

Electrospun Helical Micro-and Nanofibers of Blends of Two Polymers

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Abstract: *In this work, curled or helical structured micro- and nanofibers were fabricated from a composite of one high shrinkage polymer (thermoplastic polyester elastomer, TPEE) and one low shrinkage polymer (PBT, PET and PTT) using electrospinning technique. The blended fiber has a differential shrinkage, which can spontaneously form crimped fiber morphology on removal of the drawing tension. The morphology and the diameter of the helix of the blended helical fibers were affected by the concentrations of the two polymers and the kinds of polymers. Comparing the three blended polymers, it can be founded that the more the difference of the shrinkages are, the more the helical structures in the blended polymer are.*

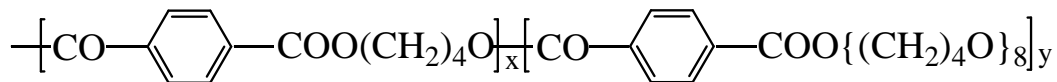
Micro-and nanoscale fibers with helical structures have attracted a great deal of attention these years because of their unique characteristics and potential applications in fields such as nanoscale sensors, transducers and resonators. Helical carbon fibers^[1, 2] and helical structures of metal oxide and silicon dioxide^[3, 4] have been produced using vapor processing methods for the above purposes. Royal *et al.*^[5] reported on the development of uniform microscale polymeric helical structures produced by electrospinning from a solution containing two dissolved polymers, of which one was conducting polymer and the other was nonconducting polymer. But preparing polymeric helical structures with much smaller diameters, especially with diameters on the order of nanometers has been a challenge.

Many methods have been used to produce helical/spiral polymer fibers, such as the contraction of a sol-gel upon solvent evaporation,^[3] the electrospinning,^[5] and vapor processing methods.^[6] Among the methods that have been used to produce helically polymer fibers, electrospinning is very attractive because of its simplicity and flexibility in producing fibers of different diameter and surface texture. Since the last decade, electrospinning has gained much attention not only due to its versatility in spinning a wide variety of polymeric fibers but also due to its consistency in producing fibers in the

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submicron range. During typical electrospinning process, a syringe-like apparatus containing the dissolved polymer solution is employed. The narrow end of the syringe is connected to a glass or Teflon capillary. High voltages are used to induce the formation of a liquid jet as being applied to an spinneret containing polymer solution. A jet is ejected from the suspended liquid meniscus at the capillary-end when the applied electric field strength overcomes the surface tension of the liquid. Near the critical point, where the electric field strength is about to overcome the surface of the liquid, the free surface of the suspended drop changes to a cone, also commonly referred to as the Taylor cone. The jet is ejected from the surface of this Taylor cone as the electric field strength is increased. The electrified fluid jet travels a short distance before the onset of a mechanical instability characterized by a rapid whipping motion. If the solution concentration is high enough for chain entanglement to occur, solid polymeric fibers are produced upon solvent evaporation and can be collected on a substrate in the form of a nonwoven mat.

In this paper, we reported on the development of micro- and nanoscale polymeric helical structures produced by electrospinning from a solution containing two dissolved polymers. The first polymer has high shrinkage, while the second polymer has low shrinkage. The objective of this study is to investigate the influence of preparation conditions on morphology and diameter of the helix of the blended fibers and the growth mechanism of the helically structures.



Thermoplastic polyester elastomer (TPEE) chosen for the electrospinning work was synthesized by Beijing Institute of Clothing Technology with the elongation at break of 300%, its chemical structure as follows:

Polybutylene terephthalate (PBT) with the elongation at break of 70% was obtained from Beijing Research Institute of Chemical Industry, polyethylene terephthalate (PET) with the elongation at break of 47% was obtained from Tianjin petrochemical corporation with an average molecular weight of 250 000, and polytrimethylene terephthalate (PTT) with the elongation at break of 40% was provided by Beijing Research Institute of Chemical Industry. Stock solution of TPEE was 13.4% by weight in trifluoroacetic acid (TFA)/dichloromethane (DCM) (80/20), and from this solution, a variety of TPEE/PBT, TPEE/PET and TPEE/PTT solutions were produced. Magnetic stirring was performed continuously to ensure the dissolution of both polymers.

The experimental configuration for the electrospinning setup was conventional. The voltage of 22kV was applied between the spinneret and the grounded electrodes using a high voltage power supply. The distance between the spinneret and the main collectors was about 12 cm. Surface images of helical nanofibers were analyzed using a field emission scanning electron microscope (JSM-6360SEM, Japan). The diameter of the helix of the blended fibers was measured by Smile View (SEM/EDS Image Report System).

For all data reported here, the TPEE concentration was fixed at 13.4% while the other polymer (PBT, PET, or PTT) concentration was varied from 0.77% to 3.75% by

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weight. Figure 1 gives SEM images of curly and helically structured morphologies of blended TPEE/PBT fibers deposited on an aluminum collector. It is found that when the PBT concentration is very low such as 0.77wt%, no curled structure is observed in the fibers excepting some irregular bending structures. With the 1.52wt% PBT concentration, the curled structures are formed. The average fiber diameter of the TPEE/PBT fibers is 1 μm , and the average diameter of the helix is about 20 μm . While the concentration of PBT is increased to 2.27wt% and 3.01wt%, more curled and helical structures are fabricated with the average diameter of the helix over 30 μm . When the PBT concentration reaches to 3.75wt%, the helical structured fibers are more regular. Beside the curled or helical structures, many straight fibers can be found from the SEM observation.

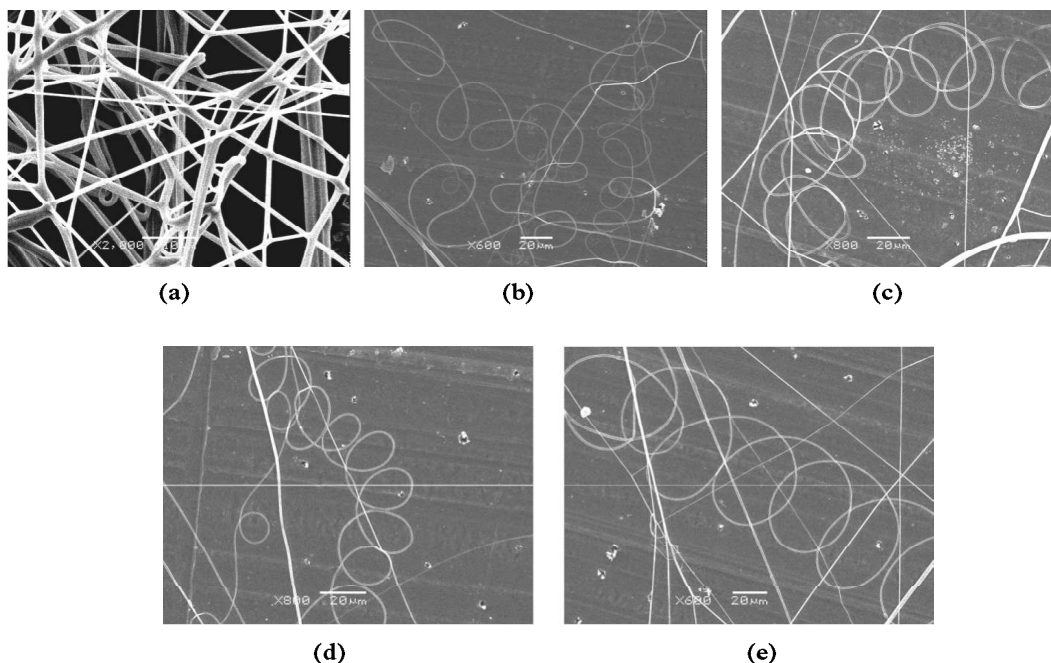


Figure 1: SEM images of microscale helical TPEE/PBT fibers. The concentration of TPEE was 13.4% and PBT was (a) 0.77%; (b) 1.52%; (c) 2.27%; (d) 3.01%; (e) 3.75%.

SEM photos of the electrospun TPEE/PET fibers are shown in Figure 2. Although there are many straight fibers, helical structures can be found under different PET concentrations. The helical loops are elliptical and the distance among these loops are unfixed. With the increase of PET concentration, the amount of helical structures increases first and then decreases, and the average fiber diameter of the TPEE/PET fibers is about 470 nm.

For the TPEE/PTT system, the morphology of the produced fibers could be observed from the SEM images in Figure 3. It is found that helical structures were fabricated, and

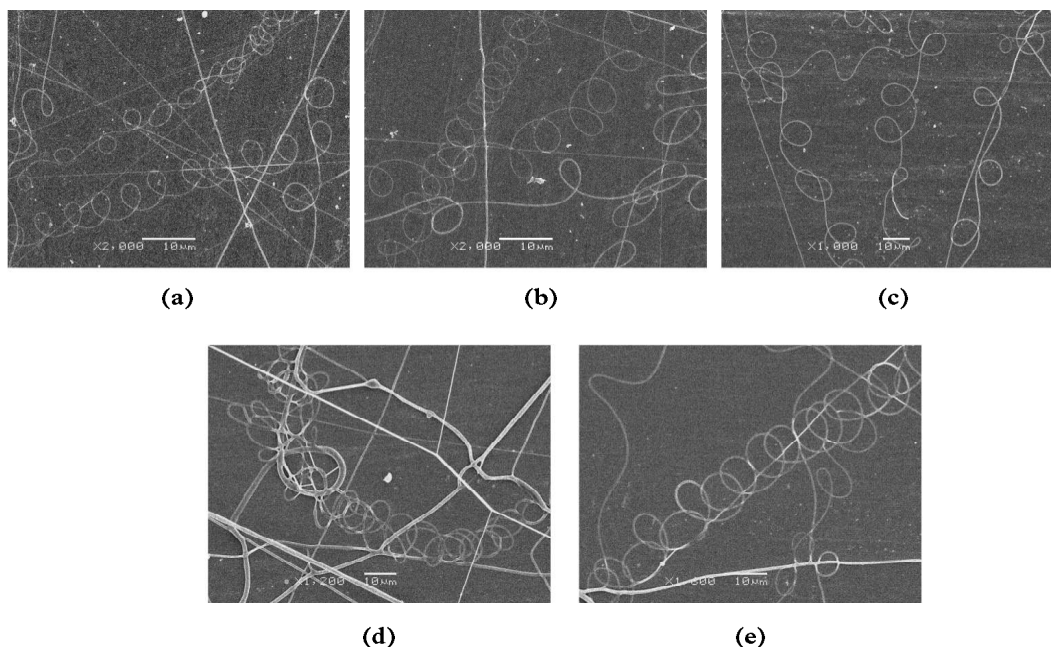


Figure 2: SEM images of nanoscale helical TPEE/PET fibers. The concentration of TPEE was 13.4% and PET was (a) 0.77%; (b) 1.52%; (c) 2.27%; (d) 3.01%; (e) 3.75%.

the average fiber diameter of the TPEE/PTT fibers is about 623 nm. When the concentration of PTT was 0.77wt%, helical structures observed in the fibers were symmetrical and sparse. With the concentration of PTT increasing, the helical structures were formed and those structures became more and more regular. But when the concentration of PTT exceeds 2.27%, the helical structures became irregular again. Comparing with Figure 1 and 2, the helical loops are more rounded and the distance among the loops is more uniform. In other words, electrospinning of blended TPEE/PTT solutions can get best helical structures among all three polymer/polymer systems. In the following part, the optimal concentration of TPEE/PTT and the growth mechanism of helical structure will be discussed.

The effect of solution concentration on the resulting helical structures was studied by measuring the average distance of the loops as a function of PTT concentration in the TFA/DCM solution. The distance of each loop within a given region on the aluminum substrate was tabulated and an average distance was calculated for the PTT concentration ranging from 0.77% to 3.75%. Here the TPEE concentration was fixed at 13.4%. Figure 4 is a histogram of the average distance of helical loops as a function of PTT concentration. With the increase of PTT concentration, firstly the distance of the helical loops decreases from 38.46 μm to 6.18 μm , then increases to 29.09 μm . Combining the results of Figure 3 and 4, it can be concluded that there is an optimal concentration of PTT to form regular helical structures. Seen from the experiments in this paper, when the concentration of TPEE is 13.4%, the optimal concentration of PTT is 2.27%.

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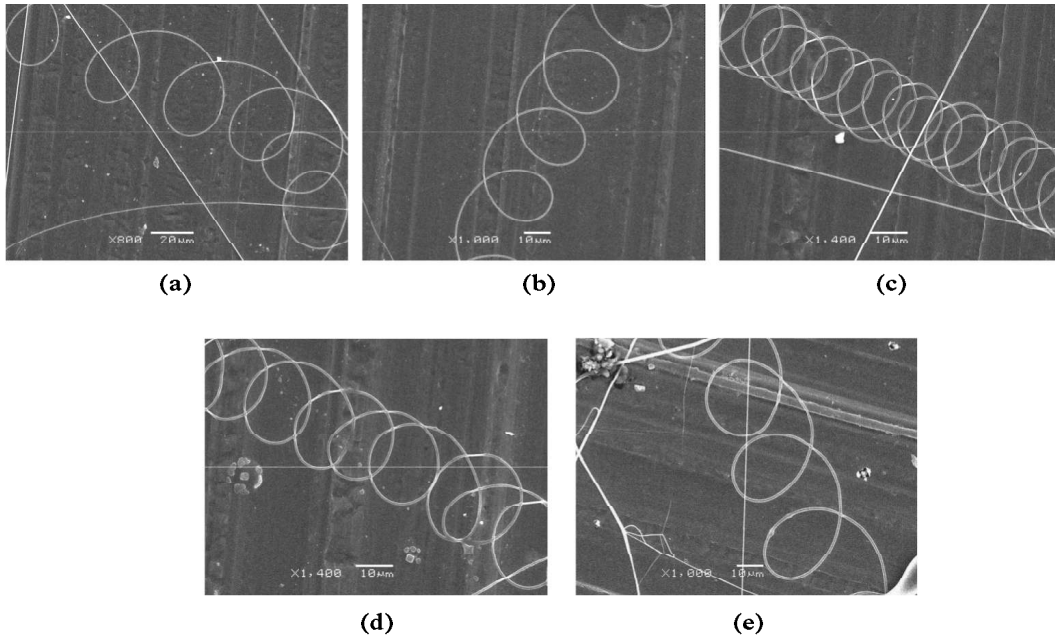


Figure 3: SEM images of nanoscale helical TPEE/PTT fibers. The concentration of TPEE was 13.4% and PTT was (a) 0.77%; (b) 1.52%; (c) 2.27%; (d) 3.01%; (e) 3.75%.

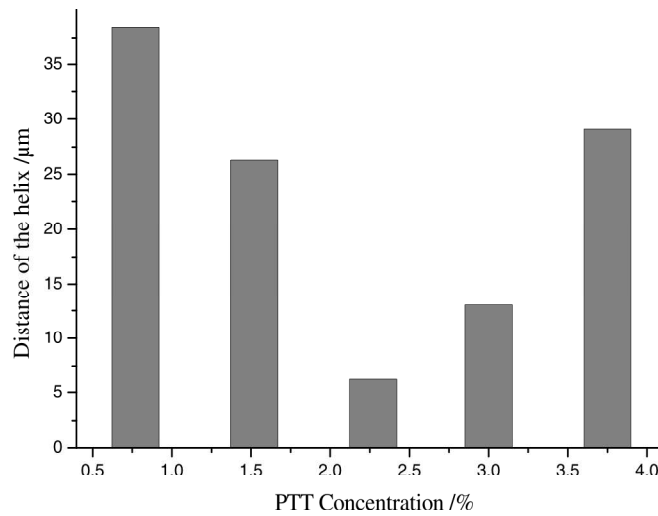


Figure 4: The relation of diameter of the helix and the mass fractions of PTT. The concentration of TPEE was 13.4%.

The result suggests a possible mechanism for the production of micro- and nanoscale curled or helical fibers. The helical structures could not be produced from a single component system,^[5] so a possible mechanism is proposed here. The curled or helical

structures are fabricated because of buckling of the compressed component in the blended fibers. TPEE is a common thermoplastic polymer, which is elastic and has high shrinkage with the elongation at break of 300%. While PBT, PET and PTT are tough and brittle, their elongations at break are only 70%, 47% and 40%, respectively. In the strong electric field, both polymers are stretched due to the electrostatic force on the blended solution. This stretching of both polymer components can lead to differential shrinkage within the fibers, which can spontaneously form crimped fiber morphology on removal of the drawing tension.

In summary, micro- and nanoscale curled or helical fibers were produced on a conductive substrate by electrospinning from a two-component solution. The morphology of the blended curled fibers was affected by the concentrations and kinds of the two polymers. A mechanism is proposed that the differential shrinkage of the two polymers can result in the formation of curled or helical blended polymer fibers during the electrospinning process.

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