Tailoring Piezoelectricity of PVDF Fibers with Voltage Polarity and Humidity in Electrospinning

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Abstract : Piezoelectric polymers have received great attention in smart textiles, wearables, and flexible electronics. Their potential applications range from devices that could operate without traditional power sources, through self-powering sensors, up to implantable biosensors. Semi-crystalline PVDF is often proposed as the main candidate for industrial-scale applications as it exhibits exceptional energy harvesting efficiency compared to other polymers combined with high mechanical strength and thermal stability. Plenty of approaches have been proposed for obtaining PVDF rich in the desired β -phase with electric polling, thermal annealing, and mechanical stretching being the most prevalent. Electrospinning is a highly tunable technique that provides a one-step process of obtaining highly piezoelectric PVDF fibers without the need for post-treatment. In this study, voltage polarity and relative humidity influence on electrospun PVDF, fibers were investigated with the main focus on piezoelectric β-phase contents and piezoelectric performance. Morphology and internal structure of fibers were investigated using scanning (SEM) and transmission electron microscopy techniques (TEM). Fourier Transform Infrared Spectroscopy (FITR), wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) were used to characterize the phase composition of electrospun PVDF. Additionally, surface chemistry was verified with X-ray photoelectron spectroscopy (XPS). Piezoelectric performance of individual electrospun PVDF fibers was measured using piezoresponse force microscopy (PFM), and the power output from meshes was analyzed via custom-built equipment. To prepare the solution for electrospinning, PVDF pellets were dissolved in dimethylacetamide and acetone solution in a 1:1 ratio to achieve a 24% solution. Fibers were electrospun with a constant voltage of +/-15kV applied to the stainless steel nozzle with the inner diameter of 0.8mm. The flow rate was kept constant at $6mlh^{-1}$. The electrospinning of PVDF was performed at T = 25°C and relative humidity of 30 and 60% for PVDF30+/- and PVDF60+/- samples respectively in the environmental chamber. The SEM and TEM analysis of fibers produced at a lower relative humidity of 30% (PVDF30+/-) showed a smooth surface in opposition to fibers obtained at 60% relative humidity (PVDF60+/-), which had wrinkled surface and additionally internal voids. XPS results confirmed lower fluorine content at the surface of PVDF- fibers obtained by electrospinning with negative voltage polarity comparing to the PVDF+ obtained with positive voltage polarity. Changes in surface composition measured with XPS were found to influence the piezoelectric performance of obtained fibers what was further confirmed by PFM as well as by custom-built fiber-based piezoelectric generator. For PVDF60+/- samples humidity led to an increase of β -phase contents in PVDF fibers as confirmed by FTIR, WAXS, and DSC measurements, which showed almost two times higher concentrations of β-phase. A combination of negative voltage polarity with high relative humidity led to fibers with the highest β -phase contents and the best piezoelectric performance of all investigated samples. This study outlines the possibility to produce electrospun PVDF fibers with tunable piezoelectric performance in a one-step electrospinning process by controlling relative humidity and voltage polarity conditions. Acknowledgment: This research was conducted within the funding from m the Sonata Bis 5 project granted by National Science Centre, No 2015/18/E/ST5/00230, and supported by the infrastructure at International Centre of Electron Microscopy for Materials Science (IC-EM) at AGH University of Science and Technology. The PFM measurements were supported by an STSM Grant from COST Action CA17107.

Keywords : crystallinity, electrospinning, PVDF, voltage polarity

Conference Title : ICNNE 2020 : International Conference on Nanotextiles, Nanotechnology and Electrospinning

Conference Location : New York, United States

Conference Dates : October 08-09, 2020