Self-Assembled Honeycomb Polyurethane Nanofibers

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ABSTRACT: Electrospinning uses a high voltage electric field to produce fine fibers. A new phenomenon of self-assembly in the electrospinning of polyurethane nanofibers is observed. This report is the first known self-assembling phenomenon in polyurethane electrospun nanofibers. Electrospun polyurethane nanofibers self-assemble into unique honeycomb patterns on the collector surface. This novel observation opens up new and interesting opportunities for electrospun fibers in the areas of drug delivery devices, protective clothing, filters, and tissue scaffolds. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3121–3124, 2006

Key words: fibers; self-assembly; nanotechnology; electron microscopy; nanolayers

INTRODUCTION

The process of producing fine fibers using electrostatic forces was first developed by Formhals[1–3] in the 1930s and 1940s. It has gained momentum in the last decade because of its ability to produce nanofibers for advanced applications such as toxic chemical filters, tissue scaffolds, and so forth. In electrospinning, a polymer solution or melt is charged with a high voltage electric field to produce fine fibers, which are collected on the oppositely charged collector screen. A viscous polymer solution charged with high voltage produces charge carriers with the polarity of the applied electric field.

These charge carriers move toward the surface of the polymer solution causing electrostatic charge repulsion due to the accumulated similar charges. Electrostatic force generated by charge repulsion pulls the polymer solution forward in the form of a cone.[4] At an applied threshold voltage, the surface tension of the polymer drop is overcome by the electrostatic forces to initiate a fiber jet formation from the cone tip.

The schematic of the electrospinning process is shown in Figure 1. Conductive polymers[5] such as polyaniline and biodegradable polymers such as polyethylene-*co*-vinyl acetate[6] and poly-L-lactide[7] can be conveniently electrospun into nanowebs that can be used as smart fabrics and tissue scaffolds. Most recently, Subbiah et al.[8] and Hussain and Ramkumar[9] have reported a detailed account on the electrospinning of different polymers and functionalized nanofibers. It is evident from these articles that earlier works have not reported any significant information on the self-assembling phenomenon in polyurethane electrospun nanofibers.

The theoretical and fundamental aspects of the electrospinning process have been well researched and documented.[10–16] Dietzel et al.[17] have reported that the accumulation of beads and beaded fibers on the collector inhibits the direct deposition of new poly(ethylene oxide) nanofibers on the mat, resulting in honeycomb meshes. The present work hypothesizes that the honeycomb patterns are influenced by the collector substrate and the charge retained on the fiber. The application potential of self-assembled polyurethane nanofibers is enormous in protective face masks and suits for chemical warfare, clean room filters, and so forth. Because the primary mechanism behind the protection in chemical protective suits is adsorption, the surface area and the arrangement of fibers play important roles. Self-assembled nanofibers have a *mesh-in-mesh* feature in addition to high surface area that are common in regular nanofibers. This unique feature is very useful in protective liners and filters for chemical warfare, because the honeycomb filters can trap and retain particles more efficiently, providing enhanced adsorption and filtration capabilities.

To the best of our knowledge, this article demonstrates the first known self-assembling phenomenon in polyurethane nanofibers. Self-assembled nanofibers align themselves into unique three-dimensional (3-D) patterns such as honeycomb meshes on a collector substrate. As briefed earlier, self-assembled nanowebs will be of enormous value in chemical countermeasure substrates such as face masks and chemical protective clothing liners because of their enhanced trapping and filtration capabilities.

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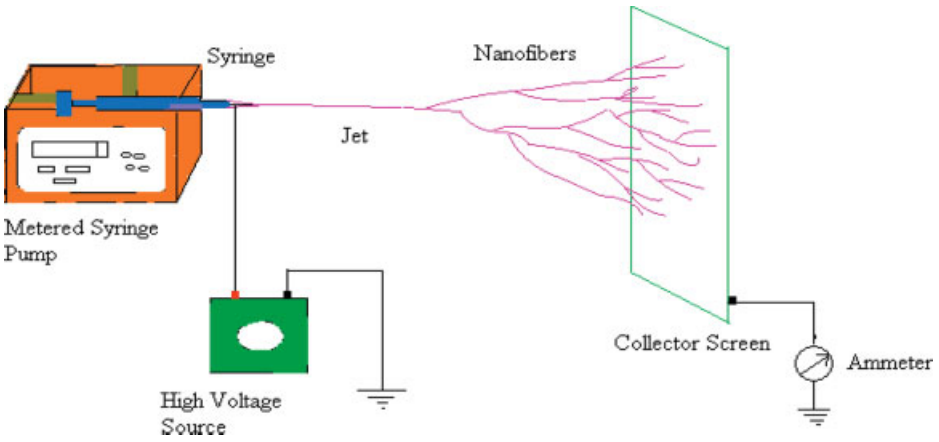

Figure 1 The schematic of the electrospinning process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

EXPERIMENTAL

Pellethane, which is a thermoplastic polyurethane from Dow Chemicals, was homogeneously dissolved in a co-solvent (60 : 40 THF/DMF mixture) at 10 wt % concentration. The aluminum foil was placed 50 mm in front of a syringe needle with its terminal grounded. Electrospun fibers deposited as an irregular nonwoven matrix on the collector surface. Surprisingly, the fibers electrospun over aluminum foil exhibited a self-aligning phenomenon, resulting in honeycomb meshes. As is evident from the SEM micrographs in Figure 2, the self-assembling nature of polyurethane nanofibers is distinctly shown in the form of a honeycomb structure.

The charge carrying electrospun fibers self-aligned on the collector to form meshlike honeycomb nanofibers. The nanofibers ranged from 80 to 300 nm in diameter. Figure 2 shows the honeycomb nanoweb with meshes clearly separated by wall-like boundaries. The boundaries are formed by the self-aligning nanofibers. The electrospun polyurethane fibers contained numerous bead structures along the fiber and it is possible that the beads formed boundaries. Further experiments are currently underway to verify this result. However, we think the charge retained on the nanofibers and the characteristics of the collector screen influence the self-assembling of the fibers, resulting in honeycomb patterns. During electrospinning, the quantity of charge carried by the fibers also depends on the medium that envelops the distance between the jet ejecting needle and the collector screen. There is a good possibility that the surface charges on the fiber jet are dissipated by the interaction with the surrounding media such as air. When a positive charge carrying fiber jet moves toward the negative collector, the fiber deposition pattern is expected to be directed by the intensity of the fiber charge and the repulsive forces exerted by the already deposited fibers. These collected fibers with higher charge intensity repel the incoming similarly charged fibers and drive them toward the nearby conducting points on the collector screen for easier charge dissipation. This was particularly visible during the electrospinning of polyurethane on aluminum foil, where the fiber deposition initially starts at one particular point and periodically covers the entire surface of the foil, resulting in honeycomb patterns. This observation emphasizes the effect of residual charges in self-aligned fibers on web formation, which in turn is influenced by the spinning environment and electrical and surface properties of the collector screen. To understand the influence of the collector screen on the formation of self-aligned nanofiber webs, different collector substrates such as metallic mesh, cotton fabric, and glass were chosen for collecting the fibers.

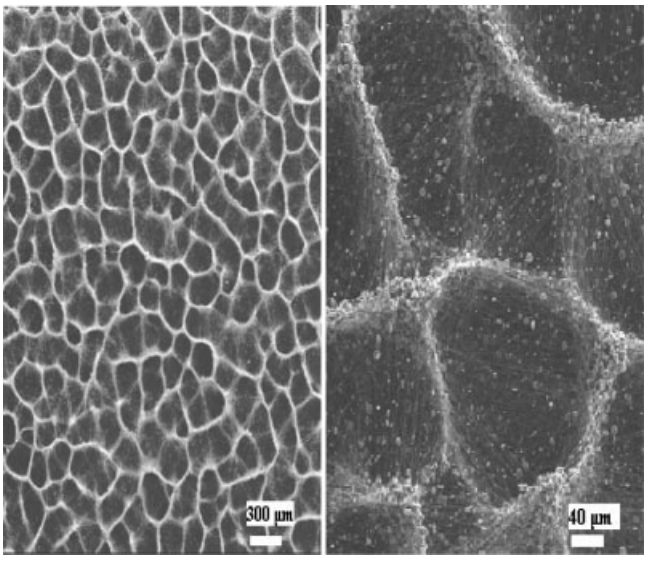

Figure 2 SEM images of self-assembled polyurethane electrospun nanofibers collected on aluminum foil obtained with a Hitachi S570 at a 12-kV accelerating voltage.

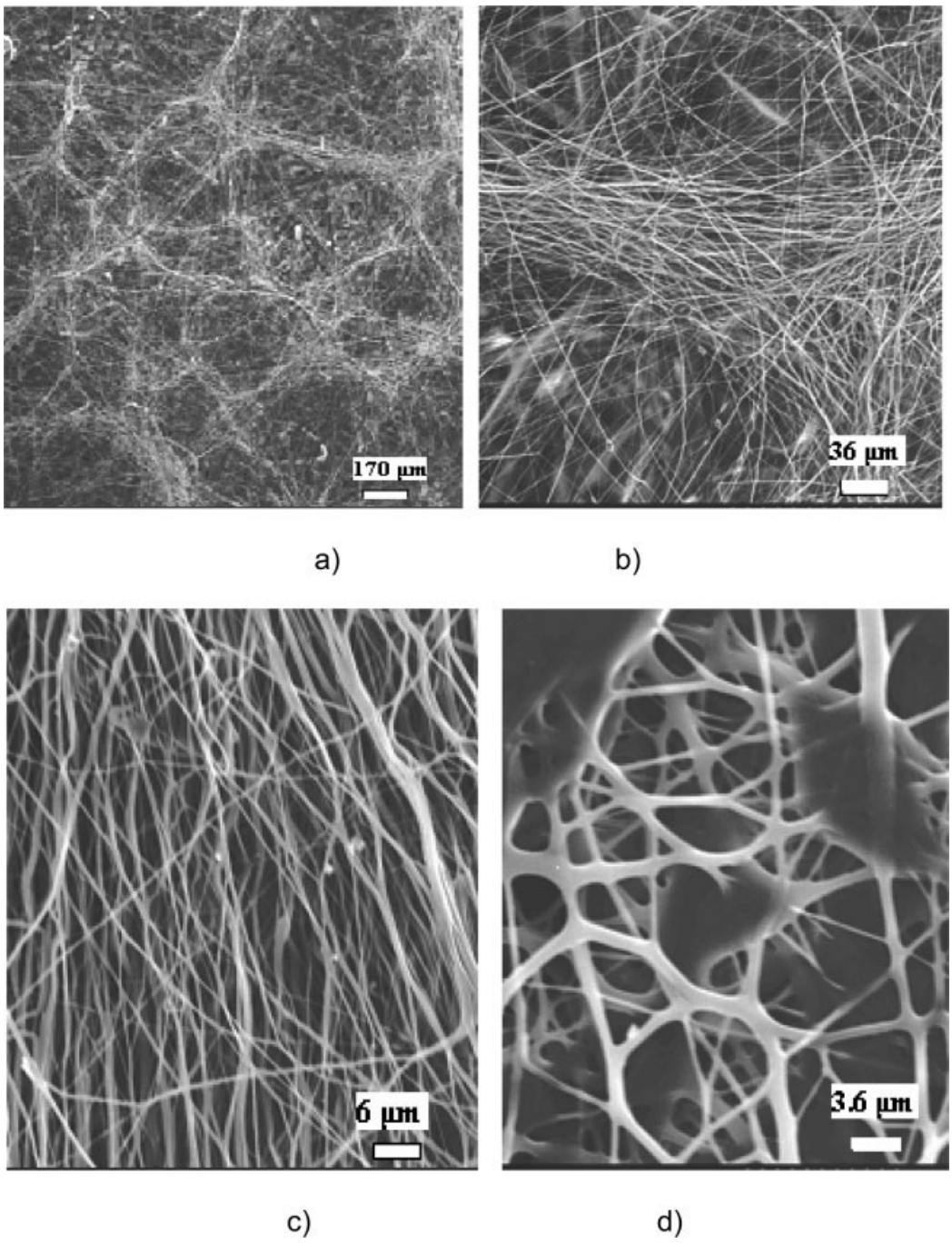

Figure 3 SEM images of electrospun polyurethane nanofibers collected on different substrates: (a) a honeycomb pattern formation over a cotton substrate; (b) self-assembled nanofibers without beads on a cotton substrate, which is a magnified image of (a); (c) straight aligned fibers on a metallic mesh; and (d) a self-assembled 3-D structure on a glass substrate.

Polyurethane nanofibers were electrospun over these substrates while keeping all other process parameters constant. The electrospun fibers aligned straight along the straight edges of the conducting metallic mesh with an irregular fiber deposition pattern over the rest of the areas. This deposition pattern was expected because the charged fibers would obviously move toward the conductive boundaries of the square mesh. When cotton, a natural fiber with very poor electrical conducting properties, was used as the collecting surface, it produced a 3-D honeycomb pattern deposition. Similar results were observed with the glass substrate. Although we are unable to provide a conclusive interpretation of the influence of the electrical properties of the collector on the self-assembling process, we demonstrated the variations in the fiber deposition pattern over different collector substrates. The SEM images in Figure 3 clearly show the

self-assembling fibers without any bead defects. This result suggests that high charge carrying beads are not solely responsible for the self-assembling process.

CONCLUSION

The results reported here demonstrated a new phenomenon of self-assembly in polyurethane nanofibers. As is evident from this study, residual charges on the collected fibers and the electrical property of the collector screen influenced the self-alignment of fibers. This self-assembling phenomenon in nanofibers opens up new and enhanced applications for nanofiber webs. The single polymer study reported here is exciting and will lead to studies on different polymers to investigate whether the self-assembly is unique to polyurethane or is due to the collector screen influence as hypothesized here.

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