

SHORT COMMUNICATION

Curled Poly(ethylene glycol terephthalate)/ Poly(ethylene propanediol terephthalate) Nanofibers Produced by Side-by-side Electrospinning

By Binfei ZHANG,¹ Congju LI,^{2,*} and Min CHANG¹

KEY WORDS: Helical Structure / Side-by-side / Electrospun / Nanofibers /

The electrospinning process is an established method for producing continuous polymer fibers with diameters on the nanometer scale. In the electrospinning process, a polymer solution is charged with a high electrical voltage. A polymer droplet at the tip of a nozzle is attracted by an electrical field, forming a so-called "Taylor cone." At the tip of the cone, when the droplet overcomes restrictions due to surface tension, a polymer jet is ejected. The charged jet then undergoes bending instability, alternatively referred to as "whipping instability,"¹ stretching itself to form very fine filaments. Solution evaporation from the filament results in dry or semi-dry nanofibers, which are deposited randomly on the collector electrode, usually in the form of a non-woven mat. The whole electrospinning process takes place in milliseconds.²

Micro- and nanoscale helical structures have been of increasing interest and have potential applications in areas, such as structure or inductive components in microelectromechanical systems devices, drug delivery systems, and advanced optical components. However, in order to generate helical structures at the micro- or nanoscale, synthesis or processing strategies must be employed. In recent studies, microscale polymeric helical structures were obtained by electrostatic spinning.³

The formation of large ribbons and loops is prevalent in the electrospinning process and can normally be attributed to the structure and motion of the electrified fluid jet.⁴ However, uniform helical structures with microscale coil diameter and the evidence for the existence of a side-by-side bicomponent fiber on morphology have not been reported. In this work, helically structured nanofibers were fabricated from two kinds of polymer solution, high shrinkage polyethylene terephthalate (HSPET) and polytrimethylene terephthalate (PTT) in trifluoroacetic acid (TFA)/methylene dichloride component solvent, by using side-by-side electrospinning system. A new structure of helical fiber with microscale coil diameter was discovered. The results of this study can provide further insight into the curling mechanism of self-crimp fibers in electrospun.

EXPERIMENTAL

The electrospinning process was conducted by connecting the positive electrode of a high-voltage power supply (DWP-P303-2AC Dong Wen Company) to the microfluidic device and the grounded electrode to the collector. Two different polymer solutions were supplied separately from two syringes through the side channels. The flow rates were controlled by two syringes through the side channels. An electrical voltage of 15 kV was used in the electrospinning process, and the DTC was 12 cm. The main collector in our system were fabricated from aluminum foil on a stainless panel. The HSPET were got from Beijing Institute of Fashion Technology and the PTT were from Royal Dutch Shell. Two kinds of solution, HSPET 14 wt.-% and PTT 11 wt.-% in a component solvent of TFA/methylene dichloride (ratio of 3 to 2 by volume) were prepared, and used after a

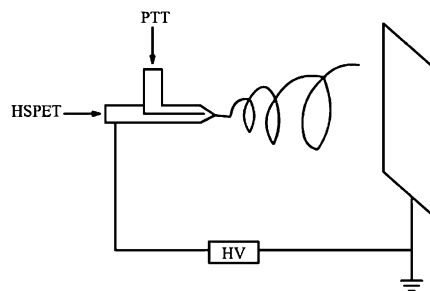


Figure 1. The structure of apparatus for co-electrospinning two polymer solutions side-by-side.

period of about 6 h for a homogenous mixture.

The morphology of the electrospun fibers were observed by SEM (JSM-6360LV).

RESULTS AND DISCUSSION

Tong Lin⁵ have reported a process for side-by-side electrospinning of two different polymers using a microfluidic device as the spinneret. Therefore, the self-regulating apparatus was chosen for our experiment according to the report. The setup for electrospinning is essentially the same as the conventional configuration except for the use of the special spinneret. The copper spinneret consists of two channels (inner diameter of 1.5 mm). Two side channels are used for delivering the different solutions, which are combined at the subuliform outlet (1.5 mm in length). The inner diameter of our spinneret tip is 500 μm . And such copper spinneret can be connected by the high-voltage power supply to provide electrical potential. Figure 1 shows the structure of apparatus we employed in our electrospun process. When the two polymer solutions are fed through the side channels and merge side-by-side within the same capillary channel, they are able to flow side-by-side with little dispersion of the liquids over a relatively long distance.⁶

Figure 2a shows an SEM image of helically structured nanofibers deposited on an aluminum collector. The average fiber diameter of the HSPET/PTT nanofibers is 800 nm. And the diameter of the helix have a so large distributed that it is difficult to indicate whether it is due to the "whipping instability" or not.

Figure 2b indicated the contrast of helically structured and straight line nanofibers. The fibers are so tightly curled that the diameter of the helix is as small as 1 μm . And the fiber of such microscale helical diameter could not be produced from a single component system or only obtained from "whipping instability." Moreover, the straight line fiber in the image have a

¹Department of Material Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100-029, People's Republic of China

²Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing 100029, People's Republic of China

*To whom correspondence should be addressed (Tel: +86-10-6428-8192, Fax: +86-10-6428-8192, E-mail: congjuli@sina.com).

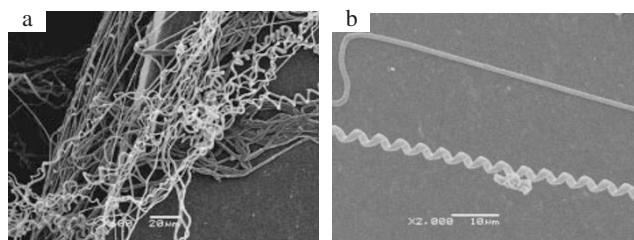


Figure 2. a) Fiber produced from HSPET (14 wt.-%) and PTT (11 wt.-%) in TFA/methylene dichloride component solvent. b) The contrast of hecially structured and straight line nanofibers.

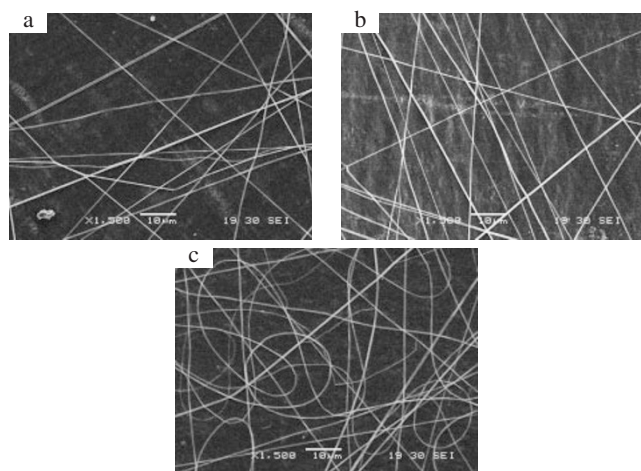


Figure 3. a) HSPET (14 wt.-%) nanofibers, b) PTT (11 wt.-%) nanofibers, c) nanofibers processed by one syringe of isopyknic HSPET 14 wt.-% and PTT 11 wt.-% mixed solution.

massive whipping, this is due to the instability in electropun process. In short, the crimp were not imposed on the fiber from the outside, but rather results from the rearrangement of the internal molecular structure of the fiber material.

In other experiment, we have got three kinds of nanofibers by electropun: (a) HSPET (14 wt.-%) nanofibers, (b) PTT (11 wt.-%) nanofibers, and (c) nanofibers processed by one syringe of isopyknic HSPET 14 wt.-% and PTT 11 wt.-% mixed solution. The former two shows straight line nanofibers. As well as the former two, the third nanofibers present straight line in the mass besides a massive whipping (Figure 3).

The HSPET/PTT bicomponent fiament has three dimensional spiral-shaped curls (Figure 4a). The scanning electron microscopy (SEM) image of the electrospun HSPET/PTT nanofibers shown in Figure 4b indicates that the as-spun fibers have curly and helically crimped fiber morphologies. The average fiber diameter of the HSPET/PTT nanofibers is 800 nm, and the diameter of helix is about 1–1.5 μm , simultaneously the thread pitch of the helical structure is only about 1.5 μm that the whole fiber present a morphology of tight spring. The crimps are born from a composite of two parallel but attached fibers with differing shrinkage or expansion properties. A side-by-side bicomponent fiber with obvious projection with the diameter of 300 nm can be seen on its surface. The projection of our

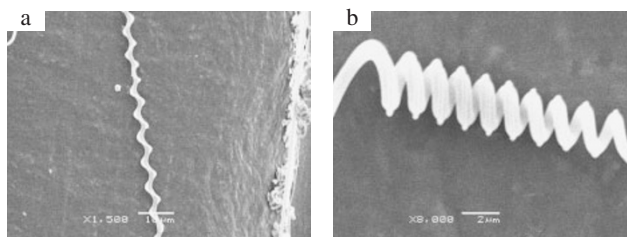


Figure 4. The SEM image of a particular structure of hecial fiber with protuberance on it's surface.

hecial fiber (Figure 4b) exactly indicate the spontaneous formation of the microscale helical structures is due to the composite nature of the fibers. In the electropun process, a side-by-side bicomponent fiber can be bent to one side, forming a crimped or helical fiber morphology, if the two component sides have a differential shrinkage.

In general, mechanical deformation or chemical process is the most widely used method for manufacturing commercial synthetic fibers. However, the crimped property always disappeared along with the service time increased. Other than synthetic fibers, the HSPET/PTT bicomponent fiber by using side-by-side electropinning have a section of two constituent, the property of which is exactly distinction in mechanical property or shrinkage. Therefore, the hecial structure of our HSPET/PTT bicomponent fiber is due to the two constituent with distinct stress-strain action, instead of causing by mechanical strategy. In theory, symmetry distribution of each component in such bicomponent fiber is the foundation to get self-crimp fibers, and the differential shrinkage belonging to the both sides of as-fiber is the immediate origin to obtain it.

In summery, self-crimping nanofibers have been obtained when the fibers are prepared from HSPET and PTT in TFA/methylene dichloride by using side-by-side electropinning. The characteristic structure of bicomponent fiament have been found, they can provide further insight into the curling mechanism of self-crimp fibers in electropun.

This study was partly supported by the 863 project (grant no. 2007AA021900), the Natural Science Foundation of China, Program for New Century Excellent Talents in University (grant no. NCET-05-0204), and PHR (IHLB).

Received: October 24, 2008
Accepted: December 23, 2008
Published: February 12, 2009

REFERENCES

1. D. H. Reneker, A. L. Yarin, H. Fong, and S. Koombhongse, *J. Appl. Phys.*, **87**, 4531 (2000).
2. Y. M. Shin, M. M. Hohman, M. P. Brenner, and G. C. Rutledge, *Appl. Phys. Lett.*, **78**, 1149 (2001).
3. R. Kessick and G. Tepper, *Appl. Phys. Lett.*, **7**, 4807 (2004).
4. S. Koombhongse, W. Liu, and D. H. Reneker, *J. Polym. Sci. Part B: Polym. Phys.*, **39**, 2598 (2001).
5. T. Lin, H. X. Wang, and X. G. Wang, *Adv. Mater.*, **17**, 2699 (2005).
6. N. Giordano and J. T. Cheng, *J. Phys.: Condens. Matter.*, **13**, R27 (2001).