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Piezoelectric properties of PVDF/MWCNT nanofiber using near-field electrospinning

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ABSTRACT

This study reports the use of near-field electrospinning to fabricate polyvinylidene fluoride (PVDF) piezoelectric nanofibers mixed with multiwalled-carbon nanotubes (MWCNT). This study also investigates the mechanical strength and piezoelectric characteristics of a single PVDF/MWCNT nanofiber. The morphology and polarization intensity of piezoelectric fiber can be controlled by adjusting the traveling velocity of the *X*–*Y* stage, the DC voltage, and the gap between the needle and collection plate. The optimal parameters of the PVDF solution, such as the PVDF powder weight percentage and MWCNT content, were also determined. X-ray diffraction (XRD) analysis shows a high diffraction peak at $2\theta = 20.8^{\circ}$ in the piezoelectric crystal β-phase structure. ANSYS finite element analysis (FEA) software with coupled field analysis was used to realize piezoelectric actuation behavior of the PVDF fibers. A nano-indentation test (NanoIndenter XP System, MTS co.) was used to investigate Young's modulus of the PVDF fiber. Finally, the fixed–fixed beam structures of PVDF composite fibers were tested using a DC voltage supply. Comparing the polarized fiber with non-polarized fibers, the measurement of the center displacements as a function of electric field was conducted and characterized.

1. Introduction

Polyvinylidene fluoride (PVDF) is a popular piezoelectric polymer because of its high flexibility, biocompatibility, and low cost. These features make PVDF attractive for energy conversion applications involving microelectric-mechanical devices, electromechanical actuators, and energy harvesters [1]. Several researchers have studied PVDF actuators in the form of thin film [2–4]. However, only a few studies have examined single PVDF fibers [5]. The current study presents a method of controllable electrospinning based on a new type of near-field electrospinning (NFES). This method can potentially be scaled down to the nanometer scale and form any shape for various sensing and actuation applications. The main advantages of NFES-formed PVDF/MWCNT composite fibers are their excellent properties, including structure scalability, greater flexibility, and greater piezoelectric strain constant ($d_{33} \sim -57.6$ pm/V) [6] compared with commercially available PVDF thin films ($d_{33} \sim -15$ pm/V) [7].

PVDF is a semicrystalline polymer consisting of four crystalline phases: α, β, γ, and δ. The non-polar α phase is most commonly found in commercially available films. Because the dipole moments in this phase have a random orientation, they cancel each other out. The β phase has dipole moments pointing in the same direction; thus, the β phase is responsible for the piezoelectric properties of PVDF polymer. Yee et al. announced a method of electrospinning PVDF fiber [8]. In a typical electrospinning process, fibers are emitted from a Taylor cone when the solution is subjected to a high-voltage electrostatic field [9]. As electrostatic force stretches the fiber, it bends into a complex path, causing chaotic whipping of the fiber jet [10]. As the fibers form in the electrospinning process, they are unstable in nature. Highly aligned fibers are therefore difficult to achieve using this method. Fennessey and Kim investigated different techniques to align electrospun fibers using a rotating collector [11,12], and Wang [13] modified the electric field. Other researchers improved the electrospinning process with fundamental physics and chemistry for better control [14].

A direct-write electrospinning technique using NFES [15,16] was developed to achieve controllable fiber deposition for various materials. Unlike the conventional electrospinning process, NFES only needs a small electric field to produce continuous fibers with fine diameters. Chang et al. reported electrospinning PVDF fibers

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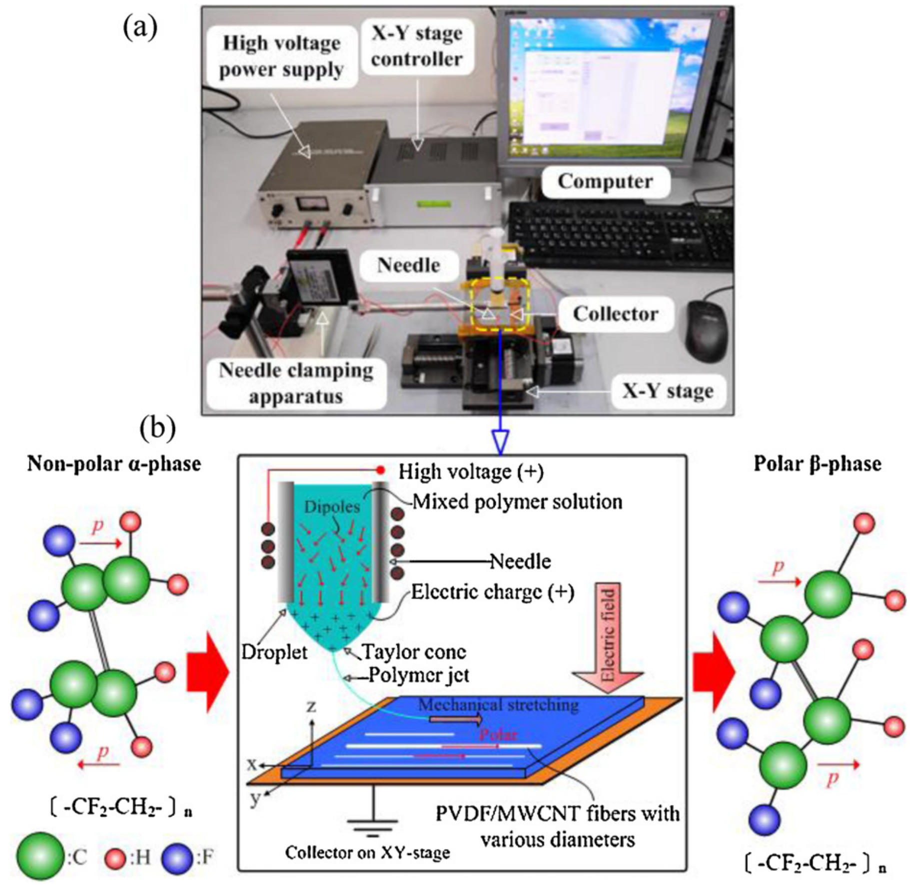

Fig. 1. (a) The photo of near-field electrospinning setup. (b) Direct-write PVDF fiber process with in situ poling: the dipoles in the non-polar, α-phase PVDF could be stretched and oriented by a high electrical field with in situ strong mechanical stretching to become the polar.

with high energy conversion efficiency for power handheld electronics through body movements [17]. This approach can be used to form PVDF fibers with in situ electrical poling. Therefore, electrospinning a PVDF solution can transform the non-polar α phase into the polar β phase [8]. Furthermore, adding modified carbon nanotubes (CNTs) to reinforce PVDF fibers can enhance the crystallinity of the β phase. Zhang et al. [18] showed that CNTs can facilitate the growth of the crystalline β phase in PVDF composite fiber, enhancing piezoelectric properties.

This study demonstrates the controllability of electrospun PVDF fibers using NEFS. This method reduces the electrode-to-collector distance, which is typically on the order of 10 cm in the conventional electrospinning process, to less than 1 mm. This is a powerful method to direct-write PVDF fibers with high controllability. The optimal parameters of the PVDF solution, such as weight percentage of the PVDF powder and multiwalled carbon nanotubes (MWCNTs), were determined to obtain the optimal β-crystalline structure and surface morphology. Under the strong extensional force in NFES process, the unique crystalline structures of the PVDF/MWCNT in orderly aligned PVDF fibers resulted by the cooperative orientation of the MWCNTs and PVDF chains were aligned in sequence along the fiber axis, which promotes the nucleation of highly oriented β-form extended-chain crystallites at the interface.

X-ray diffraction (XRD) analysis of the PVDF composite fibers shows a high diffraction peak at $2\theta = 20.8^{\circ}$ in the piezoelectric crystal β-phase structure. A single piezoelectric PVDF fiber was simulated using ANSYS FEA commercial software to determine its actuation behavior under an external electric field. The actuation property was tested using a DC voltage supply.

2. Analysis of PVDF fiber-based flexible piezoelectric actuator

2.1. Near-field electrospinning process

Fig. 1 shows the experimental NFES setup, which includes a needle, high-voltage power supply, collector (silicon wafer), *X–Y* motion stage (controlled by *X–Y* stage controller through a computer), and needle holder. The inner diameters of needles ranged from 0.15 to 0.3 mm. The anode of the high-voltage power supply was connected to the needle holder, and the silicon wafer was grounded as a collector. A high-voltage 1200 V formed a high potential between the needle and the collector. The collector was installed on an *X–Y* stage with a motion speed of 20–100 mm/s and a travel distance of 50 mm, respectively. The gap between the needle and the collector was 0.5–1 mm, and the route of the collector mounted on the *X–Y* stage was controlled by a programmed path. Under a high electric potential, the droplet overcame the surface tension of the solution and was ejected from the needle tip, spinning an extremely fine PVDF fiber out on the collector. The applied electric field generated sufficient electrostatic force to deform the polymer meniscus into a conical shape (Taylor cone) and subsequently induce a polymer jet from the tip of the Taylor cone. In the preparation of PVDF solution, dimethyl sulfoxide (DMSO) uses as the solvent for PVDF powder ($Mw = 534{,}000$), with acetone and fluorosurfactant (ZONYL®UR) to improve the evaporation rate and reduce the surface tension of PVDF solution, respectively. The proper percentage of MWCNT was dispersed in DMSO, and PVDF was dispersed in acetone simultaneously. The MWCNT–DMSO solution was sonicated for at least 1 h to break