) 5 wt% PZT, (d) 15 wt% PZT.

fibers affects the changes in the characteristics of the solution such as conductivity and surface tension, which affect the diameter of the fibers [34]. sometimes it is possible that the reaction between the ceramic particles and the PVDF polymer matrix will lead to a change in the behavior of the polymer solution, which plays an important role in reducing the diameter of the manufactured composite fibers.

The presence of ceramic particles can affect the polymer chain alignment and stretching during electrospinning, leading to thinner fibers [33]. On the other hand, the diameter of fibers containing BaTiO<sub>3</sub> particles is smaller than the diameter of fibers containing PZT particles that According to the above, BaTiO<sub>3</sub> fibers with a smaller diameter have better piezoelectric properties compared to PZT fibers.

### 3.2. FTIR analysis

The amount of  $\beta$ -phase crystal formation of samples was studied with FTIR. Table 3. Shows the different vibration band in  $\alpha$ ,  $\beta$  and  $\gamma$  phases of PVDF in FTIR. Percentage of  $\beta$ -phase of samples were calculated using Equation (1) and absorption band of  $\alpha$  and  $\beta$  [35].

$$F(\beta) = \frac{A_{\beta}}{1.26A_{\alpha} + A_{\beta}} \quad (1)$$

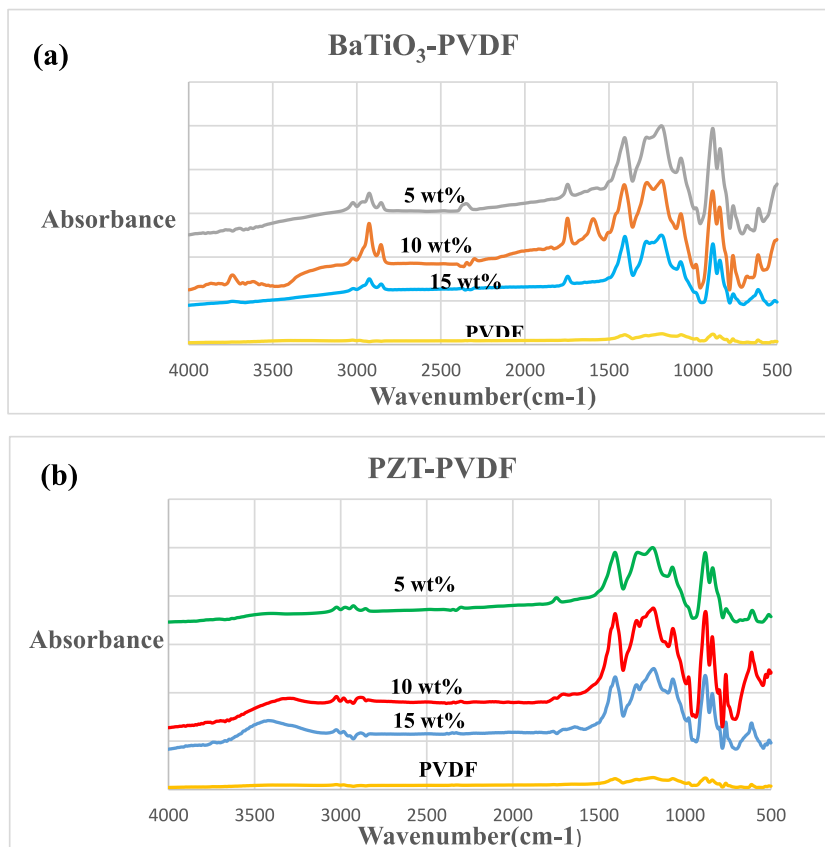
Where  $F(\beta)$  is the  $\beta$ -phase relative ratio.  $A_{\alpha}$  and  $A_{\beta}$  are calculated with the area under the FTIR peaks (763 and 840  $\text{cm}^{-1}$ ).

In pure PVDF, absorptions at 763, 766 and 976  $\text{Cm}^{-1}$  are for  $\alpha$ -phase. By adding BaTiO<sub>3</sub> intensity of them are declined and absorptions at 840 and 1273  $\text{Cm}^{-1}$  are increased. Fig. 3 shows FTIR spectrum of (a) BaTiO<sub>3</sub>/PVDF fibers compare with (b) PZT/PVDF fibers, has more influence on increasing  $\beta$ -phase. This is because of the presence of  $-\text{TiO}_3$  ( $\delta^+$ ) groups which culminates in the intense interaction between oxygen atoms and Bipolar  $-\text{CH}_2$  ( $\delta^-$ ) groups of PVDF in the composite. This reaction alters the chain structure of PVDF from  $\alpha$  to  $\beta$ .

After FTIR of the BaTiO<sub>3</sub>/PVDF composite, Abdolmaleki et al. [37] observed that the intensity of the peak representing the  $\alpha$ -phase

**Table 3**  
Vibration Absorption bands for PVDF crystal phase in FTIR [21,36].

Crystal Phase	Vibration Absorption Bands ( $\text{cm}^{-1}$ )
$\alpha$	408,489,530,532,614,615,763,764,765,766,795,796,854,855,870,975,976,1149,1210,1383
$\beta$	420,422,444,467,445,470,509,510,840,877,884,1175,1275,1279
$\gamma$	431,440,512,776,812,833,840,882,883,1117,1233,1234



**Fig. 3.** FTIR results for (a) BaTiO<sub>3</sub>/PVDF fibers and (b) PZT/PVDF fibers.

decreased remarkably with increasing BaTiO<sub>3</sub> content, indicating that more filler content deteriorated the overall crystallinity of PVDF and led to more amorphous structures [37]. also, on the other study, Kabir et al. [38] reported that the  $\beta$ -crystalline phase percentage of PVDF was increased from 59.38 % to 71.65 % by adding BaTiO<sub>3</sub>. Similarly, the piezoelectric  $\beta$ -ferroelectric phase of PVDF can increase with doping of BaTiO<sub>3</sub> [39].

Fig. 4 a) presents two prominent peaks at  $2\theta = 17.9^\circ(100)$  and  $27.92^\circ(100)$  that these peaks agreed with the PVDF  $\alpha$ -phase while the peaks at  $2\theta = 20.8^\circ(110),(200)$  and  $36^\circ(120)$  is confirmed of the existence of PVDF  $\beta$ -phase. Fig. 4 b) shows all the peaks observed from the previous figure except peak  $36^\circ$ , indicating an increase of PVDF beta phase for BaTiO<sub>3</sub>/PVDF composite fibers compared to BaTiO<sub>3</sub>/PVDF fibers. The XRD spectra for composite fibers clearly show the Reduction of  $\alpha$ -phase and increase of  $\beta$ -phase due to the addition of ceramic particles [40].

### 3.3. X-ray diffraction analysis

BaTiO<sub>3</sub> and PZT increase the peak of the  $\beta$ -phase while decreasing the peak of the PVDF  $\alpha$ -phase in composite samples, resulting in an increase in the PVDF  $\beta$ -phase and a decrease in the PVDF  $\alpha$ -phase in composite fibers as well as an improvement in the piezoelectric properties of the fibers thanks to the addition of ceramic particles. The intensity of the peaks established at low weight percentages used is the minimum due to the small amounts of BaTiO<sub>3</sub> and PZT added to the composite fibers, and the intensity of the revealed peaks increases with the increase in weight percentage. As a consequence, the investigation revealed that the characteristic peak of BaTiO<sub>3</sub> occurred at  $2\theta = 32.17^\circ(110)$  [41], and the increase in the intensity of the PZT peaks at  $2\theta = 32^\circ(110)$  and  $22^\circ(101)$  showed an increased amount of PZT in the fiber structure [42].

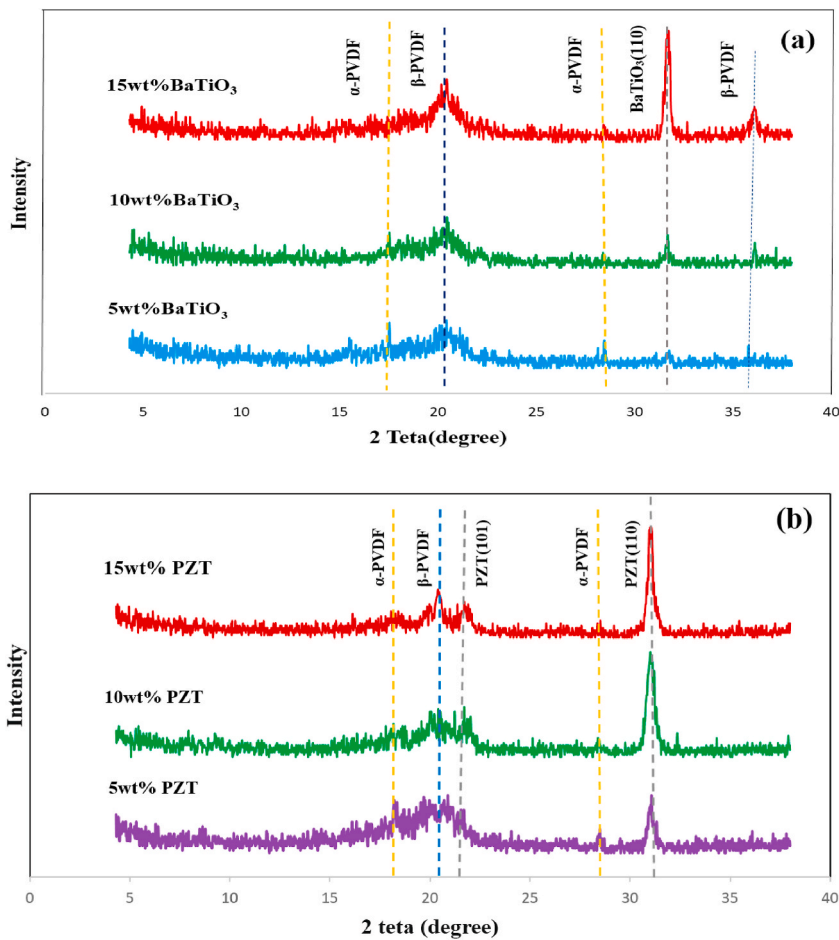


Fig. 4. XRD patterns for (a) BaTiO<sub>3</sub>-PVDF composite fibers and (b) PZT-PVDF composite fibers.

### 3.4. Dielectric properties

In order to research the Electrical properties of samples, first, Electrodes were fabricated from samples by using aluminum foil that was placed on both sides of an experimental film of electrospun fibers. Impedance analyzer was used for this test. By using the equations 2 & 3 Dielectric constant of the samples were calculated. Results which are shown in Fig. 5 showed that adding BaTiO<sub>3</sub> compare with adding PZT increase the Beta crystal phase more. As it was said previously this is due to the interaction of BaTiO<sub>3</sub> functional groups with Polymer Bipolar groups which increase the order of Bipolar groups in composite and this increases the electrical properties. Therefore, the decrease of Impedance in BaTiO<sub>3</sub> is because of increase in  $\beta$  polar phase in composite. As a result, the decline

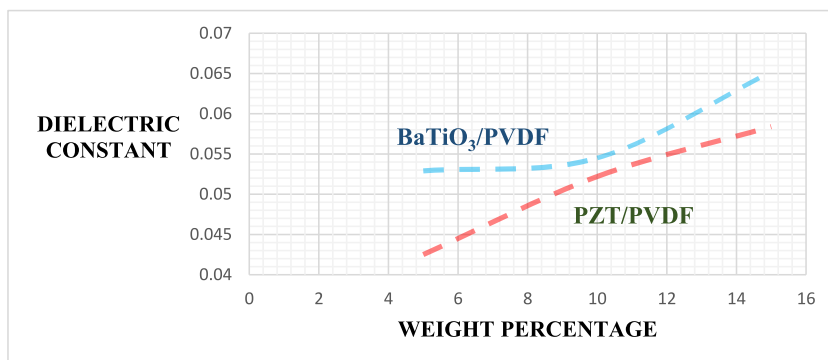


Fig. 5. Dielectric Constant-Weight Percentage of the samples diagram.

in Impedance increases the capacitance.

$$Z = \frac{1}{C\omega} \quad (3)$$

Where  $z$  is impedance,  $c$  is the capacitance,  $\omega$  is the expresses the angular frequency [43].

$$\epsilon_r = \frac{dC}{\epsilon_0 A} \quad (4)$$

where  $\epsilon_r$  is the dielectric constant,  $c$  is capacitance,  $d$  is thickness of the film,  $\epsilon_0$  is permittivity of vacuum and  $a$  is the effective electrode area [44].

PZT is filler material that can be added to PVDF fibers to enhance their dielectric properties [45]. Also BaTiO<sub>3</sub> can lead to an increase in the dielectric constant of PVDF fibers. For example, the addition of BaTiO<sub>3</sub> to PVDF can lead to a significant increase in the magnitude of the dielectric constant in PVDF/BaTiO<sub>3</sub> nanocomposite films compared to pure PVDF [46]. On the other research Yang et al. [46] added BaTiO<sub>3</sub> into PVDF fibers, they observed that their dielectric constant and breakdown strength increased, therefore resulting in improved dielectric properties.

### 3.5. Electrical sensitivity and piezoelectric effect

Sensitivity was measured with handmade device that shown in Fig. 6. Aluminum foils as Electrodes were put in the device. The ball with specified weight and distance from electrode applied tension and Preamplifier measured the produced voltage.

Results showed that increase in ceramic particles, increase the voltage. PZT-PVDF produces higher voltage than BaTiO<sub>3</sub>-PVDF. This is because of the Presence of Pb in PZT which brings about higher structure deformation which makes them to produce higher voltage. Table 4 shows the voltage values obtained in different percentages of BaTiO<sub>3</sub> and PZT used in the films of composite fibers.

This is because PZT has a higher piezoelectric coefficient than BaTiO<sub>3</sub>, which means it can generate a higher voltage output in response to mechanical stress [29,38].

## 4. Conclusion

PZT/PVDF and BaTiO<sub>3</sub>/PVDF piezoelectric composite fibers were successfully fabricated by Electrospinning method with 5, 10 and 15 wt percentage and their crystalline phase properties and piezoelectric characteristic were compared. The SEM studies showed a smooth, uniform and free bead fibers, which indicated the success of manufacturing composite fibers containing BaTiO<sub>3</sub> and PZT with PVDF. Also, due to the addition of PZT or BaTiO<sub>3</sub> particles, the fiber diameter decreased, which led to an increase in piezoelectric properties and an increase in PVDF Beta crystalline phase. Also, the decrease in the diameter of BaTiO<sub>3</sub> fibers was more than the fibers containing PZT, which increases the piezoelectric properties of BaTiO<sub>3</sub> fibers. FTIR studies conducted and showed, adding BaTiO<sub>3</sub> increases the  $\beta$ -crystalline phase more than adding PZT which is because of the better interaction of BaTiO<sub>3</sub> with PVDF. Also, BaTiO<sub>3</sub> increases higher Dielectric constant compared with PZT. X-ray diffraction also showed that as the amount of BaTiO<sub>3</sub> and PZT particles increased, the amount of  $\alpha$ -phase of PVDF decreased and the amount of  $\beta$ -phase increased also the number of  $\beta$ -phase peaks observed in the BaTiO<sub>3</sub>/PVDF samples was higher than in the PZT/PVDF samples. As a result, the piezoelectric properties of the fibers were enhanced. However, the presence of Pb in PZT/PVDF causes larger deformation than BaTiO<sub>3</sub>/PVDF which culminates in greater sensitivity which makes them produce e higher Voltage. Among all the samples, 15 % weight percentage ceramic phase showed a better sensitivity, and PZT/PVDF and BaTiO<sub>3</sub>/PVDF specimens produced 10.14 and 9.34 voltage respectively. Therefore, due to the good piezoelectric properties of lead-free BaTiO<sub>3</sub>/PVDF composite fibers, these fibers can be used for various applications such as body

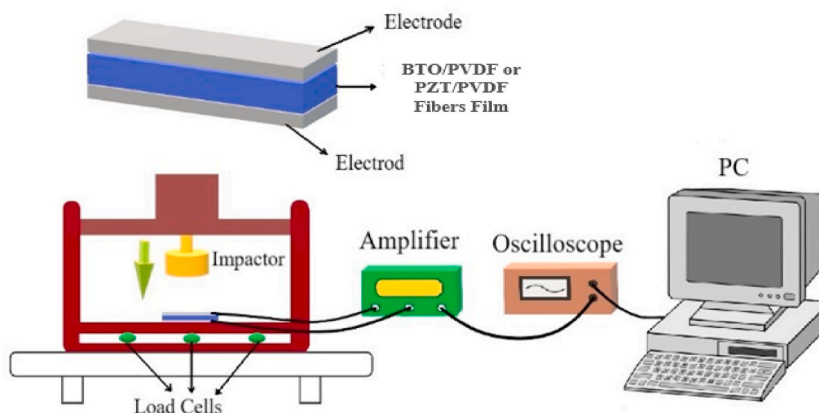


Fig. 6. Handmade device for studying samples sensitivity.

**Table 4**  
Produced voltage by the samples.

Wright Percentage	5 %	10 %	15 %
PZT-PVDF	8.04 (v)	9.75(v)	10.14(v)
BaTiO <sub>3</sub> -PVDF	8.39(v)	8.78(v)	9.34(v)

health monitoring devices and energy harvesting tools.

#### Data availability statement

Due to the nature of the research, due to legal restrictions, supporting data is not available.

#### Additional information

No additional information is available for this paper.

#### CRediT authorship contribution statement

**Shahram Mahboubizadeh:** Writing – original draft, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Saman Taghavi Dilamani:** Writing – original draft, Investigation, Formal analysis, Data curation. **Saeid Baghshahi:** Writing – review & editing, Validation, Supervision, Project administration, Data curation, Conceptualization, Formal analysis.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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