CHARACTERIZATION OF PVDF NANOFIBERS CREATED BY THE ELECTROSPINNING METHOD

Tatiana Pisarenko
Master's Degree Program (1), FEEC BUT
E-mail: xpisar04@stud.feec.vutbr.cz

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

Abstract: The work investigates structure and properties of composite fibers created by the electrospinning method for piezoapplications. Polyvinylidene fluoride (PVDF) was used as a precursor. As an electrospining parameter, the collector speed of 300 and 2000 rpm was selected, which significantly affects the properties of nanofibers. The structure of fibers was investigated by scanning electron microscopy (SEM) using focused ion beam (FIB). Morphology and piezoelectric domains was observed using piezoresponse force microscopy (PFM). Phase composition was identified using Raman spectroscopy and by Fourier-transform infrared spectroscopy (FTIR). Found results are essential for the design and construction of piezoelectric based structures.

Keywords: PVDF, electrospinning, nanofibers, characterization, PFM, FTIR, SEM

1 INTRODUCTION

Piezoelectric materials are materials exhibiting a phenomenon of electrical polarization under mechanical stress. Therefore, mechanical energy is converted to electrical energy. The advantage of piezoelectric polymers compared to piezoceramics is their high flexibility and easy processability. Another advantage is their low toxicity and possible processing into nanostructures. Compared to piezoceramics, piezopolymers have orders of magnitude lower values of piezoelectric parameters.

Polyvinylidene fluoride (PVDF) is a semi-crystalline polymer with high mechanical strength, thermal stability, good chemical resistance and aging resistance. Compared to carbon and hydrogen, fluorine has a larger radius of the van der Waals effect, causing the dipole moment of the PVDF monomer. It also depends on the configuration of the homopolymer chain. PVDF exists in five phases: α, β, γ, δ and ε. The phases α and ε are non-polar, the remaining phases β, γ and δ are polar. Three of these phases illustrates Figure 1. Thus, all polar phases exhibit piezoelectric properties, but most strongly β. The phases differ by the configuration of the chain, the difference between the phases α and β is usually presented in literature as these phases are the most common as result of electrospinning preparation procedure. In this work, the results are shown to prove that electrically active β phase is formed during electrospinning and the domains could be observed in nanometer scale [7].

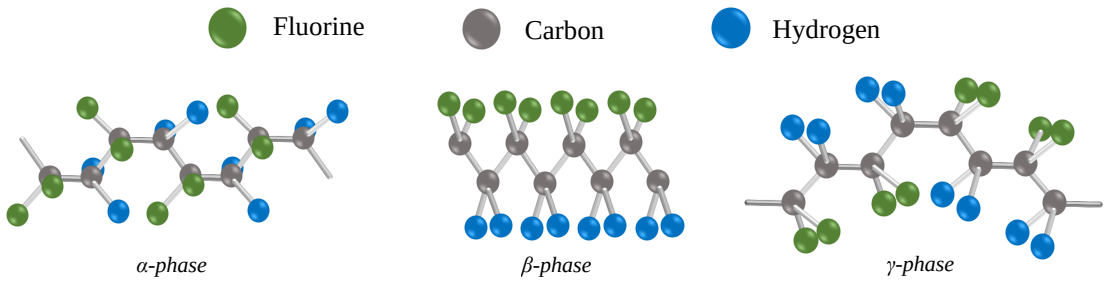


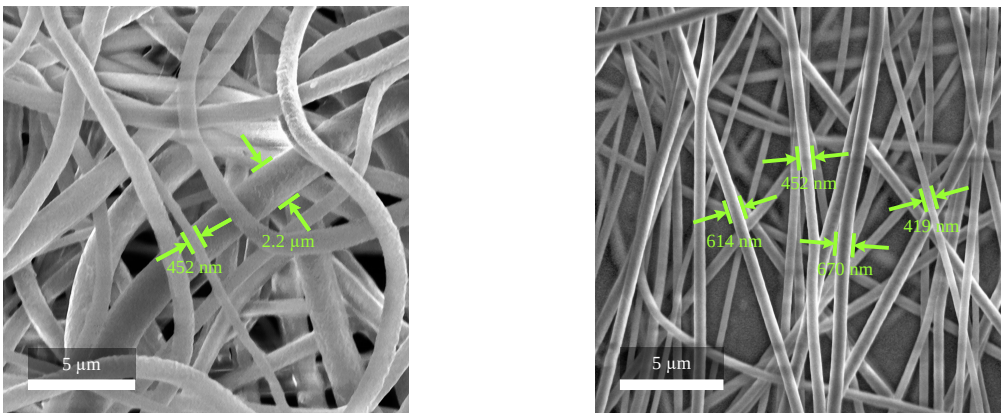
Figure 1: Representation of the chain conformation for the alpha, beta and gamma phases.

Electrospinning is one of the processes by which polymer nanofibers can be prepared. The basic parts of the manufacturing device are a high voltage source, a collector (rotating drum) and an emitter (syringe filled with precursor and needle). Gradual extrusion of the precursor creates a drop of spun material at the end of the needle. Due to the high voltage, the charge is transferred from the needle to the precursor and subsequently repelled, causing the drop to deform. The result of the process is influenced both by the properties of the precursor, as well as by the set parameters and external conditions [8, 6].

2 MATERIALS AND METHODS

The samples were prepared by electrospinning method on the firm gold-coated silicon substrates with square dimension of 10×10 mm. The results after fabrication at collector speed of 300 and 2000 rpm were compared. Piezoresponse force microscopy (NTEGRA Prima microscope) with bias voltage of 5 V was used as characterization method for investigation of morphology and piezoelectric domains. The gold surface was used as a contact for characterization of PVDF-fibers by electrical modes. Scanning electron microscopy (FEI Helios NanoLab 660 microscope) with acceleration voltage of electron beam of 5 kV and current 1.6 nA was used for observation of nanofibers arrangement and FIB at 30 kV and 2.5 nA for cross-section investigating of individual fibers. Raman spectroscopy (WITec alpha300 R) was used to monitor the phase formation described in Section 1. Transmission experiment was performed by Fourier infrared spectrometer Vertex80v, also for phase investigations [4].

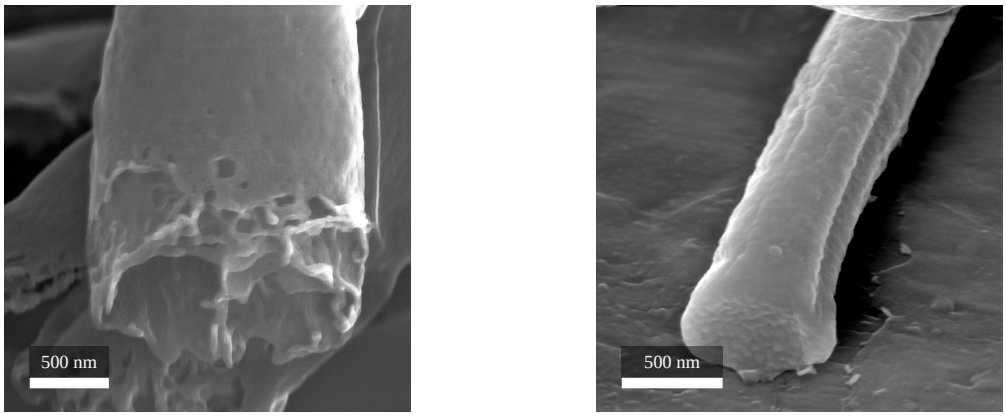
From the results below, several findings affecting the material properties are evident. In Figure 2 and 3, nanofibers are observed by SEM imaging with clearly different thicknesses. It can be seen from Figure 2 that at different collector speeds, the arrangement and shape of the nanofibers is very different. Thus, a higher collector speed causes thinning of the fibers [4]. These differences affect the outcome of piezoelectric behavior. Interestingly, in Figure 2b fiber diameters is relatively similar compared to Figure 2a where fibers vary from 452 nm to 2.2 µm.



a) b)

Figure 2: SEM image of PVDF fibers prepared at a) 300 rpm and b) 2000 rpm collector speed. The differences in fabrication are particularly noticeable in the arrangement and thickness of the fibers.

In addition to the different nanofiber thicknesses, the individual fibers in Figure 3 are seen with greater view field. There is also a different porosity visible in the cross-section of these fibers. Higher porosity predominates in the fiber in Figure 3a with pore size up to 500 nm in diameter [3].



a) b)

Figure 3: Individual fibers of PVDF material. Fiber a) with 300 rpm fabrication collector speed shows an increased porosity compared to fiber b) with 2000 rpm fabrication collector speed, where the pores are almost noticeable.

Typical Raman spectra of PVDF material in Figure 4 describes a molecular parameters in the range of 150 cm^{-1} to 3150 cm^{-1}. Attention was focused especially on the spectrum in the range of 760 cm^{-1} to 880 cm^{-1}, where α and β phase peaks are illustrated in detail and differences in their ratio are measured.

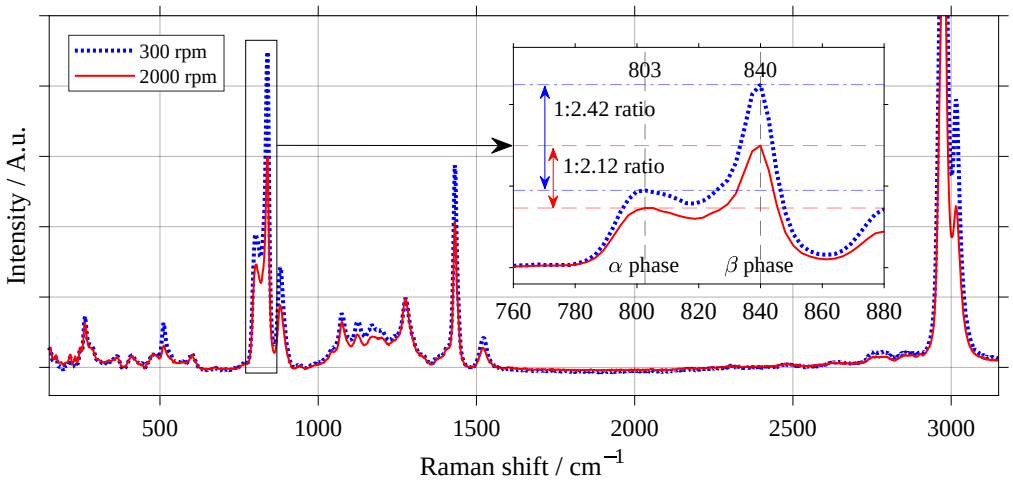


Figure 4: Nanofibers PVDF material investigated using a Raman spectroscopy with focus to 760 cm^{-1} to 880 cm^{-1} region.

Another measurement using piezoresponse force microscopy monitors the exact morphology (Figure 5a) of the fiber and its electrical parameters (Figure 5b), which vary mainly along its perimeter up to 1 nA. In this case the presence of electrostatic interaction should be taken into account. By this reason it is possible to follow only qualitative difference of the fibers appearance after applying large voltages. The response of vertically oriented domains is observed in Mag-signal.

Spectra of FTIR in Figure 6 shows dependence of the transmittance on the wavelength of the whole sample between 1500 cm^{-1} to 400 cm^{-1}. The β phase is strongly visible at 840 cm^{-1} [1].

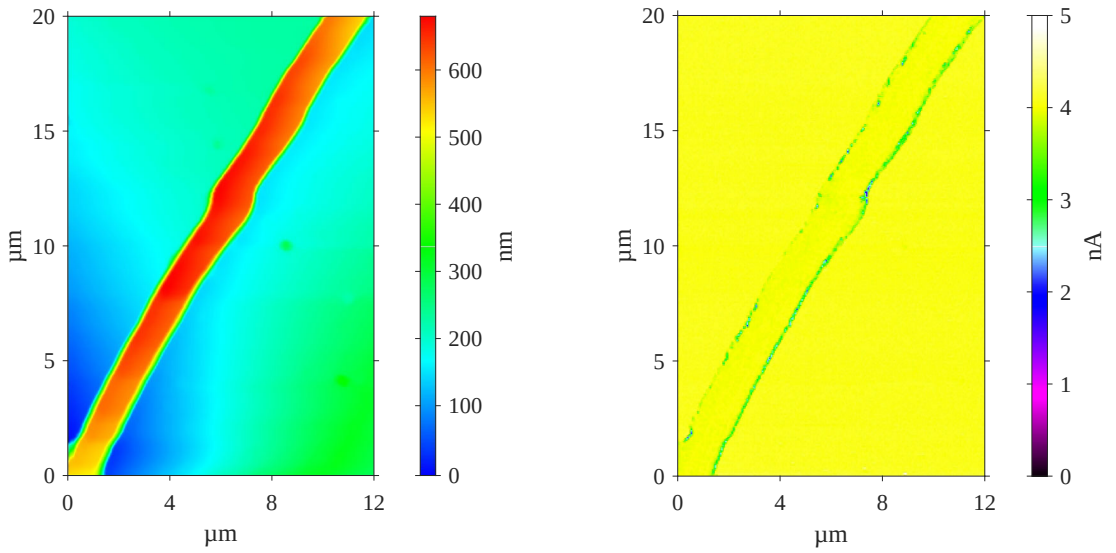


Figure 5: Measured a) morphology and b) electrical response of vertically oriented domains of single fiber by PFM method.

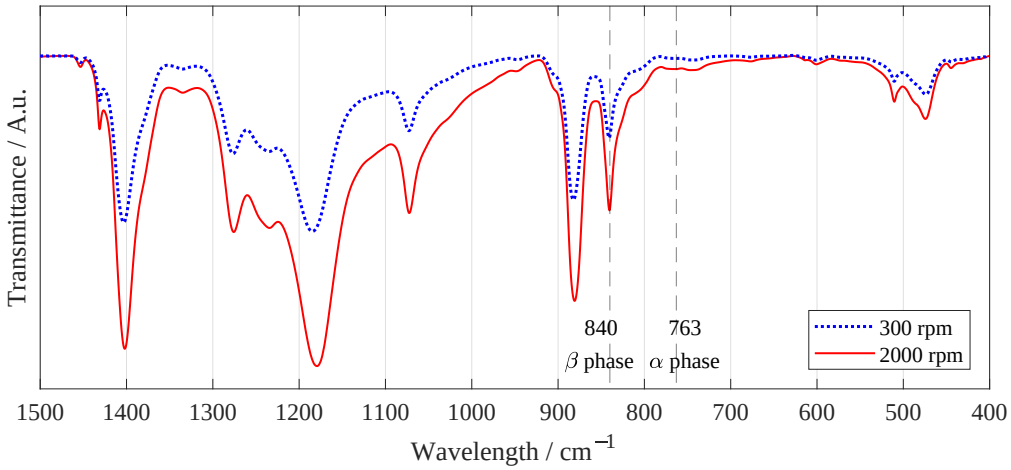


Figure 6: FTIR transmittance spectrum of PVDF nanofiber sample with 300 rpm and 2000 rpm collector speed. Emerging phases α and β are indicated by a dashed line.

3 CONCLUSION

Structural, molecular and electrical properties of PVDF nanofibers at different collector speed were measured. This characterization of nanoelectromechanical behavior is essential for design of NEMS and MEMS on the basis of new prospective materials. The resulting findings show that after fabrication at 300 rpm collector speed the structure is composed of non-uniform electrospun fibers. Also, the diameter and orientation of these observed nanofibers are not completely uniform and have higher porosity unlike fibers with fabrication at 2000 rpm collector speed, which are more uniform. However, the uniformity of nanofibers can be achieved by many other changes, for example by increasing the amount of polymer in electrospinning, leading to more interactions between polymer chains in solution [6].

According to FTIR and Raman spectroscopy was evaluated the phase composition and all α, β and γ are present. Raman spectroscopy provides information from the surface and near-surface area. Whereas FTIR spectra were collected in trasmission mode at the samples of tens microns. According to calculations from FTIR, the thinner fibers has larger amount of β phase [2]. For the PFM, the response of vertically oriented domains is observed mainly on the edges of the fiber where a variation of current occurs. The results of this characterization of PVDF nanofibers contribute in a relatively new scope in the form of better fabrication processes of this promising material.

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