Using in-situ X-ray Scattering to identify the mechanical properties and piezoelectric properties of electrospun P(VDF-TrFE) nanofibers

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Abstract

In this study, we investigated the effect of annealing on the morphology and crystal phase changes of electrospun poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) nanofibers. We also identify the underlying deformation mechanisms of as-spun and annealed P(VDF-TrFE) nanofibers during stretch-hold deformation via *in-situ* synchrotron small and wide angle X-ray scattering (SAXS and WAXS). Annealing process induces an transformation from α to β phase crystalline. The transmission X-ray microscopy (TXM) exhibits the fiber orientations with different strain. In the end, our results demonstrate that annealing is an effective method to improve the piezoelectric response in electrospun P(VDF-TrFE) nanofibers.

Keywords - electrospun, piezoelectricity, small and wide angle X-ray scattering, transmission x-ray microscopy

Introduction

Semi-crystalline polymer, poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) copolymer is a high mechanical flexibility piezoelectric material and availability in large areas that would be difficult to achieve by conventional materials. P(VDF-TrFE) has been reported by various research studies that the more the β phase crystalline, the better the piezoelectric performance1,2,3. Furthermore, annealing treatment can induce a higher crystallinity and a better mechanical performance of polymers4,5,6.

In this work, we extensively examined the deformation mechanisms at the nanoscale behavior of nanofibers alignment under uniaxial loading through mechanical, structural and morphological characterizations for as-spun and annealed P(VDF-TrFE) nanofibers fabricated by electrospinning.

Experiments

Sample preparation

DMAc and MEK were used as solvents for the P(VDF-TrFE), and then use a typical far-field electrospinning setup. The as-spun membrane was annealed at 120˚ C for 2 hours, named as annealed membrane.

Transmission X-ray microscopy

TXM has large penetration depth and superior spatial resolution. The TXM provides two-dimensional imaging at energy 8-11 keV with a spatial resolution of 50-60 nm at beamline BL01B of the Taiwan Light Source.

Synchrotron small and wide angle X-ray scattering

The non-destructive X-ray scattering techniques were implemented with the wavelength of 1.24 Å (10 keV) at beamline BL23A, NSRRC, Taiwan. The SAXS and WAXS scattering patterns were collected from a two-dimensional (2D) detector.

Piezoelectric test

The output short-circuit current and open-circuit voltage of the Piezo-electric Nanogenerator (PENG) were measured using a low-noise current preamplifier, a low-noise voltage preamplifier, and a Keithley 6514 programmable electrometer.

Results

To identify the main deformation mechanism during the strain, we first examined the mechanical behavior in associated with the structural changes of as-spun and annealed P(VDF-TrFE) membranes shown in Figs. 1 and 2. Figs. 1 and 2 describe the *in-situ* uniaxial tensile loading coupled with 2D SAXS and WAXS, together with TXM images for the as-spun and annealed P(VDF-TrFE) membrane.

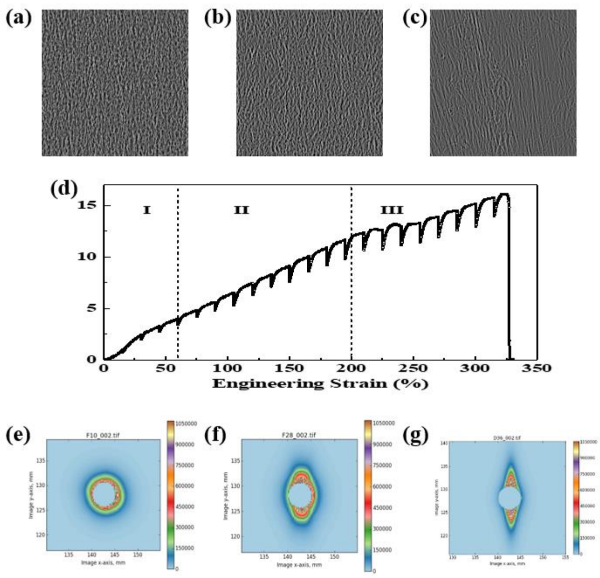

Fig. 1. (a-c) TXM images of underneath as-spun P(VDF-TrFE) nanofibers orientation during the three regions of uniaxial tensile test. (d) The engineering stress-strain (S-S) curve. (e-g) The 2D SAXS patterns.

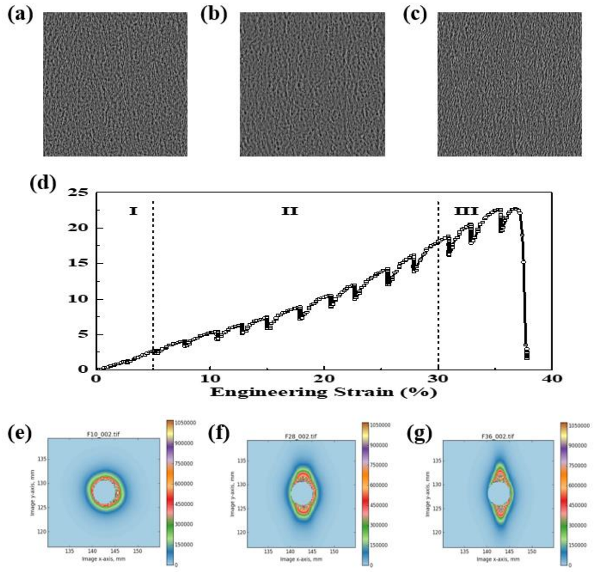

Fig. 2. (d-f) (a-c) TXM images of underneath annealed P(VDF-TrFE) nanofibers orientation during the three regions of uniaxial tensile test. (d) The engineering stress-strain (S-S) curve. (e-g) The 2D SAXS patterns.

Discussion

TXM images in Figs. 1 (a)-(c) describe the alignment of electrospun nanofibers under loading. After stretching, P(VDF-TrFE) nanofibers align along the loading direction. The 2D SAXS in Fig. 1 (e)-(g) confirm the increasing strain, the SAXS patterns revealed an anisotropic orientation and perpendicular to the loading direction. The 2D WAXS also show the intensity of β phase increase compared with α phase, indicating that stretching leads to a phase transition from α to β phase crystalline. The SAXS in Fig. 1 (g) indicates a preferred alignment perpendicular to the loading before fracture.

During the deformation of the annealed membrane, no big difference in the morphology of nanofibers was detected by TXM, seen in Figs. 2 (a)-(c). During loading, the SAXS patterns depict the orientation of crystalline lamellae perpendicular to the loading direction, as shown in Fig. 2 (e)-(g).

The as-spun P(VDF-TrFE) has better elongation while the annealed sample has higher strength. Meanwhile annealing treatment results in an increase of the Young modulus and harder elasticity behavior of P(VDF-TrFE).

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References

[1] Chen, S., Lou, Z., Chen, D., Jiang, K. & Shen, G. Polymer-Enhanced Highly Stretchable Conductive Fiber Strain Sensor Used for Electronic Data Gloves. *Advanced Materials Technologies*, 1600136, (2016).

[2] Guo, H. et al. In-situ synchrotron SAXS and WAXS investigations on deformation and α–β transformation of uniaxial stretched poly(vinylidene fluoride). *Cryst Eng Comm* 15, 1597, (2013).

[3] Huang, E. W. et al. Visible-Light Modulation on Lattice Dielectric Responses of a Piezo-Phototronic Soft Material. *Adv Mater* 27, 7728-7733, (2015).

[4] Jiang, Y. et al. Aligned P(VDF-TrFE) Nanofibers for Enhanced Piezoelectric Directional Strain Sensing. Polymers 10, 364, (2018).

[5] Ivan Dmitriev, V. B., Viktor Lavrentyev, Galina Elyashevich. Structure and Deformational Behavior of Poly(vinylidene fluoride) Hard Elastic Films. *Acta Chim. Slov.* **54**, 784–791 (2007).

[6] Baniasadi, M. et al. Effect of thermomechanical post-processing on chain orientation and crystallinity of electrospun P(VDF-TrFE) nanofibers. *Polymer* 118, 223-235, (2017).