PVDF — AN IDEAL CANDIDATE FOR USE IN NANOGENERATORS

Tatiana Pisarenko
Master's Degree Program (2), FEEC BUT
E-mail: xpisar04@stud.feec.vutbr.cz

Supervised by: Dinara Sobola
E-mail: sobola@vutbr.cz

Abstract: In this work, the PVDF composite, also known as polyvinylidene fluoride in the form of thin nanofibres, was created. Subsequently, a single-fibre characterization was performed, which proves its piezoelectric properties and describes its structure. Electron microscopy, atomic force microscopy and X-ray photoelectron spectroscopy were chosen as characterization methods. The discussion in this paper deals with the ability of these fibres to use PVDF as a nanogenerator.

Keywords: PVDF, electrospinning, nanofibres, characterization, PFM, STEM, SEM, XPS

1 INTRODUCTION

Polyvinylidene fluoride (PVDF) is a very promising semi-crystalline polymer for various industries, such as medicine, textile industry, electronics, energy harvesting, and many more. Widespread use is in the form of nanofibers. Its unique properties lie in the strong ability to polarise, i.e., the ability to exhibit a piezoelectric effect. Piezoelectric responses are characterized mainly by polar phases: γ, δ, and especially the most decisive β phase [1]. The individual phases differ in the configuration of the homopolymer chain. It very much depends on the parameters of the fibre for the successful formation of the β phase. Thus, if the final product results are to give satisfactory performance, it is desirable to focus directly on the processes already occurring in the single fibre itself [2, 3].

2 MATERIALS, METHODS AND RESULTS

In this experiment, the synthetic 20 % PVDF 275 DMSO/AC fibres were produced by electrospinning method in Contipro 4SPIN device. The properties of the produced nanofibres depend on many parameters set during spinning. For analysis, the samples were created using a continuous rotating collector. These samples differed mainly in the diverse number of spins per minute of the collector drum. The number of 300 rpm was chosen for the first sample and 2000 rpm for the second sample type. Other essential parameters during spinning were temperature 24 °C, humidity 51 %, and 20 cm distance of the emitter from the collector at a voltage of 50 kV. The collector used was a 17 GA needle with a set dose of flow of 30 µl/min. Different collector speeds affect the resulting β phase of the fibres, their organisation, and the average thickness.

The shape of the fibre was described by NTEGRA Prima atomic force microscope (AFM). The scan was performed in the region of 10×10 µm on a single fibre. Scan velocity was from 8.04 to 13.94 µm/s. It can be seen that not every fibre is necessarily circular in its diametre. It is visible in Figure 1 that both fibres are affected at speeds of 300 rpm and 2000 rpm. The resulting shape can be influenced, for example, by the collector voltage or the type of needle used.

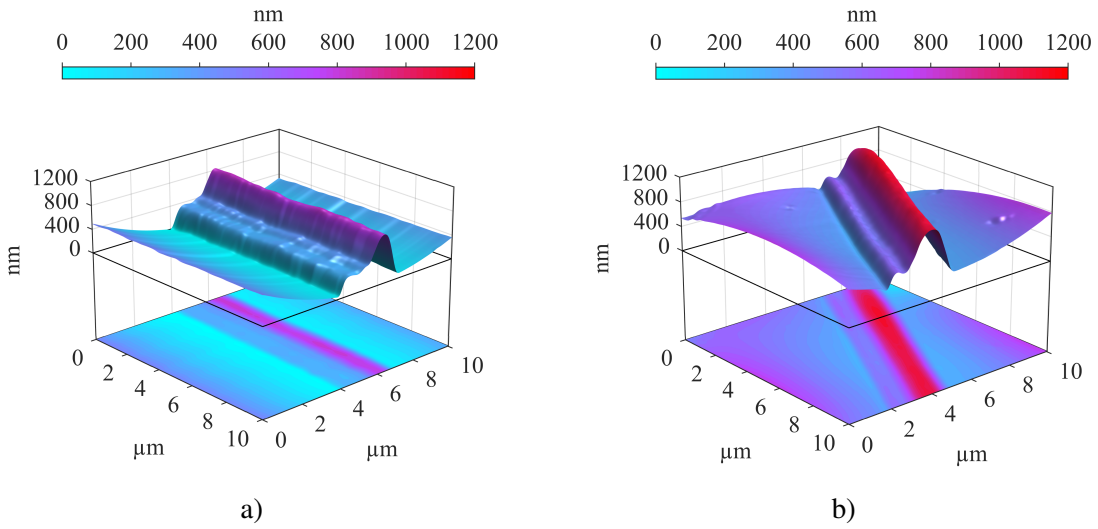


Figure 1: Three and two-dimensional imaging of the fibre at drum speeds of a) 300 rpm and b) 2000 rpm using the AFM microscope.

The piezoelectric response of the fibre were confirmed by piezoelectric force microscopy (PFM) measurements. This was used for the fibre with a more decisive β phase – at the collector cylinder speed of 2000 rpm [4]. The change in polarisation is most visible along the edges of the fibre, described in Figure 2. Here, the colour of these edges changes from light green to deep red in the form of a thin line. The voltage was varied from -5 to 5 V [5].

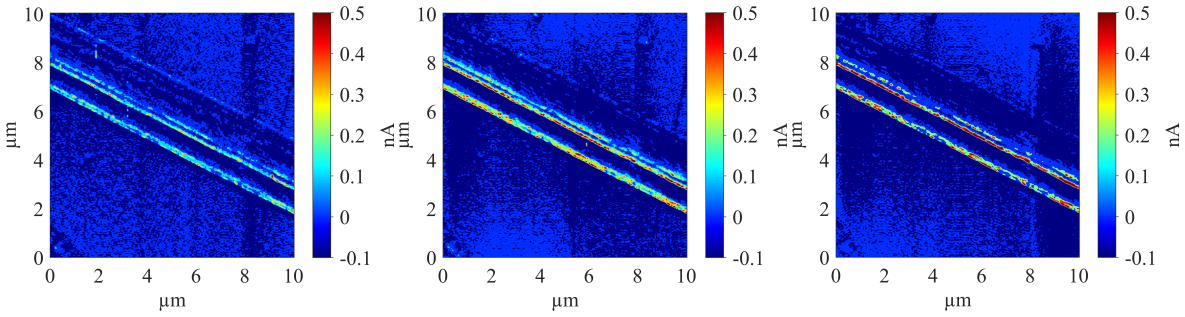
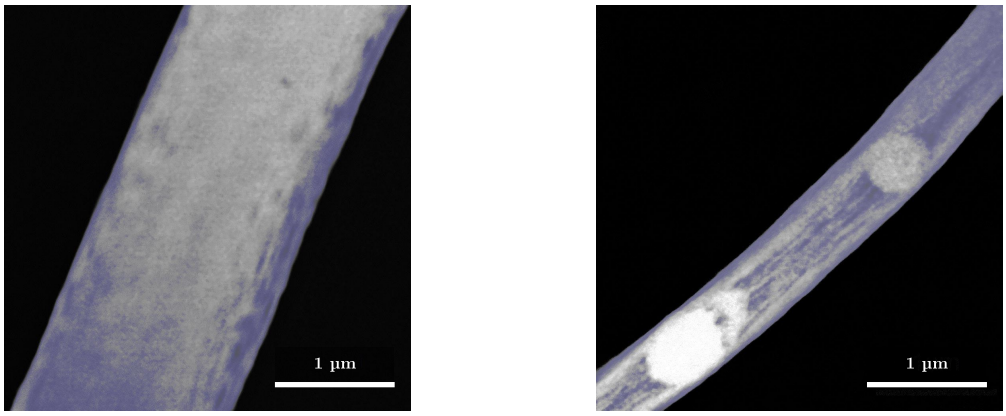


Figure 2: PFM method used in observation with AFM. A differently polarised fibre is observed mainly at its edges during biasing of a) -5 V, b) 0 V, and c) 5 V. Dipole changes are observed, which are influenced by hysteresis.

Specific parameters of PVDF fibres were observed by scanning electron microscopes (SEM). The first – scanning transmission electron microscope (STEM) – FEI Helios NanoLab 660, monitored the fibre composition using a high-angle annular dark-field (HAADF) imaging detector. The accelerating voltage was set to 30 kV and the current 50 pA, which is a sufficient value for electrons that pass through the polymer fibre.

Figure 3a shows the fibre produced at 300 rpm and Figure 3b at 2000 rpm. The purplish tone of the fibre highlights a different structure that needs to be emphasized. In addition to the variety in different fibre thickness, which is different at first glance, the fibre structure affects not only the strength but also the piezoelectric properties. It is also important to mention the imperfections in the form of balls in the fibre in Figure 3b.

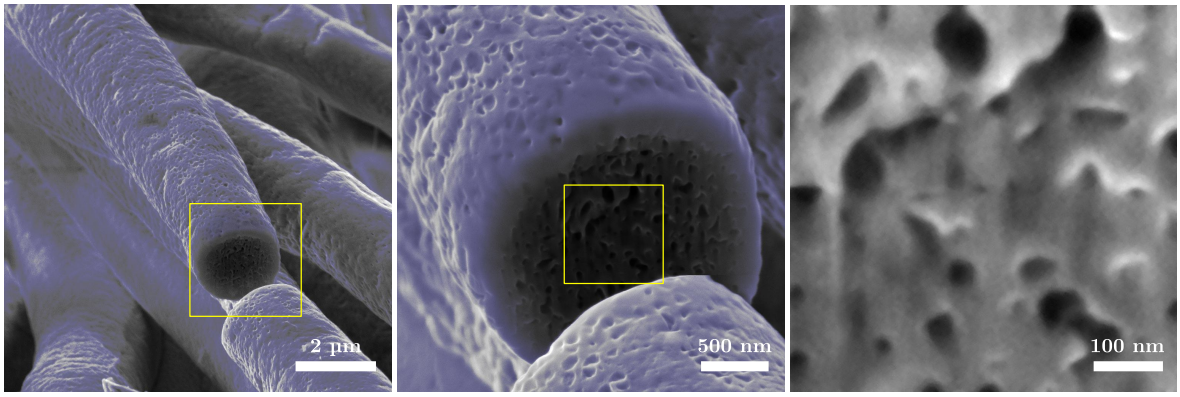


a) b)

Figure 3: Internal fibre structure at drum speeds a) 300 rpm and b) 2000 rpm observed by STEM and HAADF method.

The second – microscope with a focused ion beam (FIB) was the Tescan Lyra3. Here, the fibres were not observed longitudinally, as in the previous case, but as a cross-section. The accelerating voltage was set to 5 kV for SEM observation. When cutting, the FIB high voltage was 30 kV, and for precise fibre separation, the current was 50 pA. This is a small value for cutting, as the fibre had to be cut very finely to avoid defects. A thin layer of 20 nm thick carbon was also coated before observing due to fibre fixation and preventing charge accumulation.

The cross-section in Figure 4 from a view field of 10 to 0.6 µm confirms the fibre's porous structure, which was also indicated during the observation on STEM. The purplish colour here does not describe significant changes in structure but a thin carbon layer [6]. A similar porous structure occurs in both types of fibres.



a) b) c)

Figure 4: Cross-section of one fibre divided into three different magnifications. The yellow border shows the area that was investigated in the following figure. In Figure a) several fibres can be seen, in Figure b) it is already focused on the specific fibre, and its core in Figure c).

Observations of the structure and electrical properties were also supplemented by AXIS Supra Kratos X-ray photoelectron spectroscop (XPS) to determine the fibre's elemental composition and its chemical state. It was focused on the study of the carbon band bonds of the C1s spectrum in Figure 5. The most significant change is almost half the decrease of the $C-C/C-H$ peak [7].

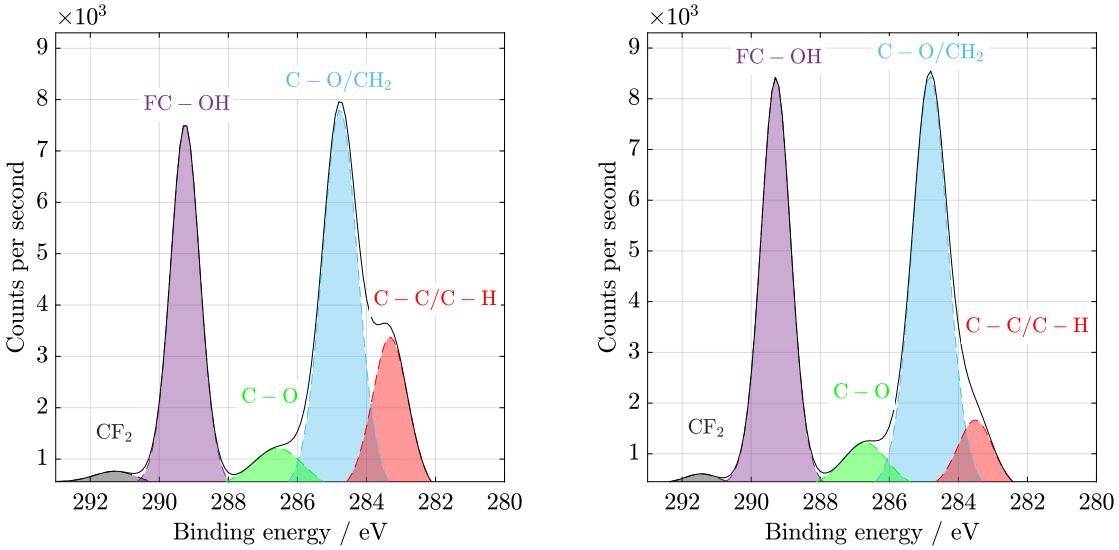


Figure 5: XPS spectra represented the C1s high-resolution energy band's expressed by an envelope, fitted and divided into individual peaks of certain bonds in the material. A more substantial $C-C/C-H$ binding (red peak) is recognised on the fibre produced at a) 300 rpm compared to the fibre produced at b) 2000 rpm.

3 CONCLUSION

This work described the structural, electrical, and chemical characteristics of PVDF. Standard results from publications are based on the entire sheet of nanofibers. The repeatability of these results is often challenging due to the whole specimen's uniformity and many other parameters, which must be constant. The main core of this work was to understand the function of PVDF based on the single fibre and its unique behaviour and properties at the nanoscale, thanks to which it is possible to create a complex structure of an electric energy generator.

ACKNOWLEDGEMENT

Research described in the paper was financially supported by the Grant Agency of Czech Republic under project No. 19-17457S, and by the Ministry of Education, Youth and Sports of the Czech Republic under the project CEITEC 2020 (LQ1601). Part of the work was carried out with the support of CEITEC Nano Research Infrastructure supported by MEYS CR (LM2018110).

REFERENCES

[1] ISLAM, A.; KHAN, A.; SHAKIR, F.; ISLAM, K. Strengthening of β polymorph in PVDF/FLG and PVDF/GO nanocomposites. *Materials Research Express*, 2020, 7, issue 1. ISSN: 2053-1591.

[2] PISARENKO, T. Characterization of PVDF nanofibers created by the electrospinning method. *Proceedings I of the 26th Conference STUDENT EEICT 2020*. Brno: 2020. s. 287-291. ISBN: 978-80-214-5867-3.

[3] XIN, Y.; ZHU, J.; SUN, H.; XU, Y.; LIU, T.; QIAN, C. A brief review on piezoelectric PVDF nanofibres prepared by electrospinning. *Ferroelectrics*, 2018, 526, issue 1, p. 140–151. ISSN: 0015-0193.

[4] UEBERSCHLAG, P. PVDF piezoelectric polymer. *Sensor Review*, 2001, 21, issue 2, p. 118–126. ISSN: 0260-2288.

[5] SENCADAS, V., C. RIBEIRO, I. K. BDIKIN, A. L. KHOLKIN a S. LANCEROS-MENDEZ. Local piezoelectric response of single poly(vinylidene fluoride) electrospun fibers. *Physica status solidi (a)*. 2012, 209(12), 2605–2609. ISSN 18626300.

[6] MOTAMEDI, A.S.; MIRZADEH, H.; HAJIESMAEILBAIGI, F. et al. Effect of electrospinning parameters on morphological properties of PVDF nanofibrous scaffolds. *Progress in Biomaterials*, 2017, 44, issue 3, p. 113–123. ISSN: 2194-0517.

[7] KASPAR, Pavel, Dinara SOBOLA, Klára ČÁSTKOVÁ, Alexandr KNÁPEK, Daniel BURDA, Farid ORUDZHEV, Rashid DALLAEV, Pavel TOFEL, Tomáš TRČKA, Lubomír GRMELA a Zdeněk HADAŠ. Characterization of Polyvinylidene Fluoride (PVDF) Electrospun Fibers Doped by Carbon Flakes. *Polymers*. 2020, 12(12), 2766.