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Poly(γ-benzyl α, *l*-glutamate) in Cylindrical Near-Field Electrospinning Fabrication and Analysis of Piezoelectric Fibers

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In this study, a cylindrical near-field electrospinning (CNFES) process was used to fabricate poly(γ-benzyl α, l-glutamate) (PBLG) fibers with permanent piezoelectricity. To analyze the piezoelectricity of various PBLG fibers, PBLG weight percentage, rotating tangential speed, electric field, and fiber diameter were investigated. The average diameter of the electrospun PBLG fiber is in the range from 4.37 to 25 μm with the optimum parameters (PBLG concentration: 18 wt%, tangential collection velocity: 942.4778 mm/s, and electric field: 6×10^6 V/m). Fourier transform infrared spectroscopy (FTIR) was used to characterize PBLG nonwoven fiber fabrics (NFFs) made by the CNFES process. The PBLG NFFs with high absorption peak at 1650 cm^{-1} corresponding to α-helix piezoelectric structures were demonstrated. In the experiment, the electrical energy output of one single PBLG fiber was characterized. The maximum power output is 138.42 pW with a load resistance of 8 MΩ. However, one single polyvinylidene fluoride (PVDF) fiber was also tested under the same condition and measurement. The power output is up to 265.81 pW with a load resistance of 6 MΩ. The results show that the power generation of the PVDF fibers exceeds that of PBLG fibers by 68%.

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1. Introduction

In recent years, functional piezoelectric materials have attracted increasing attention from researchers. The piezoelectric materials could be applied to different areas and also played important roles in this field. Piezoelectric materials could be used in flexible structures and under amplitude working conditions.[1]

In 1999, Vinogradova studied polyvinylidene fluoride (PVDF) fibers and researched their ferroelectric and mechanical properties.[2] PVDF fibers show excellent piezoelectric properties, chemical resistance, and mechanical properties.[3] PVDF fibers exhibit a smooth surface morphology, a high content of β-phase structure, and a high content of piezoelectric crystal structure. Under a high *in situ* electrical poling, PVDF fibers have strong mechanical stretching capability.[4] However, the PVDF piezoelectric materials contain fluorine, which is toxic and not suitable for biomedical materials. By contrast, poly(γ-benzyl α, l-glutamate) (PBLG) is a synthetic polypeptide molecule and contains no fluorine. PBLG could be applied biomedically directly to animal and human tissues, body fluids, and blood. In this study, we present a nonpolluting piezoelectric fiber process to enhance the piezoelectric properties for energy-harvesting purpose. In 2004, Papadopoulos and Floudas used differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), Fourier transform infrared spectrometry (FTIR), nuclear magnetic resonance spectroscopy (NMR), and analytic instruments to analyze PBLG.[5] In 2011, Farrar *et al.* used electrospun PBLG fibers to measure the d33 piezoelectric coefficient of 25 pC N^{-1}.[6] In 2012, Kuo and colleagues studied PBLG combined with fluorescent substances.[7]

The main concept of this research is green energy. We investigate the piezoelectric characteristics of PBLG for power generation using cylindrical near-field electrospinning (CNFES).[8] The size of piezoelectric PBLG fibers could be reduced to micro- and nanometer levels.[9] The piezoelectric PBLG fibers are characterized as having high flexibility, high toughness, high electric dipole density, and good thermal stability.[6] The PBLG fibers show excellent piezoelectric properties that could be applied in the field of microcomponents.

2. Experiment

In this study, we focus on the CNFES process to produce piezoelectric PBLG fibers. The properties of PBLG piezoelectric fibers were analyzed by FTIR. Then, we used the same process condition to fabricate PVDF piezoelectric fibers. The performance of energy harvesting was analyzed. The experimental process is shown in Fig. 1. PBLG and PVDF were spun under the same condition.

2.1 *Solution configuration*

During the electrospinning process of the PBLG, alcohol with dehydration reaction was used to form BLG. Triphosgene cyclization added by an n-butylamine ring-opening polymeric initiator was carried out to form PBLG powder with α-helix. The main ingredient of the powder is PBLG with a molecular weight (MW) of 48,822, uniformly dispersed in dichloromethane. We used a magnet stirrer for 30 min. Next, the PBLG solution was put into a syringe. In the PVDF part, PVDF with a MW of 534,000 was

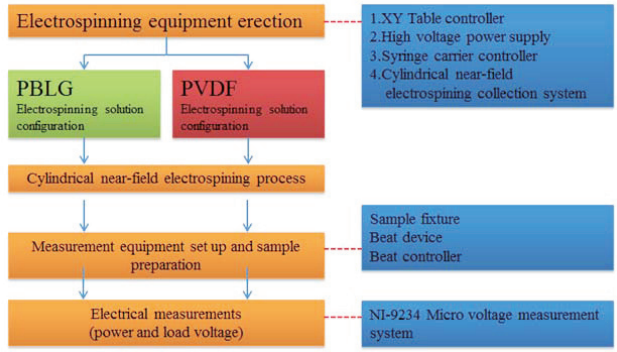


Fig. 1. (Color online) Experimental process.

used. The solvent of acetone was uniformly dispersed with dimethyl sulfoxide (DMSO). To make the electrospinning more smooth, an appropriate surfactant was added to change the surface tension of the solution. Then, the PVDF solution was put into the syringe.

2.2 *Cylindrical near-field electrospinning process*

The devices of the CNFES process are shown in Fig. 2. A syringe was used as a container filled with solution. The syringe was injected using a precision flow control pump. The devices of the CNFES process can be pulled out continuously and smoothly, which were linked to an XY-axis digital control platform. A computer was used to execute signal conversion. The platform moving distance and speed were controlled by computer software. The speed was fixed at 2 mm/s. A high-voltage power supply provided a maximum output voltage of 40 kV.

PVDF and PBLG solutions were filled in a syringe. Then, the syringes were connected to a metal needle injector with copper wire to contact a high-voltage power supply. Under the high-voltage electric field, the conical prominent drops in the needle gradually became a cone, called the Taylor cone.[10] PBLG and PVDF electrospun fibers were collected by a collection plate in the XY-axis digital control platform and cylindrical collector. The electrospun fibers were collected by a cylindrical collector as shown in Fig. 3.

2.3 *Piezoelectric properties measurement*

The energy-harvesting device is shown schematically in Fig. 4(a), which exhibits a 20×40 mm^2 flexible polymide (PI) substrate and copper conductive tape to form a structure. The actual PGLG and PVDF energy-harvesting devices are shown in Figs. 4(b) and 4(c), respectively. The energy-harvesting device was packaged on flexible PI tape as the substrate, and was characterized under periodical external strains by using a tapping device at 18.33 Hz to control the deformation magnitude of the PI flexible structure. The estimated strain from the bending of the PI flexible packaging structure by the tapping device is increasing by 0.05%. A schematic diagram of the tapping measurement system is shown in Fig. 5. The instrument of NI9234 (set the maximum sampling frequency per channel at 51.2 kS/s, 24-bit resolution, and 102 dB) was used to measure voltage.

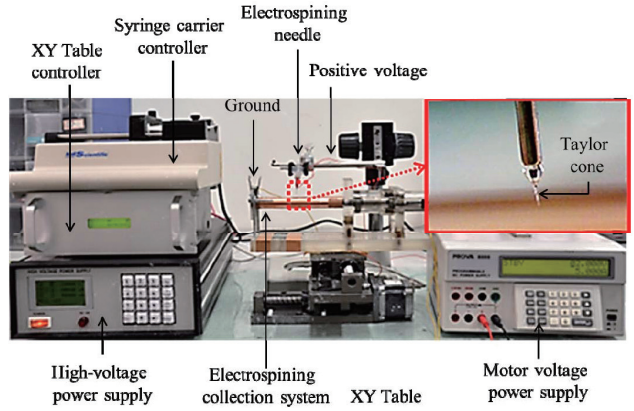
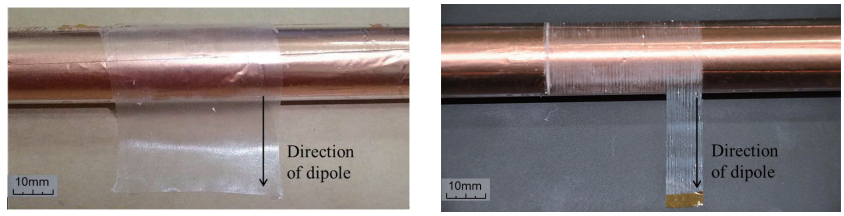
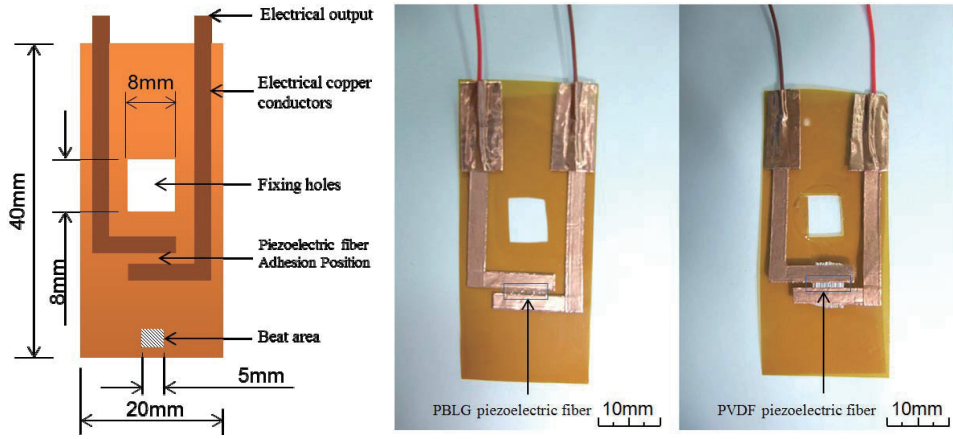


Fig. 2. (Color online) Devices of CNFES process.



(a) (b)

Fig. 3. (Color online) Piezoelectric fiber obtained by CNFES process: (a) PBLG material and (b) PVDF material.



(a) (b) (c)

Fig. 4. (Color online) Prototypes of energy-harvesting devices: (a) device description and dimensions, (b) PBLG device, and (c) PVDF device.

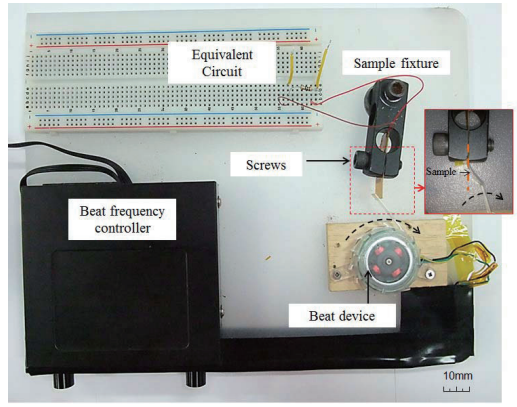


Fig. 5. (Color online) Equipment of voltage measurement system.

3. Results and Discussion

3.1 *PBLG piezoelectric fiber*

A scanning electron microscope (SEM) was utilized to observe the surface morphology of the PBLG fibers and measure its diameter. The measurement result is shown in Fig. 6. The PBLG diameter ranges from 2.5 and 6 μm. It shows that the PBLG fiber surface is clear and untangled.

PBLG is a synthetic polypeptide molecule. Since the hydrogen bonds interact with the α-helical structure, it could be formed under stable condition. In the α-helical structure, the hydrogen bonds are parallel to the center axis of the helical structure. Under the permanent dipole force, amino acids can produce high-electric-density dipoles and transform into the permanent polarity with piezoelectric characteristics. The fibers were measured by FTIR. At 1650 cm^{-1}, the PBLG piezoelectric fibers show an intense α-phase helical structure, as shown in Fig. 6. The increase in the electric field had a positive impact on the PBLG piezoelectric characteristics of the α-phase helical structure that enhances its strength up four times. The electric field caused the α-phase helix to rearrange and enhance the piezoelectric properties.

3.2 *Relationship between concentration and fiber diameter*

To investigate the effect of concentration on the diameter of the fibers, the experimental parameters were fixed as follows: MW of 48,822, rotating tangential velocity of 523.6 mm/s, motion X-Y stage velocity of 2 mm/s, electric field of 6×10^6 V/m, precision flow control pump of 2 ml/h, and inner diameter of needle of 0.2 mm. Only the concentrations of 10–18 wt% were changed. The diameters of piezoelectric fibers are between 17.25−43.85 μm. It shows that the higher the concentration of the solution, the smaller the diameter. The relationship between concentration and diameter is shown in Fig. 7(a).

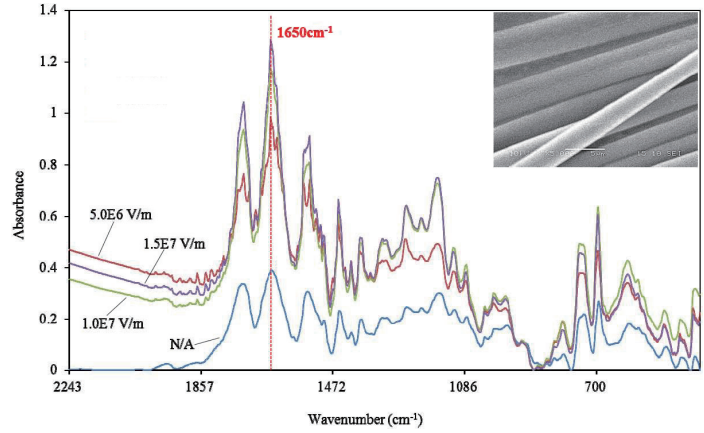


Fig. 6. (Color online) SEM and FTIR results of PBLG piezoelectric fibers using CNFES process.

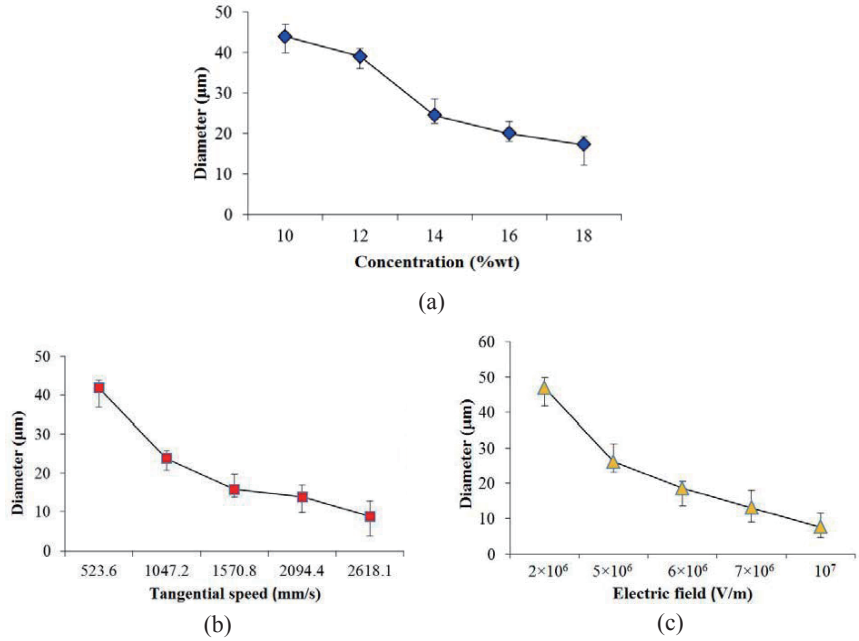


Fig. 7. (Color online) Different experimental parameters and their relationship with fiber diameter: (a) relationship between concentration and fiber diameter, (b) relationship between rotating tangential velocity and fiber diameter, and (c) relationship between electric field and fiber diameter.

3.3 *Relationship between rotating tangential velocity and fiber diameter*

To investigate the relationship between rotating tangential velocity and fiber diameter, the experimental parameters were fixed as follows: MW of 48,822, concentration of 18 wt%, motion X-Y stage velocity of 2 mm/s, electric field of 6×10^6 V/m, precision flow control pump of 2 ml/h, and inner diameter of needle of 0.2 mm. Only the rotating

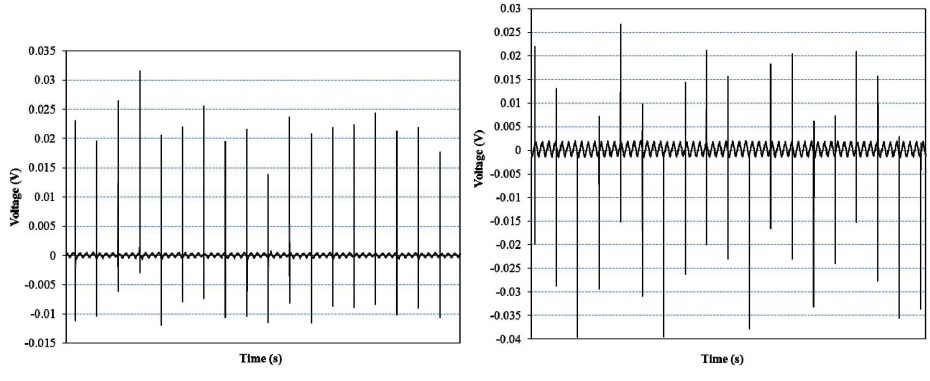
tangential velocity was changed from 523.6 to 2,618.1 mm/s. The result shows that the diameters of piezoelectric fibers were between 41.81 and 8.74 μm. As the piezoelectric fiber deposits on the cylindrical tube after being ejected, when the speed of collection is slower than the speed of ejection, it might cause the fiber flexural phenomenon that yields a rougher diameter. When the rotating tangential velocity is faster than the speed of ejection, the piezoelectric fiber deposits on the cylindrical tube. Therefore, the velocity affects the diameter of the piezoelectric fiber. The relationship between rotating velocity of the cylindrical tube and diameter is shown in Fig. 7(b).

3.4 *Relationship between electric field and diameter*

To investigate the effect of the electric field on the diameter of the fiber, the experimental parameters were fixed as follows: MW of 48,822, concentration of 18 wt%, motion X-Y stage velocity of 2 mm/s, rotating tangential velocity of 2618.1 mm/s, precision flow control pump of 2 ml/h, and inner diameter of needle of 0.2 mm. Only the electric field of 2×10^{6}–1×10^{7} V/m was changed. The result shows that the diameter of the piezoelectric fibers is between 7.51 and 46.85 μm. Therefore, when the electrospinning process is in normal operation, a higher electric field can result in a smaller fiber diameter. The relationship between electric field and diameter is shown in Fig. 7(c).

3.5 *Piezoelectric properties measurement*

By periodically stretching and releasing this harvester at 18.33 Hz vibration, a maximum peak voltage of 33 mV in forward connection can be obtained, as shown in Fig. 8(a). When the measuring system was connected in reverse, all the response signal outputs are reversed, as shown in Fig. 8(b). The peak voltage was about −38 mV in reverse connection. This test is important to validate results coming from the piezoelectric responses instead of artificial effects. When the signal is coming from the noise or other forms instead of piezoelectric responses, the shape of the response should remain the same even if the polarity of the contacts has been changed. Since the induced piezoelectric response has its own polarity based on the electrical poling direction,[11] the electrical measurements should have reversed responses when the polarity of the contacts was reversed.



(a) (b)

Fig. 8. Voltage measurement of energy-harvesting device of PBLG piezoelectric fibers in 18.33 Hz vibration: (a) positive and (b) negative.

To investigate the maximum power transport, a load resistor of 8 MΩ (effective voltage exhibits impedance) was chosen because of the 8 MΩ internal resistance of the single-fiber PBLG nanoharvester. The maximum load voltage is 33.27 mV [Fig. 9(a)], and the maximum power is 138.42 pW. Figure 9(b) shows the PVDF single piezoelectric fiber measurement result. When the impedance is 6 MΩ and the load voltage is 39.94 mV, it produces the maximum power output of 265.81 pW. Thus, the result shows that the PVDF power output is more than the PBLG power output by 68% because the piezoelectric coefficient of the piezoelectric PVDF fibers is higher than that of the piezoelectric PBLG fibers.

4. Conclusions

In this study, we used the CNFES process to fabricate permanent piezoelectric PBLG fibers. When the electrospinning process is in normal operation, a higher electric field can result in a smaller fiber diameter. The increase of the electric field has a positive impact on the PBLG piezoelectric characteristics of the α-phase helical structure that enhances its strength up to four times. The experimental result shows that the PBLG

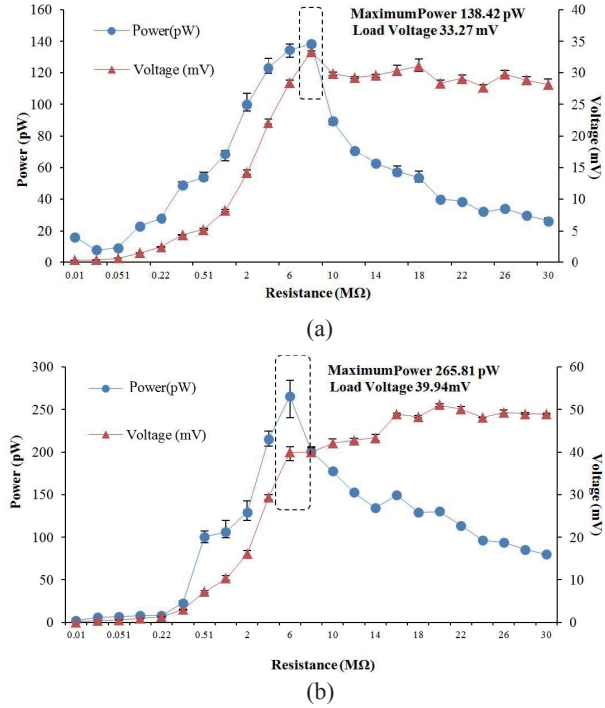


Fig. 9. (Color online) PBLG and PVDF piezoelectric fiber measurements of power and load voltage: (a) PBLG material and (b) PVDF material.

energy-harvesting device has a maximum power output of 138.42 pW (the impedance is 8 MΩ). By contrast, the result shows that the PVDF energy-harvesting device is 68% better than the PBLG energy-harvesting device in generating electrical energy. We have successfully developed new nontoxic fibers with piezoelectric effect. PBLG can be applied to biomedical research.

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