

Direct Formation of “Artificial Wool” Nanofiber via Two-Spinneret Electrospinning

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ABSTRACT: To reproduce the excellent characteristics of natural fibers like wool and proteins, a novel two-spinneret electrospinning technology was demonstrated in this communication, which can generate three-dimensional self-crimp fibers of HSPET/PTT, HSPET/PAN and PU/PAN directly. In the apparatus, two spinnerets were used to prevent gel formation or precipitation of the polymer, and the voltages of

opposite polarities were applied to the spinnerets respectively. And the electrospun fibers morphology was observed by using scanning electron microscopy (SEM). © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2992–2995, 2012

Key words: microstructure; morphology; nanotechnology; three-dimensional self-crimp; electrospinning

INTRODUCTION

The behavior of self-crimp fibers or helix action exists widely in natural materials such as wool and proteins. It endows natural fibers with strong flexibility and high porosity. To reproduce the excellent characteristics of natural fibers in synthetic materials, people began to imitate the process in natural fibers to fabricate self-crimp fibers. In the early 1960s, DuPont (Wilmington, DE) synthesized the first self-crimp yarn—Polypropylene (PP). Several decades past, self-crimp yarns have been produced vastly in the fiber industry.^{1–5} Nevertheless, the diameters of self-crimp fibers produced in industry are limited to the micrometer scale.⁶ Nowadays, people are in need of smaller and more sophisticated materials, and the demand of nanomaterials in the market is likely to be immense. Micro- and nanoscale helical structures have been drawing great attention because they have potential applications in many fields, such as structural or inductive components in microelectromechanical systems devices, drug delivery systems,

advanced optical components, and so on.⁷ However, there is no general method for generating helical structures at micro- or nanoscale so far.^{8–12} New techniques need to be developed to achieve that.

The electrospinning technique has been recognized as an effective, versatile, and mature method for the production of fibers with high surface-to-volume ratio and small diameters.¹³ So several improved electrospinning techniques have emerged in some research groups. Recently, microscale polymeric helical structures have been generated from a solution containing two dissolved polymers by electrostatic spinning.^{7,14,15} However, the formation of large ribbons and loops is prevalent in those electrospinning processes, and the percentage of microscale helical structures is quite low due to the difficulties in controlling the structure and motion of the electrified fluid jet.¹⁶ Lin et al.⁶ produced self-crimp nanofibers using a micro-fluidic device as a spinneret during the electrospinning process, and they proved the existence of side-by-side bicomponent fiber morphology by dissolving one of the polymer components from the bicomponent fibers. In our previous work,¹⁷ a similar improved electrospinning apparatus was also used to generate helical fibers. Both of the methods can be used to fabricate more or less self-crimp fibers, but it still has some drawbacks. The gel formation and precipitation of the polymer always affect the coelectrospinning process, thus it is quite difficult to generate a stable polymer jet by using these methods. Moreover, it requires two kinds of polymers which could be dissolved in the same solution, which has limited the applications of some polymers without the same solubility in one solution.

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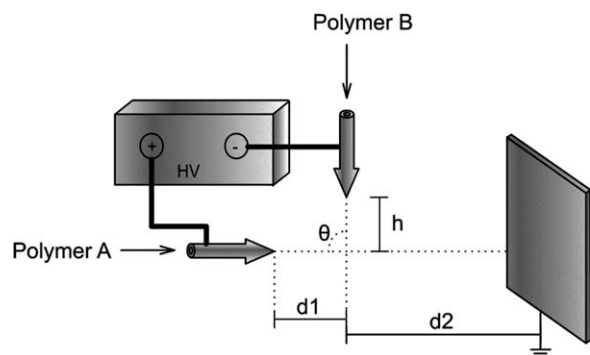


Figure 1 The scheme of two-spinneret electrospinning apparatus for generating self-crimp composite polymer fibers.

This communication demonstrates a two-spinneret electrospinning method that can generate three-dimensional self-crimp fibers directly. In this process, two spinnerets were used to prevent the solutions from getting the gel formation or precipitation of the polymers. And the voltages of opposite polarities were applied to the spinnerets, respectively. The electrospun fibers with opposite charges would attract each other, stick together, and then form compound fibers.¹⁸

MATERIALS AND METHODS

The setup of two-spinneret electrospinning is essentially the same as the conventional configuration except for the use of two spinnerets with opposite voltages. Two high-voltage DC power supplies (DW-SA303-2ACE5 Dong Wen Company) were employed to provide opposite voltages. High shrinkage polyethylene terephthalate (HSPET) was supported by Beijing Institute of Fashion Technology, and polytrimethylene terephthalate (PTT) was purchased from Royal Dutch Shell. Both of them were dissolved in trifluoroacetate acid (TFA)/meth-

ylene dichloride (DCM) (volume ratio, 3 : 2). Polyurethane (PU) and polyacrylonitrile (PAN) were also supported the Beijing Institute of Fashion Technology. The solvent used for PU and PAN was *N,N'*-dimethylformamide (DMF).

The morphology of the electrospun fibers was observed by scanning electron microscope (SEM, JSM-6360LV) at an accelerating voltage of 10 kV. The scheme of the two-spinneret electrospinning apparatus was illustrated in Figure 1. The solutions were held into two plastic tubes which were connected to copper spinnerets, respectively. The inner diameter of the copper spinnerets is about 3 mm. The aperture of spinneret tip is about 500 μm . Two high-voltage DC power supplies (with positive and negative high-voltage supplies) were used to provide voltages to the copper spinnerets. The flows were controlled by outward electric pressure, air pressure, and gravity. The distance between the positive spinneret and the collector along the straight horizontal ($d_1 + d_2$) could be adjusted from 12 to 20 cm. The horizontal distance between the two spinnerets was present as d_1 , and the vertical distance was present as h . The angles (θ) could be adjusted manually. In general, the positive voltage applied to spinneret A was higher than that of the negative voltage applied to spinneret B. The electric field was mainly produced by the positive voltage to make the jet out. The produced fibers with opposite charges attracted each other, stuck together, and finally formed compound fibers. The compound fibers would be driven by the electric field between the spinneret A and the collector along the horizontal direction and finally would deposit on the collection screen which was covered with a piece of aluminum foil.

The solutions of HSPET (14 wt %) and PTT (11 wt %) were prepared under vigorous stirring for about 6 h, both of which were dissolved in a

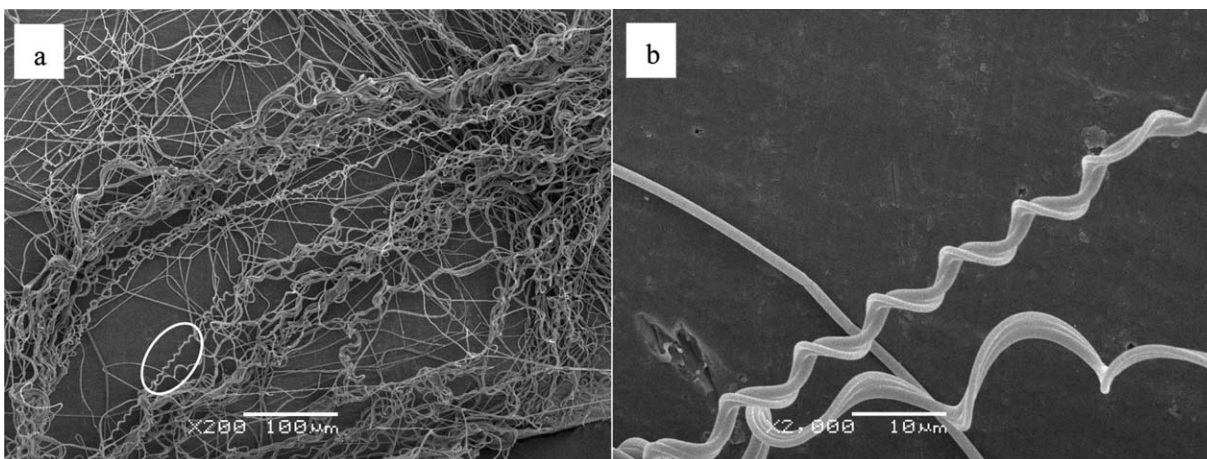


Figure 2 SEM images of (a) the electrospun HSPET (14 wt %)/PTT (11 wt %) fibers and (b) enlargement image of such fibers.

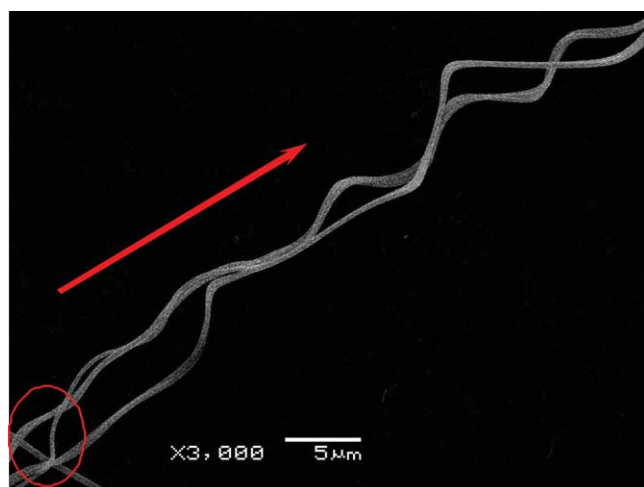


Figure 3 The SEM image of HSPET/PTT fibers shows the process of forming self-crimp fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mixed solvent of TFA/DCM (volume ratio, 3 : 2). HSPET solution as the higher shrinkage percentages component was fed into spinneret A with a positive voltage, while PTT solution as the lower shrinkage percentages component was fed into spinneret B with a negative voltage.

It was different from the above case that HSPET (14 wt %) was dissolved in TFA/DCM (volume ratio, 3 : 2), while PAN (13 wt %) was dissolved in DMF. The shrinkage percentage of HSPET is higher than that of PAN, and its solution was connected with a positive voltage. And the PAN solution was connected with a negative voltage.

Both PU and PAN could be dissolved in DMF, but the solution concentrations were a little different—PU (13 wt %) and PAN (11 wt %). The shrinkage percentage of PU is higher than that of PAN. PU solution was connected with a positive voltage, while PAN solution was connected with a negative voltage.

In general, the positions of the two spinnerets and the collector were adjusted to the following scales: $5 \text{ cm} < d_1 < d_2 < 20 \text{ cm}$, $3 \text{ cm} < h < 8 \text{ cm}$, and $40^\circ < \theta < 90^\circ$. The positive voltage was from +15 to +22 kV, while the negative voltage was from -8 to -3 kV.

RESULTS AND DISCUSSIONS

The scanning electron microscopy (SEM) image of the electrospun HSPET/PTT fibers in Figure 2 indicates that the as-spun fibers have visibly curly and helically fiber morphology [Fig. 2(a)]. The average diameter of the HSPET/PTT fibers is about 800 nm.

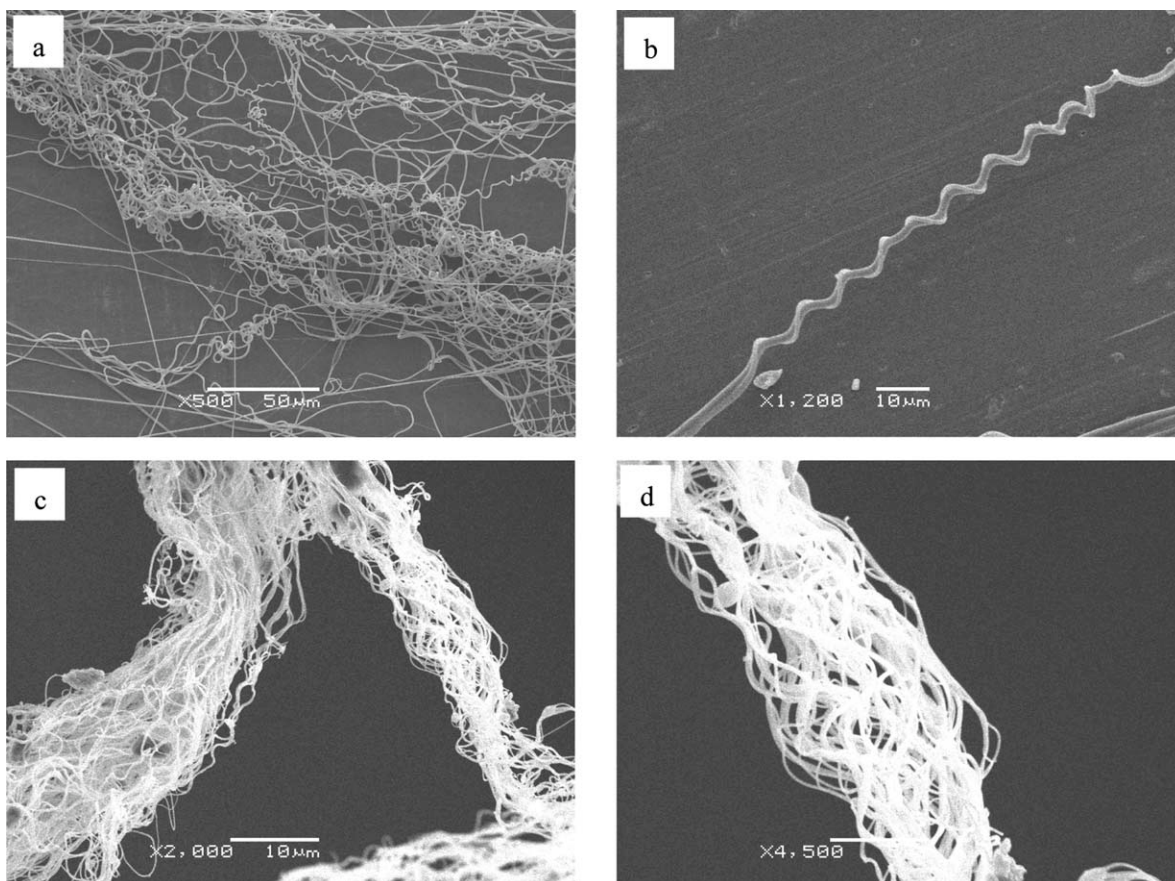


Figure 4 SEM images of (a,b) HSPET (14 wt %)/PAN(13 wt %) bicomponent nanofibers (HSPET in TFA/DCM and PAN in DMF), and (c, d) PU (13 wt %)/PAN(11 wt %) bicomponent nanofibers (PU and PAN in DMF).

The enlarged image [Fig. 2(b)] shows the side-by-side structure on the fibers' surface, which indicates that the curly fibers consist of two or three different phases. As a contrast, the fiber with a single phase is straight. The side-by-side structure indicates that the spontaneous formation of the microscale helical structures is mainly due to the recombination property of the fibers. If the two polymers have different shrinkage percentages, a side-by-side bicomponent fiber can be bent to one side to form crimped or helical fiber morphology in the electrospinning process.

The process of forming self-crimp fibers is shown in Figure 3. When the two fibers stuck together, they became more curly along with the extension of as-spun composite fibers. At first, the two fibers were nearly straight which could be seen from lower left corner in Figure 3, then the curly fibers were shown clearer along with direction of arrow. Reneker et al.¹⁹ reported the formation of nanofiber garlands during the electrospinning of polycaprolactone and confirmed that the garland morphology originated from the contact and merging of segments in different loops of the electrospinning jet while the jet was in flight. However, in our work, the extensive three-dimensional spiral-shaped curls and the side-by-side structure of single crimped fibers demonstrated that the crimping was not imposed on the fibers from external disturbance. The mechanism behind the formation of crimped and helical structure is similar to that of seersucker, which is formed from two fibers with different shrinkage ratios, such as cotton fiber and polyester fiber.

Two-spinneret electrospinning method can be used as a general method for generating three-dimensional self-crimp fibers. So many kinds of bicomponent self-crimp fibers can be obtained as long as the two components have different shrinkage percentages and can be electrospun individually, even if they need to be dissolved in different solutions. Figure 4 shows abundant curly fibers of HSPET/PAN and PU/PAN. They were all with extensive three-dimensional spiral-shaped curls and the side-by-side structures of single crimped fibers. It is worth to mention the determination of the concentrations of the different polymers. In our previous work, the concentrations of these polymers which could be electrospun have been determined, and the concentration was usually between some ranges. But when two different polymer solutions are electrospun together, the optimal concentration may change a little in its concentration range, such as PAN in HSPET/PAN (13 wt %) and PU/PAN (11 wt %) systems. The concentrations of the differ-

ent polymers nearly did not change during electrospinning processing, because the process was conducted in a short time. Thus, the concentration need not to be controlled.

CONCLUSIONS

Three-dimensional self-crimp fibers of HSPET/PTT, HSPET/PAN and PU/PAN have been obtained in abundance using a novel two-spinneret electrospinning technology. The electrospun processing conditions of these polymer systems were selected respectively, such as concentration, voltage, the positions of the two spinnerets and the collector (d_1 , d_2 , h , θ) and the types of the two polymers. This method provides us a new method for the preparation of "Artificial Wool" with different components. And it also provides us a new method for the preparation of inorganic nanofibers. Furthermore, the self-crimp nanofibers have some potential applications. If they could be triggered by an external stimulus, such as optical irradiation, temperature, or some chemicals, these fibers could be used as nanotweezers.²⁰

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