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ELECTROSPINNING AS THE FABRICATION TECHNOLOGY FOR THE ENERGY HARVESTING COMPOSITES

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Abstract: *This paper presents the electrospinning technology as used for the fabrication of the energy harvesting composites, including the review of ceramic-based and polymer-based piezoelectric composites and their electrical outputs for the energy harvesting applications. Energy harvesting is a method for obtaining electrical energy from the environment to be used for powering autonomous electronic devices. Current trend of reducing the size of the devices has led to the increasing number of new energy harvesting materials. Basic principles of fiber fabrication via electrospinning were presented, as well as material characterization methods. The special focus was given to the electrical properties of energy harvesting composites with a review of methods for detecting and measuring electrical outputs of these materials. Electrical performance of the electrospun piezoelectric nanogenerators was discussed.*

Keywords: *Energy Harvesting, Electrospinning, Piezoelectric Composites, Kinetic Energy Harvesting, Piezoelectricity.*

1. INTRODUCTION

Piezoelectric properties of the electrospun materials have been studied for applications in nanogenerators [1], [2], different sensors [3], including smart and wearable sensors and devices [4]–[8], for the monitoring of mechanical and acoustic signals [9], self-powered tissue cultures [10], or novel treatments [1], [11], [12], that is, in diverse biomedical applications [13].

Piezoelectric nanogenerators can exhibit high energy conversion efficiency [14]–[16]. Development of the efficient devices for energy harvesting is of the utmost importance for the development of micro-electro-mechanical systems (MEMS) [7], [8], [17], and especially related to the biomechanical and biochemical energy harvesting [18], [19].

There are different production technologies for piezoelectric materials [20], but the electrospinning is low cost and rather simple technology that can efficiently fabricate vast variety of materials and related structures, including piezoelectric materials [20], [21].

Unlike traditional methods of preparing the piezoelectric materials, which required additional steps to improve the piezoelectricity, the electrospinning method, that was first patented in 1934 by Anton Formhals [22], [23], is now extensively used for production of the piezoelectric nanofibers. Original electro-spinning process was further improved through the change in collectors, distance between polymer jet and collector and differences in voltage supply, thus creating new, near- and far-field electrospinning technologies [17], [24]–[26]. Initially, instead of the plate-like collectors, a revolving collector was introduced as a collector [26], [27]. Further control improvements were investigated with the use of fast-spinning collectors in the shape of drums [26], [28], wheel-like disks [29], and wire drums [30], with varying degrees of effectiveness.

In this paper, the review of electrospinning technology for the fabrication of piezoelectric materials is presented, including the mostly used composites. Material properties, especially electric properties and the dependence on the fabrication method are discussed. Advanced material characterization techniques, FTIR, XRD, PFM, are described. Different approaches in characterization of piezoelectric properties are evaluated, including artifacts used in output signal measuring. Electrical performance of the electrospun piezoelectric nanogenerators is discussed.

2. ELECTROSPINNING PRINCIPLE

The process of electrospinning was long discovered with first polymer filaments utilizing electrostatic force [22], [23]. In its most basic version, the electrospinning process consisted of a pipette to contain the polymer solution, two electrodes, and a DC voltage source in the kV range. Because of the high voltage, a polymer drop from the tip of the pipette was pulled into a fiber. The jet was electrically charged, and the charge caused the fibers to bend in such a way that the diameter of the polymer fiber decreased with each loop. The fibers were gathered in the form of a web of fibers on the surface of a grounded target. This is represented in Figure 1 [23].

Here, a syringe pump maintains a constant flow rate of polymer solution which is dispensed through a needle connected to a high voltage supply and acts as a cathode, whereas collector acts as an electrode that collects electrospun nanofibers.

Like other technologies, electrospinning does not have only one principle. For example, collector shown in Figure 1 does not have to be a plate. It can also be a drum collector as shown in [26]. In general, there are two types of electrospinning: near-field (NFES) and far-field electrospinning (FFES).

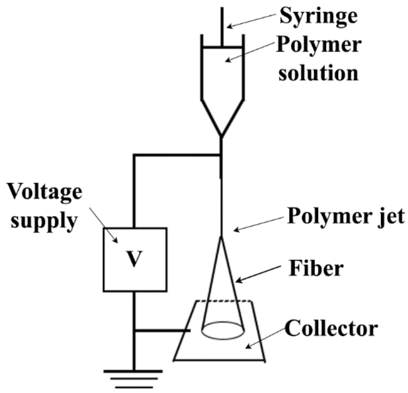

Figure 1. Schematic diagram of electrospinning process [23]

2.1 Far-field electrospinning

As it was already mentioned, a typical electrospinning setup includes a syringe pump, polymer solution, a dispense needle, high voltage supply unit and a collector [17], [24], [25]. A strong electrostatic field is formed between the needle tip and the collector electrode when a high voltage is applied. The electrostatic force draws the polymer melt from the needle and is balanced by the fluid's surface tension force. This produces a droplet with a conical form, known as a Taylor cone. When the electrostatic force exceeds the surface tension force, the droplet ejects a thin liquid/melt jet toward the collecting electrode. If the collection electrode is situated far enough away from the needle tip (tens of centimeters), the jet will undergo a whipping and chaotic process to deposit nanofibers randomly on the collector electrode, as is the case with traditional far-field electrospinning (Figure 2).

The average inner diameter of the dispense needle for far-field electrospinning is a few hundred micrometers, the applied voltage is several tens of kilovolts, and the needle-to-collector distance (*h*) is tens of centimeters. Main characteristic of the far-field electrospinning is the chaotic and random distribution of nanofibers on collector.

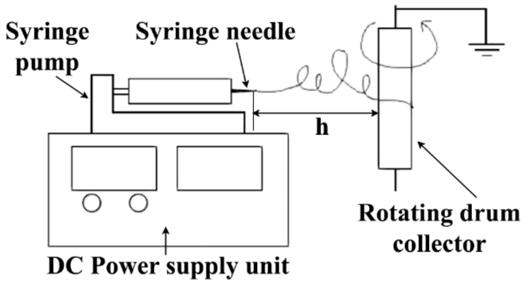

Figure 2. Schematic diagram of the electrospinning setup

The deposition of the nanofibers has significant influence on the energy generation efficiencies of the nanofiber nanogenerators. Thus, many attempts were made in order to control the deposition of nanofibers. At first, a rotating collector was added as a collector instead of a plate-like collectors, as shown in Figure 2 [26], [27]. Further enhancements of the control were examined with the use of fast-spinning collectors in the shape of drums [26], [28], wheel like disks [29] and wire drums [30], which had a various levels of success.

2.2 Near-field electrospinning

Another approach for controlling the deposition of nanofibers is near-field electrospinning, in which the needle-to-collector distance (parameter *h* shown in Figure 2) is decreased to improve the controllability of a fiber deposition. The needle-to-collector distance is decreased to a few millimeters, and the applied voltage is reduced to around 1 kV. By exploiting the stable liquid jet area, the reduced distance and enhanced electric field (as a result of considerably shorter distances), controlled nanofiber deposition on the collector is enabled. A dip-pen method was used in the early stages of the near-field electrospinning process, as illustrated in the experimental findings [31].

To refill the system in this scenario, repeated dips into a polymer solution were required. Continuous near-field electrospinning was later developed utilizing a syringe rather of a probe, as illustrated in [32], so that polymer solution could be fed constantly to deposit continuous nanofibers. These novel changes enable NFES to retain the continuous features of traditional FFES while providing greater control over deposition sites. These and other related NFES techniques can be used to build nanofiber nanogenerators previously unattainable by FFES, such as parallel arrays of nanofibers for nanogenerators [17].

3. MATERIAL AND STRUCTURAL CHARACTERIZATIONS

As piezoelectric properties strongly rely on the material structure, tools and techniques for its analysis are necessary to characterize the crystal/molecular structure for optimal parameters. Instruments such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis (XRD) and piezoresponse force microscopy (PFM) have been used for this purpose and will be briefly described in this chapter.

3.1 FTIR

FTIR Fourier transform infrared spectroscopy (FTIR) can be used to characterize both the dipole orientation and crystallographic structure of nanofibers. Mandal et al. [26] used FTIR to examine the dipole orientation of electrospun P(VDF-TrFE) nanofibers. They have discovered that the dipoles were aligned in the direction of the electrical field during the electrospinning process. A comparison between the FTIR spectra of an as-spun fiber and a heat treated (above the Curie temperature to assure the random dipole alignment) electrospun fiber resulted in a different absorbance of perpendicularly polarized light. Baji et al. [33] also confirmed the presence of the crystal beta-phase using FTIR.

3.2 XRD

The X-ray diffraction (XRD) technique is commonly used to examine the crystalline structure of materials. Using XRD, Baji et al. [33] observed PVDF fibers fabricated by far field electrospinning. The beta-phase was found to be the most prevalent in electrospun PVDF nanofibers, while other crystalline forms were also detected. Smaller diameter nanofibers, fabricated via electrospinning, were found to have higher contents of beta-phase probably as a consequence of the stretching effect. McCann et al. [34] have also utilized XRD to analyze the structure of polycrystalline barium titanate nanofibers.

For PZT fiber based piezoelectric composites, XRD can be used to detect the presence of the perovskite phase of the material, being essential for the piezoelectric effect [35].

3.3 PFM

Piezoelectric force microscopy (PFM) is based on the detection of a voltage induced deformation of the piezoelectric structure. The PFM principle can be compared to AFM (atomic force microscopy), bringing a micro tip in contact with the surface while applying a sinusoidal voltage. In the case of a piezoelectric material, direction parallel to the PFM voltage direction, leads to a detectable deformation of the material due to the piezoelectric response [17]. PFM, compared to other characterization tools, is well suited for the investigation of individual nanofibers, as it allows piezoelectric measurements at the local level. Isakov et al., 2010 [36] used PFM to generate images of triglycine sulfate based nanofibers. Similar analyses were conducted by Baji et al. for electrospun PVDF nanofibers [33]. PFM has also been used for the characterization of PZT fibers, for example to characterize the polarization domains of the electrospun PZT fibers [37].

4. ELECTRICAL PROPERTIES OF ENERGY HARVESTING COMPOSITES PRODUCED BY ELECTROSPINNING

When a mechanical stress is applied to the piezoelectric materials, it causes transitory surface charge fluctuations and, as a result, electrical potential variations in the material. The output voltages can vary in the range of hundreds of mV and up to a hundreds of V, with the peak currents usually in nA ranges and power delivered by the device in mW [17], [38]. Besides the open-circuit output voltage, short-circuit current and power measurements, a significant criterion for selecting the proper piezoelectric nanofiber nanogenerators for energy harvesting applications is the piezoelectric energy conversion efficiency. This may be determined as the ratio between the measured output electrical power, calculated as the product of measured open-circuit voltage and closed-circuit current, and the estimated generated mechanical energy from the applied strain [17]. Furthermore, it is important to quantify several other characteristics of the piezoelectric materials as relevant for their application. These include impedance, permittivity, dielectric properties at different frequencies, piezoelectric displacement, resonance, and piezoelectric coefficients d_{33} and d_{31}.

4.1 Typical methods for measuring the electrical properties of piezoelectric materials

Generally, the properties of piezoelectric materials may be characterized using commercially available measurement equipment. For example, the dielectric constant and dielectric loss of nanogenerators were measured by an impedance analyzer (Alpha-A High Performance Frequency Analyzer, Novocontrol) between 102 and 106 Hz [39]. The impedance and dielectric constant of the nanocomposite fibers in [40] were measured by an impedance analyzer (Agilent 4194A) between 0.1 Hz and 10 kHz. Other commercial impedance analyzers, Solartron 1296, HP/Keysight 4294A and N4L PSM3750, were also used in the works of Cain et al. [41], Briscoe et al. [42] and Chen et al. [43] respectively. Moreover, a custom built impedance analyzer was used in [44] to measure the impedance of PVDF nanofiber mats as a function of the frequency between 70 Hz to 4 kHz at the room temperature. The method and measuring circuit for *in situ* measurements of the piezoelectric voltage coefficient, g_{31}, which shows the voltage generated by a piezoelectric under applied force, along with measurements of g_{32} were described in [45]. Furthermore, the frequently reported d_{33} and d_{31} piezoelectric coefficients can be determined using the well-known Berlincourt method comprehensively described by Stewart et al. [46]. The other measuring protocols and practices for characterization of piezoelectric materials are summarized in [47] and include testing at high temperatures, electromechanical coupling factor, relative permittivity, dielectric loss, ferroelectric hysteresis and material degradation.

Additionally, recent publication by Alexander et al. [48] showed that the atomic force microscopy (AFM), depending on the different forces between the probe tip and sample, can also be used for extracting electrical properties from the piezoelectric materials. The AFM electrical modes, which are all based on probing of the electrical force, may be used to measure variations of electrostatic forces, surface potentials and dielectric permittivity. They include non-contact electrostatic force microscopy (EFM), piezo response force microscopy (PFM), Kelvin force microscopy (KFM), probing of capacitance gradients as well as Maxwell stress microscopy.

Furthermore, energy harvester experiment setups are mostly custom-built combination of several devices and measuring instruments. They usually include signal generators, synthesized function generators, amplifiers, electrodynamic shakers, dynamic mechanical analyzers (DMA), accelerometers, digital voltmeters, ammeters, charge amplifiers, electrometers, digital oscilloscopes, rheostats, and laser-vibration meters [16] [49] [40] [47]. In addition, the control of these experimental rigs is usually done manually by taping the piezoelectric device [44] [16] or with a custom LabView [50] code or the proprietary software of the Keithley measurement system [51].

4.2 Artifacts in measured output signals

Electrical outputs generated by piezoelectric nanogenerators are usually extremely small and may have very low signal-to-noise ratio. This is particularly challenging when working with the small single nanofiber constructions [17]. For example, while measuring output signals from the nanogenerators, changes in the capacitance could result from a distance between the contact electrodes and potential electrical coupling of the measuring device. These changes may be larger than the actual nanofiber signal. Furthermore, the noise from the surrounding experimental environment and different resistances of the measuring equipment, can introduce artifacts in the signal. As a result, a measured signal must be filtered to remove the noise. Moreover, it is a good practice to conduct the additional tests while measuring the output signals. One of the tests is the switching polarity test, which shows if the polarity of the nanogenerator is fixed, i.e., connecting the measuring instrument's wires shouldn't influence the direction flow of the electrons. When altering the polarity of the measuring equipment, it should result in the output signals being reversed. Additionally, it is important to check the linear superposition principle, which should result in voltage response as the sum of the devices connected in series with the same polarity or a zero-voltage response if the devices are with opposite polarity [17].

The current "gold standard" is "*BS EN 62830-3:2017*" that describes the measurement protocols for electrical characterization of flexible energy harvesters. It includes tests for short circuit current (I_{SC}), open circuit voltage (V_{OC}), power delivered to a resistive load, and optimal electrical load. Additionally, a universal and easy-to-use standard for the voltage measurement of piezoelectric devices was recently proposed by Su et al. [52]. In their work, the inner resistance of voltmeter was set to be larger than a critical value in terms of impedance, loading frequency and accuracy requirement of measured voltage, thus making it a resistance-independent voltage measurement method.

4.3 Electrical performance of electrospun piezoelectric nanogenerators

According to some reports, electrospun nanofibers have the potential to exhibit high energy conversion efficiency in nanogenerator applications such as PVDF [14], [53] or PZT nanofibers [16]. Overview of the commonly used piezoelectric materials and their electrical outputs for energy harvesting applications is given in Table 1.

In the experiments conducted by Chang et al. [14] PVDF nanofiber nanogenerators were tested by varying a diameter from 600 nm to 6.5 mm and a length from 100 to 600 mm. The average conversion efficiency was calculated to be 12.5%, although the maximum voltages were ~30 mV. Even higher conversion efficiency of 13.62% was reported in [54] for a membrane device of randomly oriented electrospun PVDF nanofibers with the area of 2 cm^2 at a compression frequency of 10 Hz while generating up to 2.21 V. This is a considerably higher value than the conventional devices made from piezoelectric PVDF thin films (0.5–4%) or commercial PVDF thin films (0.5–2.6%) tested under the same conditions [17]. In general, nanogenerators with the smaller diameters have higher energy conversion efficiency even if the piezoelectric properties change due to the slight differences in the processing conditions. Recent work of Fang et al. [55] showed that using the needle electrospinning method to produce the nanofiber web from 16% PVDF solution can increase the conversion efficiency by 14% compared to nanofibers produced by disc electrospinning but the voltage and current dropped from 2.6 V to 2.05 V and 4.5 μA to 3.12 μA. Also, increasing PDVF solution to 20% led to a similar electrical output. Some of the nanogenerators with the highest voltage outputs were produced by Shi et al. [53] and Guo et al. [56]. They demonstrated that by combining the 15wt% of $BaTiO_3$ nanoparticles with 0.15wt% of graphene nanosheets the generated open-circuit voltage was 11 V and electric power 4.1 μW under a compression frequency of 2 Hz and 4 mm strain. However, during the finger pressing, the nanogenerator managed to produce a peak voltage of 112 V. Moreover, the hybrid nanogenerator produced by pairing the two components: electrospun silk nanofibers and PVDF [56], managed to generate the open-circuit voltage of 500 V, short-circuit current of 12 μA, and power density of 0.31 mW cm^{-2}, respectively. The list of other electrical outputs of nanogenerators with various material combinations is given in Table 1.

Electrical performance of the piezoelectric materials is of the utmost importance for several other applications, besides energy harvesting. Their possibility to influence a healing process of the tissues has been proven, even though this approach is still largely in its research phases. For example, bone healing process under the influence of the electric stimulations has been long proven. Such approach is already widely used in regenerative clinical medicine, but only by using externally applied devices that stimulate the tissues over the skin. Novel piezoelectric materials has opened up new directions in these treatments, due to the possibility to harness the energy stored within the material itself and use it for some type of treatments that otherwise would engage some externally powered device. Further research in the development and application of the piezoelectric materials will surely enable significant advancements in several fields, including medical treatments in regenerative medicine.

Table 1. Overview of the commonly used piezoelectric materials and their electrical outputs for energy harvesting applications

Fabrication method	Material combination	Typical applications	Output power/voltage/current	Ref
Disk electrospinning needle electrospinning	PVDF in DMF-acetone solvent	Nanogenerators for microelectronic devices, powering LEDs, photodetectors, smart textiles	Voltage: 1 – 3 V Currents: 1.4 – 4.5 μA	[55]
Electrospinning	BNT-ST embedded into PVDF-TrFE	Power for wearable devices or sensors for health monitoring	Voltage: up to 3 V	[57]
	Coated zinc oxide/PVDF	Human motion tracking	Voltage: 83.3 mV/(m/s) Power: 134 nW	[4]
	BaTiO3/PVDF	Human motion monitoring, wearable electronics	Voltage: 0.1 V Current: up to 300 nA	[58]
	Polycarbone acrylate di-epoxide (PCADE)/PVDF	Energy harvesting, biosensors	Not reported	[59]
	GK Graphite powder/PVDF	Biosensors	Voltage: 1.5 V, Current: 100 nA, Power: up to 5.5 nW	[60]
	PVDF/PZT	Nanogenerators		[17]
	NFC, NFCh, CNC, MFS	Human motion monitoring, nanogenerators, smart materials	Voltages: up to 500V, Current: up to 12 μA Power: up to 0.31 $mWcm^{-2}$	[56], [61]
	Ag/PVDF	Sensors	Not reported	[62]
	TiO2	Solar cells, Li-ion batteries, supercapacitors, fuel cells	Not reported	[63]
	PLLA	Strain sensors, human motion energy harvesting	Voltage: 0.55 V Current: 230 pA Power: 19.5 nW	[64]
Far-field electrospinning	PZT	Biosensors, medical treatments with small currents	Voltage: up to 1.6 V	[16], [50], [51]
Electrospinning (far or near field)	PVDF	Harvesting energy from human movements, biosensors	Voltages: 2.21 V [54], 30 mV [14], 24.6 V [49], 11 V to 112 V [53]	[14], [31], [38], [49], [53], [54], [65], [66]
Electrospinning	CNT/PVDF	Mechanical motion control	Voltage: 9 V Current: 0.01 A	[67]

5. CONCLUSION

In this paper the electrospinning principle is briefly described and its application in energy harvesting, as the method for obtaining energy from environment. Furthermore, the material characterization techniques, FTIR, XRD, PFM, commonly used for determining the composite structures, are described. Brief review of piezoelectric composite materials, their application and electrical characteristics was given. The review of typical methods for detecting and measuring the electrical outputs and electrical performance of electrospun piezoelectric nanogenerators were presented, with artifacts used in output signal measuring.

Unlike traditional methods of preparing the piezoelectric materials, which required additional steps to improve the piezoelectricity, the electrospinning method can be efficiently used for production of the piezoelectric nanofibers. Through mechanical stretching and poling of the polymer solution, this method leads to an increase in the electrical potential of the material due to the higher content of β-phase. Modern electrospun piezoelectric nanofiber devices have been vastly improved by modifying polymers and forming of composite structures, in order to enhance their piezoelectric properties.

Advanced characterization techniques such as standard or customized FTIR, XRD, PFM technologies can provide valuable directions for improvements of the piezoelectric materials and their properties, as well as for the design of novel composites with piezoelectric properties.

Further research is important, related to piezoelectric materials, their fabrication technologies and characterisation methods, considering that the need for energy in the world constantly grows, especially for self-sustaining devices, also including energy generation and storage systems.

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