

# ENERGY DISPERSIVE X-RAY SPECTROSCOPY OF DOPED PVDF FIBERS

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**Abstract:** This work aims to further improve properties of Polyvinylidene fluoride (PVDF), one of the most promising electroactive polymers, by the inclusion of powders of piezoelectric materials. PVDF was formed by electrospinning into fibres with a thickness of 0.5 – 1.5 μm and then examined in a scanning electron microscope including energy-dispersive X-ray spectroscopy. The obtained properties of doped PVDF could be used in the design of sensors. Before that, it is essential to perform a series of analysis to support or deny the use of adjusted fibres for sensor design.

**Keywords:** PVDF, energy dispersive X-ray spectroscopy, scanning electron microscopy, electrospinning, composition, morphology, piezoelectricity

## 1 INTRODUCTION

PVDF is a semicrystalline polymer having five crystalline polymorphs, including  $\alpha$ -,  $\beta$ -,  $\gamma$ -  $\delta$ - and  $\epsilon$ -phases. The  $\beta$ -PVDF-phase exhibits excellent ferroelectric and piezoelectric properties, making PVDF useful in a wide range of applications (including actuators, biosensors, energy harvesting materials, audio devices and many more). Piezoelectric materials generate an electric charge in response to applied stress or slight mechanical deformation, thus eliminating the need for external power sources for electrical stimulation. Therefore, it is possible to obtain a high dielectric constant by doping PVDF with piezoelectric ceramics. As a result, polymer-ceramic composites can be an excellent choice to achieve miniaturisation of energy storage devices.

The fibres were doped by five types of piezoelectric ceramics. This paper, because of its required length, focuses only on two resulting composites – on fibres doped by barium calcium zirconate titanate ((Ba,Ca)(Zr,Ti)O<sub>3</sub>, BCZT) and barium titanate (BT). Both of the ceramics are lead free, environmentally friendly ferroelectric materials applicable in a variety of applications, due to its excellent dielectric, ferroelectric and piezoelectric properties. [1]

## 2 ELECTROSPINNING

For the preparation of PVDF fibres doped by ceramics was used the method called electrospinning. Electrospinning is a simple method to produce nanoscale fibres both in a laboratory and industrially. The fabrication process starts with the application of a high electric field to the polymer or solvent solution. A Taylor cone is formed at the surface of the polymer solution extrusion and above critical voltage electrostatic repulsion overcomes the surface tension of polymer droplet. The charged polymer jet is then ejected from the needle tip towards a grounded collector, forming randomly oriented fibres. The droplet is refilled by pumping new polymer solution to the needle tip through the needle.

The fibre diameter and porosity of the fibrous scaffolds depend on the processing parameters such as applied voltage, solution flow rate, type of solvent, polymer concentration in the solution, and the distance between the needle and collector. Electrospun fibres can be aligned by controlling the

fabrication parameters. Because of the chaotic trajectory of the polymer jet, the fibres collected on a grounded collector generally exhibit random orientation.

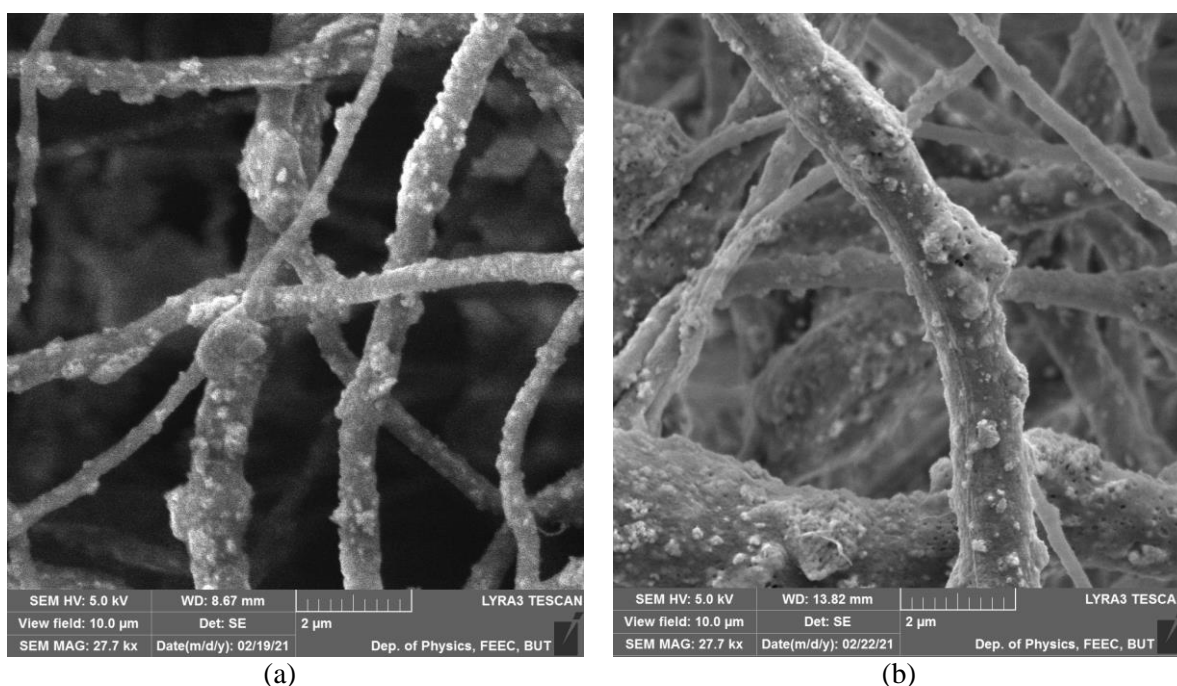
collector voltage	50 kV
distance between the needle and collector	20 cm
collector speed	300 rpm
duration of the process	100 min

**Figure 1:** The electrospinning processing parameters for manufacturing PVDF fibres doped by piezoelectric ceramics BCZT and BT

### 3 SCANNING ELECTRON MICROSCOPY

The morphology of the nanofibers was characterized by scanning electron microscopy. A SEM microscope uses a fine beam of focused electrons to scan a sample's surface; the process is based on applying kinetic energy to produce signals on the interaction of the electrons. [2] Electrons reflected by the specimen are used to form a magnified, black and white three-dimensional image.

When working with a scanning electron microscope, proper sample preparation plays an important role. While metals do not require complicated preparation, non-metals need to be coated with a conductive material to interact with electrons. [3] To ensure conductivity, resp. for charge dissipation, samples were sputtered with a thin layer of gold or carbon (10 nm) before the analysis. The images were taken on a Tescan Lyra 3 scanning electron microscope at an accelerating voltage of 5 or 10 kV.



**Figure 2:** SEM micrograph of PVDF doped by (a) BCZT (b) BT

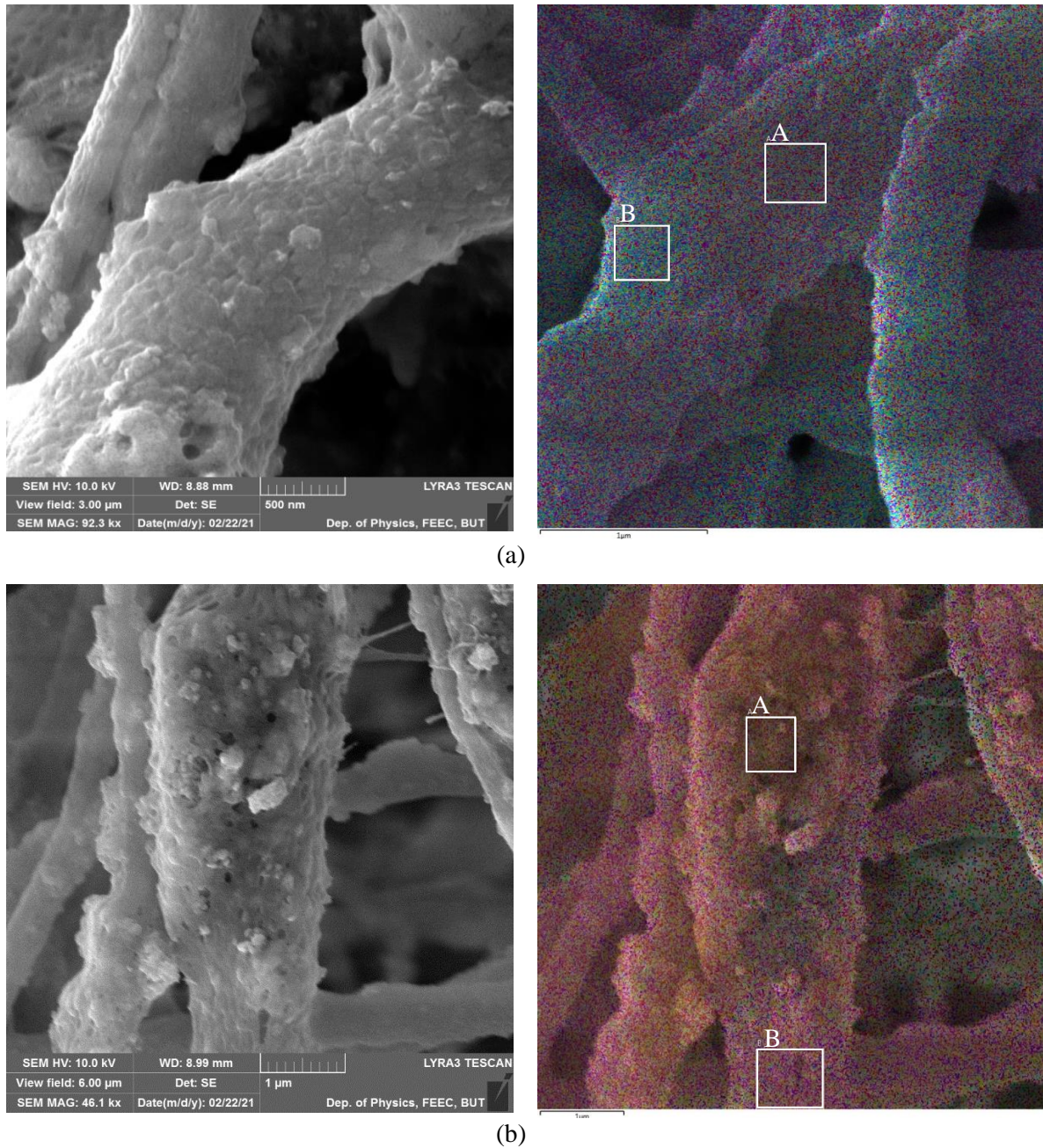
The fibres have an inhomogeneous diameter; the thin fibres are predominantly smooth, while the wider fibres have a rough texture with a layered structure. It suggests that the ceramic particles have been incorporated into the fibres; however, to support this argument, EDX analysis must be performed.

### 4 ENERGY DISPERSIVE X-RAY SPECTROSCOPY

The presence of ceramic particles in the fibres were confirmed by mapping using energy dispersive spectroscopy (EDX mapping, Tescan Lyra 3, AZtec software). The measurement was performed at

an accelerating voltage of 10 kV and energies of 0–10 keV were measured. For sample A (doping by BCZT), it was barium, calcium, carbon, fluorine, oxygen, titanium, and zirconium, and for sample B (doping by BT), it was barium, carbon, fluorine, oxygen and titanium. The aim was to create as homogenous composite as possible, where properties are uniform throughout the fibre, i.e. they do not depend on the position inside the fibre body.

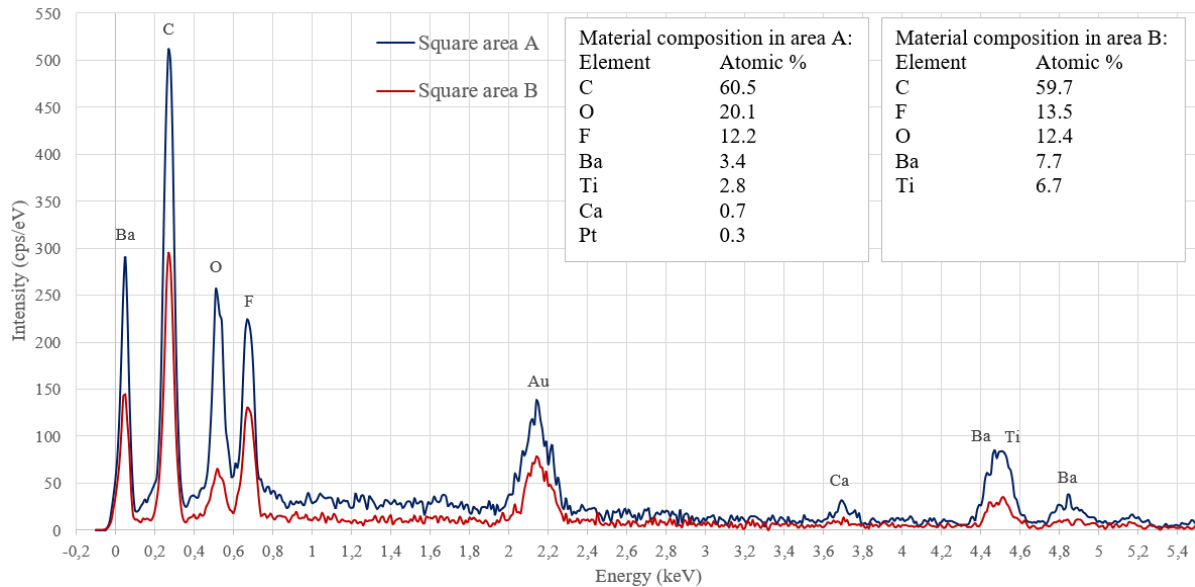
Figure 2 presents a map analysis of the major elements; these elements are colour-coded by EDX software. It is visible that the added ceramic relatively homogeneously copies the structure of PVDF nanofibers, which means that the additive is homogeneously dispersed in the polymer fibres formed by electrospinning; thus, the desired result was obtained. Similar results were obtained for the remaining samples of nanofibers (TiO<sub>2</sub>, ZnO, KNN), the analysis of which is not part of this article.



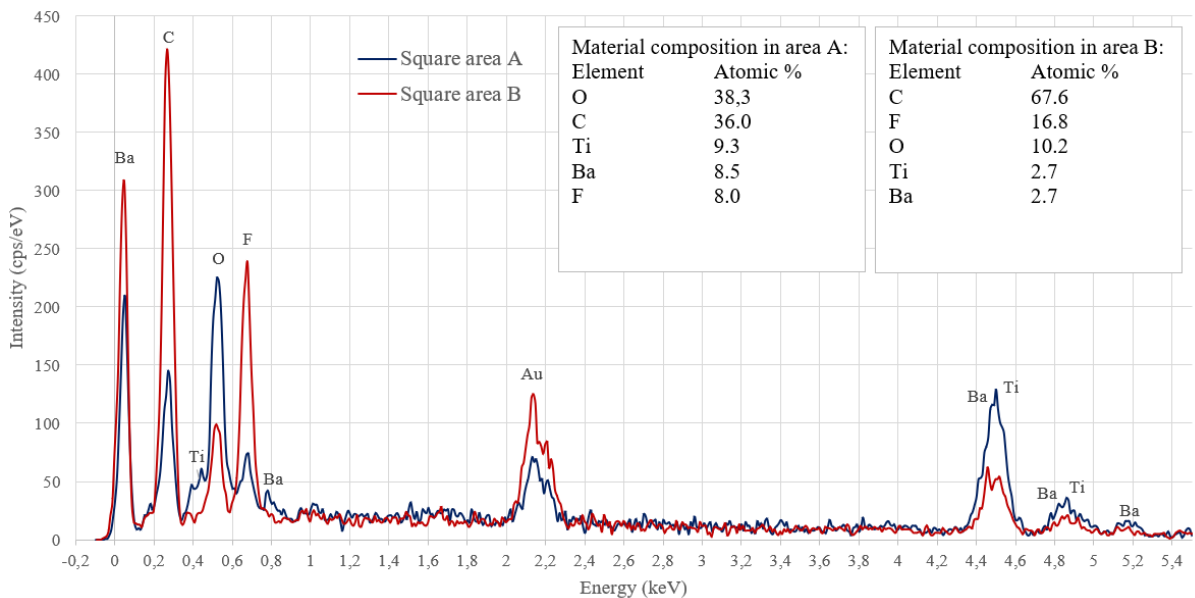
**Figure 2:** SEM and EDX micrographs of PVDF fibres doped by (a) BCZT (b) BT

EDX analysis also presents a spectrum that plots the number of X-rays detected versus their energies. In other words, it displays the peaks correlated to the elemental composition of the investigated sample and allows the identification of elements present in the sample.

Using the AZ software, it is also possible to concentrate only on a specific fibre section. This feature is ideal for comparing elemental compositions of various fibres areas - see Section A and Section B highlighted in EDX micrographs. These sections are further investigated in figures 3 and 4.



**Figure 3:** EDX spectrum of PVDF fibres doped by barium calcium zirconate titanate (BCZT)



**Figure 4:** EDX spectrum of PVDF fibres doped by barium titanate (BT)

See also the atomic percentage of each section in the upper right corner of each graph. These reveal the atomic composition of each area, not influenced by the weight of each element. Only a slight difference in atomic percentages of elements in each section's composition supports the previous arguments. It can be concluded that fibres have been doped successfully with even distribution.

## 5 CONCLUSION

Principally, the modification of materials provides additional features and aptitudes while maintaining the fundamental characteristics of the materials. By improving polyvinylidene fluoride properties by the inclusion of piezoelectric ceramics, it is possible to induce  $\beta$ -phase in PVDF. Therefore, polymer-ceramic composites can be an excellent choice to achieve miniaturisation of energy storage devices by combining the merits of polymers and ceramics.

After fabricating the fibres from the polymer solution, the fibres' morphology was characterised by a scanning electron microscope. SEM offered a transparent picture of thin fibres enriched with ceramics particles; fibres exhibited a rough texture with a layered structure and, therefore, proposed that the ceramic particles were uniformly distributed throughout the fibres.

The presence of ceramic particles in the fibres was later confirmed using energy dispersive spectroscopy. EDX provided mapping of the elements of doped ceramics using a colourful micrograph. It is possible to distinguish building elements of the doped fibres in the pictures and their even dissipation in the fibres. By exporting data from AZtech, an EDX software, it was possible to create a series of spectra, revealing the element composition in percentage. Comparison of elemental compositions of various fibres areas is sufficient evidence of satisfactory dopant distribution. Therefore, it is possible to continue with development of doped PVDF fibres.

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