Chapter 9

Applications of Electrospun Nanofibers in Current and Future Materials

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Abstract

The search for practical applications of electrospun microfibers and nanofibers is primarily concentrated on filters, membranes, and biomedical devices. This chapter reviews current progress towards developing new applications of electrospinning. The production of submicron as well as nanometer sized fibers by electrospinning was reported early in the 20th century (*1-5*). Over the intervening decades, research has continued around the world, resulting in over one hundred patents and publications. Research today continues to focus on new methods of producing nanofibers, including an increased understanding of electrospinning and its applications. These studies have resulted in process improvements that have increased the speed of electrospinning, increased the strength of the resulting nanofiber web, and may lead to better control of electrospun membrane features such as fiber size, fiber orientation and porosity for future applications.

Introduction

Most commonly reported nanofibers are solid continuous fibers of material with diameters ranging from a few hundred nanometers down to tens of nanometers, exhibiting lengths of a few microns up to meters, depending upon the manufacturing process. Such fine diameters result in fibers that are at least an order of magnitude thinner than commercial microfiber fabrics, as shown in Figure 1. Fabrics of nanofibers may have the appearance and the properties of porous membranes in the case of many organic nanofibers (*6*), or may exhibit the consistency of high loft batting materials in the case of rigid organic fibers and inorganic fibers (*7*). Nanofibers have been reported to be hollow (*8,9,10*), but are usually produced as dense solid fibers or multi-component composite fibers consisting of more than one material within the fiber (*11,12*). Organic nanofibers have been produced by various methods, but one easy fiber forming process is electrospinning (*13*). The application of an electric force to the surface of a polymer solution produces a continuous stream of extremely fine fiber without the use of mechanical extrusion or temperature changes. Methods of applying the field, influencing the spinning by external forces and collecting the fibers continue to be developed, and some recent processing discoveries are discussed in other chapters of this book.

Advantages of Electrospun Fibers

One of the most cited advantages of electrospun fibers that motivate research and the search for applications is the high surface to volume ratio of nanofibers. Based on the surface area of the cylinder, a fabric of 10 nm fibers will have a surface area of roughly 350 m^2/g, whereas 10 μm fibers will be 0.35 m^2/g. Although high surface areas in excess of 2,000 m^2/g can be realized with meso and nanoporous materials such as adsorbent granules and powders, fibers are more easily handled and manipulated than powders. Another advantage of these high surface area organic fibers is the filtration efficiency that has been observed with nanofibers. Electrospun nanofibers can be produced from a wide range of polymers allowing a range of fiber types for filtration and other applications.

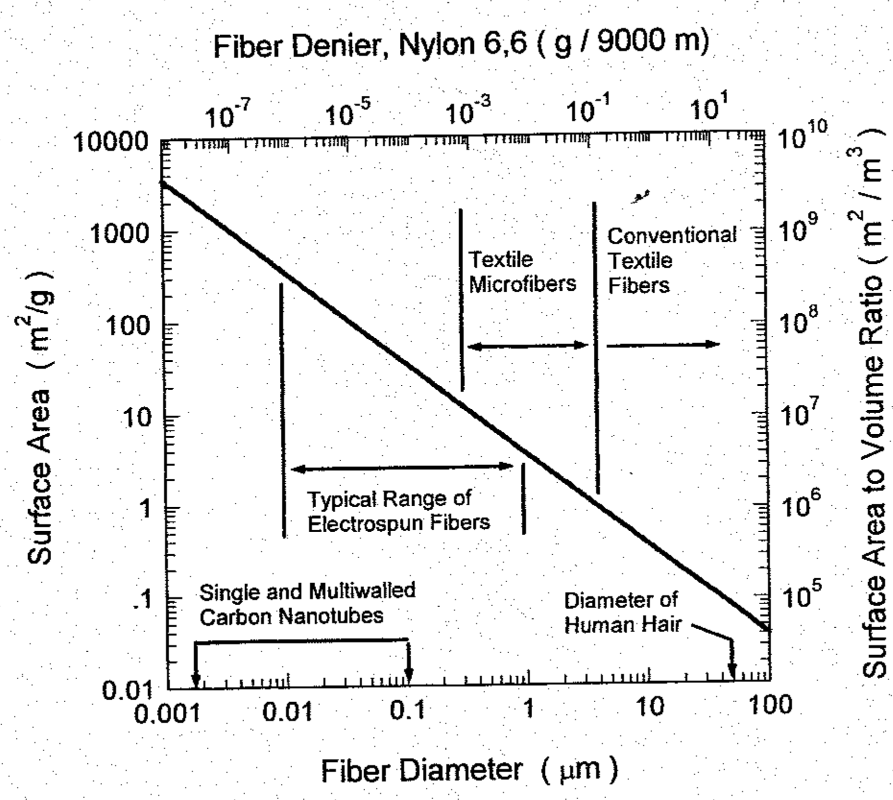


Figure 1. Inverse relationship between fiber diameter and surface area of fabrics calculated for fibers of density 1.14 g/cc. (Reproduced with permission from reference 18. Copyright 2002 Journal of Advanced Materials.*)*

One of the most significant advantages of electrospun fibers is the filtration efficiency that can be realized from the porous membrane-like fabrics and the high surface area available for airborne particle capture. In the case of filtration, electrospun fibers of nylon and polycarbonate have been applied in thin layers to the surface of typical filter fabrics of natural and synthetic nonwovens (*14-16*). High filtration efficiencies result from low levels of electrospun fibers (*17,18*). However, electrospun fibers of glassy and semi crystalline polymers are fragile and require supporting substrates for reinforcement during use; thus rigidly held filters have been the first successful commercial application for electrospun fibers. Shown in Figure 2, thin layers of electrospun nylon fibers coated onto the surface of a carbon-loaded foam exhibit good airflow properties while still providing high aerosol filtration

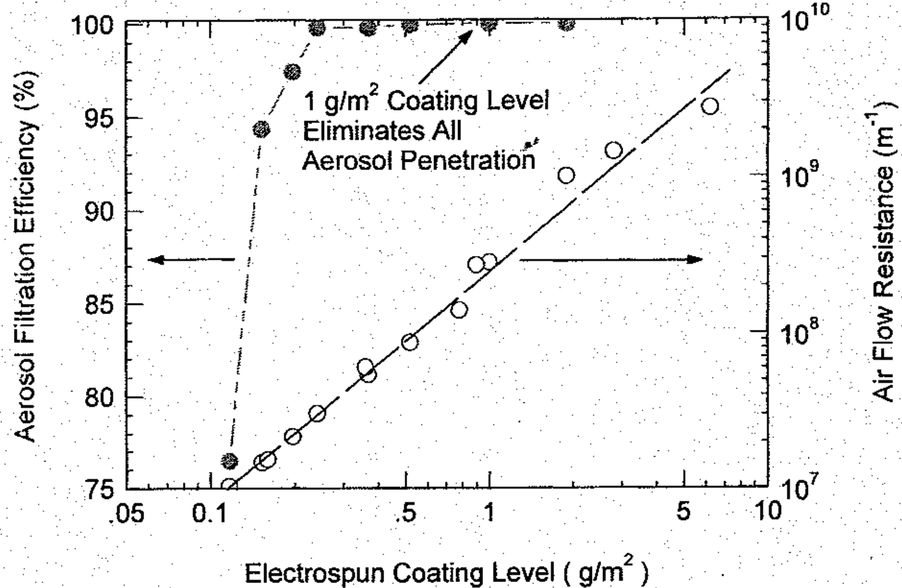


Figure 2. Aerosol filtration and air flow resistance as a function of nanofiber coating level on carbon foam substrate. Aerosol consists of potassium iodide particles with diameters of 0.5-20μm. (Reproduced with permission from reference 18. Copyright 2002 Journal of Advanced Materials.*)*

Another advantage of electrospinning is the ability to produce submicron fibers from a wide range of organic polymers. This enables the production of microporous membranes comprised of nanofibers from elastomers, glasses, and semi crystalline materials, and, recently the preparation of ceramic nanofibers (*19, 20*). The advantage to producing a microporous membrane by electrospinning is the simplification of manufacturing steps; instead of multiple processing steps involving film formation and manipulations such as expanding, foaming or partially dissolving components in the films to produce micro pores, electrospinning allows a direct spray-on application of the final microporous structure onto a wide range of substrates, including release papers, screens, fabrics, and even living tissue. Recent patent applications have proposed the formation of electrospun membranes onto expandable wire frames for biomedical applications, as well as tubes and stents (*21-23*). Chemical surface modification, crosslinking and other chemical treatments of electrospun microporous membranes can be easily achieved in order to produce functionalized surfaces and tailored properties within the membranes (*15, 16, 24*). Surfaces have been functionalized with enzymes (*25*), and recently the co-spinning of electrospun membranes with cells for tissue growth has been reported (*26, 27*). Other advantages to electrospinning as a fiber manufacturing method include the ability to cover complex three-dimensional surfaces with a uniform fibrous layer. The mild processing temperatures involved in solution electrospinning enables the blending of temperature sensitive components such as drugs, biological materials aqueous domains into the fibers (*28, 29*).

Disadvantages of Electrospinning

Slow fiber production speed has been one of the most difficult technical problems to overcome. Whereas typical fabric coating line speeds of up to 60 meters/min produce adhesive patterns of 2 g/m^2 weight onto substrates, electrospinning, in contrast, produces only 100mg fiber/min for a 100-hole spinneret system. This translates into a line speed of approximately 120 g/min for adhesive patterning, and 0.1 g/min for electrospinning onto a 1-meter wide web. Recent improvements in electrospinning with the use of forced air at the spinnerets have been reported, resulting in electrospinning speeds of up to 1 g/min from 100 spinnerets (*26*). Another approach to increase production rates of electrospun fibers has been recently patented, utilizing a method of charge injection into a polymer solution or melt in order to produce submicron and nanometer-sized fibers at rates of 60g fiber/min from a single orifice (*30*), resulting in a rate of nearly 1kg/min at production widths of 1 meter. The phenomenon of electrospinning is not limited to the use of spinnerets or nozzles to generate the nanofibers. Using electric and magnetic fields normal to the free surface of a polymer solution layered on a magnetic fluid, Yarin and Zussman (*31*) report that fiber production can be increased 12-fold over electrospinning from multiple nozzles.

While production speeds have been reportedly improving, other disadvantages to the electrospinning process that have been deterrents to manufacturing on a large scale include safety and environmental issues of the solvents used in the spin dopes and the voltages involved in the electrospinning process. Solution spinning has been shown to be the only way to achieve fiber diameters below 1μm. However, many polymers dissolve in highly volatile and toxic solvents that pose explosion hazards in the presence of the high voltages required for electrospinning. Solvent removal and recovery increase manufacturing costs. The best approach is to develop polymer/solvent systems that are benign in terms of safety and environmental impact. In recent patents, Donaldson Company cites preferred solvents of water, alcohol, acetone and Nmethyl pyrrolidone in their electrospinning production of filtration media (*15-17*).

Web strength is another disadvantage for electrospun fibers. Selection of polymers that dissolve in nonhazardous solvents can limit the fiber strength and toughness in the final electrospun web, or membrane. The use of crosslinking chemistry has improved strength of the final membrane and improved bond strength between the electrospun fibers and the substrate material (*16, 17*). In the case of electrospun Pellethane®, a thermoplastic polyurethane supplied by Dow Chemical, it has been found that solvent type can influence the strength of the final random fiber mat in the membrane-like layer, as shown in Table I, reprinted from the Journal of Advanced Materials (*18*).

Table I. Effect of Electrospinning vs. Cast Film on Tensile Properties

Sample	*Specific Modulus* (MPa)*	*Ultimate Tensile Strength* (MPa)*	*Elongation (%)*
Pellethane® Film	3	15.5	979
Espun Membrane -(Spun from tetrahydrofuran)	3	9.50	360
Pellethane® Film	3	24.7	730
Espun Membrane -(Spun from n-dimethyl formamide)	12	54.5	160

*Normalized by web density (30% fiber) of the electrospun membrane.

Data in Table I suggest that the more volatile solvent, tetrahydrofuran produces a slightly weaker fiber mat than the lower volatility solvent, n-dimethyl formamide, possibly due to the fusing of wetter fibers during the formation of the electrospun mat.

Prospects for Future Research and Applications

The utility of electrospun fibers to provide high surface areas in applications such as filtration can also be an advantage for biomedical devices and for catalyst supporting membranes, as evidenced in recent patent applications (*32-*

41). Some of the recent claims involve methods to electrospin highly porous fibers (*40*) to further increase surface area and to use the fiber as a carrier for a catalyst or preparing composite fibers of polymers with a mesoporous molecular sieve components (*20*).

Use of electrospun fibers in medicated stents has been proposed in recent patent applications (*36, 37*), and in other medical applications involving cell implantation and growth, the characteristic high porosity and high surface area of the fibrous layers is a desirable feature. However, there are few methods to control the pore size of electrospun fiber mats. We speculate that one method would be to incorporate two materials into the electrospun fiber structure, followed by the removal of one material. Spinning blends of two polymers, or co-mingling two fiber streams into a single mat could be two possible approaches, but there have been difficulties in accomplishing this blending of permanent and removable materials in electrospinning. Co-spinning separate polymer solutions from different spinnerets causes field interference between the streams and prevents intermingling of the fiber streams into a final fiber mat, as shown in Figure 3. In this figure, we see polycarbonate fibers collecting into a small spot while the polyacrylonitrile fibers remain segregated from the polycarbonate. This repulsion between different polymeric fibers electrospun simultaneously is an effect that could be caused by a difference in charge density of the different fibers. A higher charge density can result from fibers of smaller diameter, so the higher charge density of the smaller polyacrylonitrile fibers results in strong repelling forces acting against larger fibers of lower charge density.

However, the use of a single spinneret that has been divided to accommodate two polymer solutions has been reported to be a successful design that combines two polymers into single fibers and also produces fiber mats containing separate fibers of each material (*9, 11, 43*).

Other approaches to controlling pore size and total porosity in an electrospun mat involve simply collecting fibers of different diameter. Measurements done on melt blown nonwovens have shown that larger fiber diameters produce larger pore sizes within fiber mats (*43*). This relationship, between fiber size and pore size has been derived and is useful in the indirect measurement of an effective fiber size from air permeability measurements, rather than microscopic measurements (43).

Figures 4-6 show the dramatic differences in apparent fiber size in two electrospun examples and the corresponding difference in mean pore size compared to a melt blown sample of the polyurethane, Estane®, produced by Noveon Corporation.

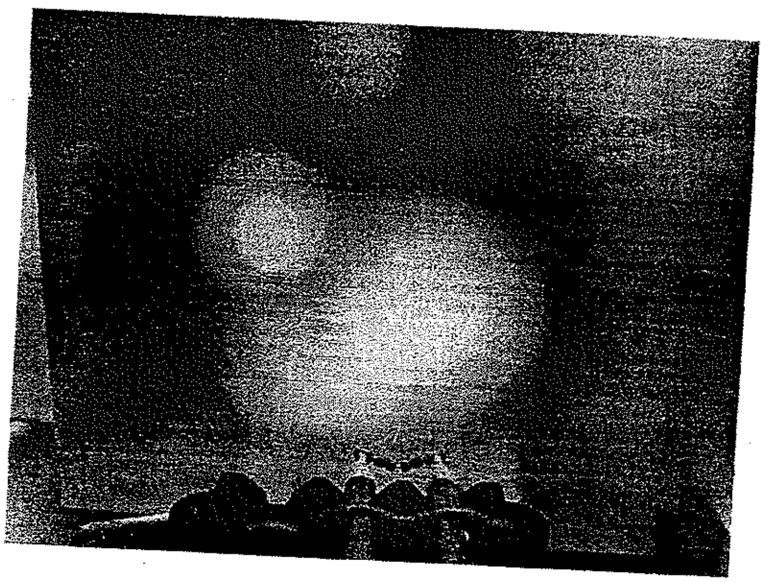


Figure 3. Electrospinning of polycarbonate solution in the left collection spot and polyacrylonitrile in the right. (Reproduced with permission from reference 42. Copyright 2003.)

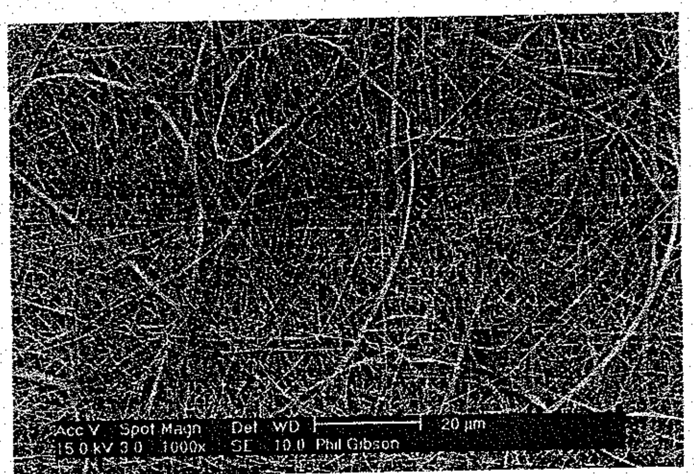


Figure 4. Electrospun Nylon® 6,6 average fiber diameter 0.13µm and mean pore size 0.1-0.2 µm.

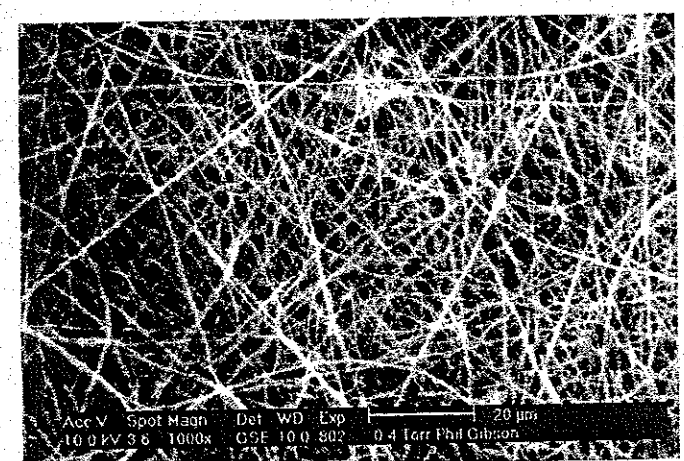


Figure 5. Electrospun Estane®, average fiber diameter 0.43µm and mean pore size 0.4µm

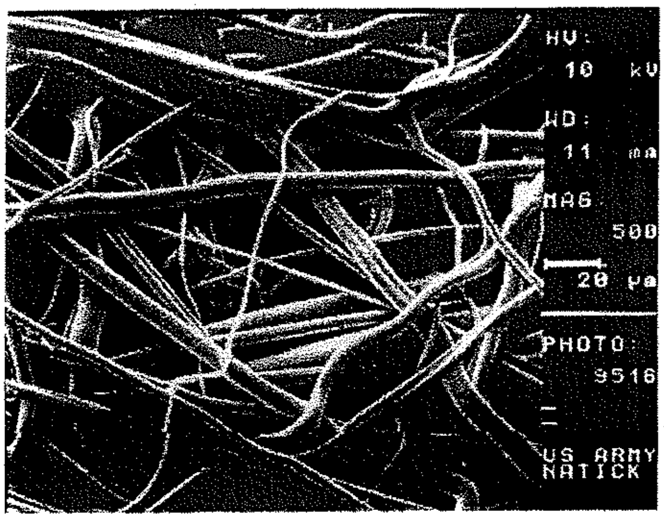
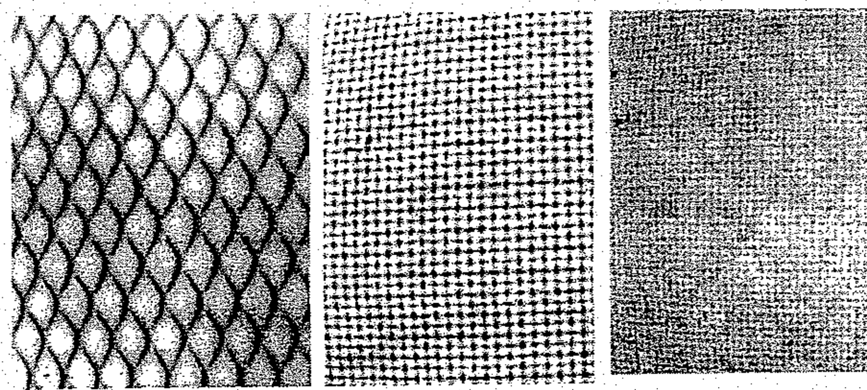


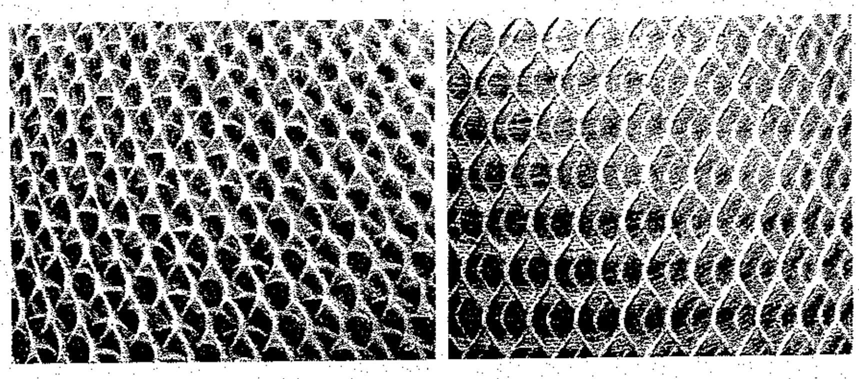
Figure 6. Melt Blown Estane®, average fiber diameter 10-20µm and mean pore size 30µm.

Combining high surface area nanofibers with larger diameter textile fibers would be expected to accomplish two objectives: achieve a controlled average pore size based upon the average fiber size and provide reinforcement of the nanofiber mat with larger fibers integrated into the structure. Research is ongoing in an effort to combine electrospinning with large nonwoven spunbonding or melt blowing processes to achieve the intermingling of electrospun and nonwoven fiber sizes, but success has been limited and more work needs to be done on fiber intermingling of these two processes.

Charged electrospun fibers can be organized into a patterned arrangement through the use of secondary electric fields such as electrostatic lenses (*44-47*) and patterned collectors (*48*). These techniques can be used to develop new fibrous architectures and are being applied in an effort to develop processing methods to control the porosity of electrospun membranes and provide mechanical reinforcement to increase toughness of the electrospun membrane. Figure 7 shows that different patterns from a grounded collector surface will influence the deposition of charged electrospun fibers and impose a fibrous pattern on the membrane.



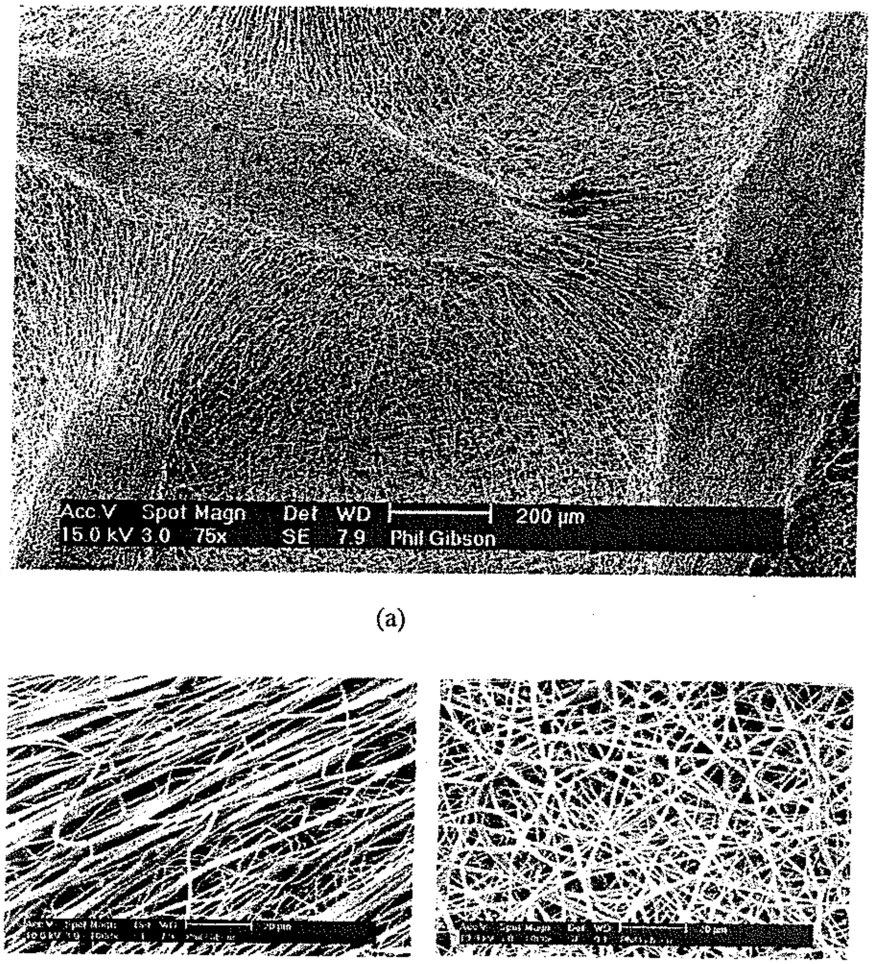
(a) Coarse Grid (b) Medium Grid (c) Fine Grid



(d) Pattern Rotated (e) Pattern Shifted Laterally

Figure 7. Grid patterns used for electrospun polyurethane fiber collection. These images are electrospun membranes that display the original grid pattern. (Reproduced with permission from reference 48. Copyright 2003 e-Polymer.*)*

The fiber patterns in Figure 8 show that the fibers orient in some areas in the grid, and remain random in other areas. Figure 8 (a) shows a magnified image of the fiber orientation on the medium grid of Figure 7 (b). Figure 8 (b) shows orientation of the electrospun polyurethane fibers near the grid junctions, while Figure 8 (c) shows that the electrospun fibers are random in areas between the grid junctions.

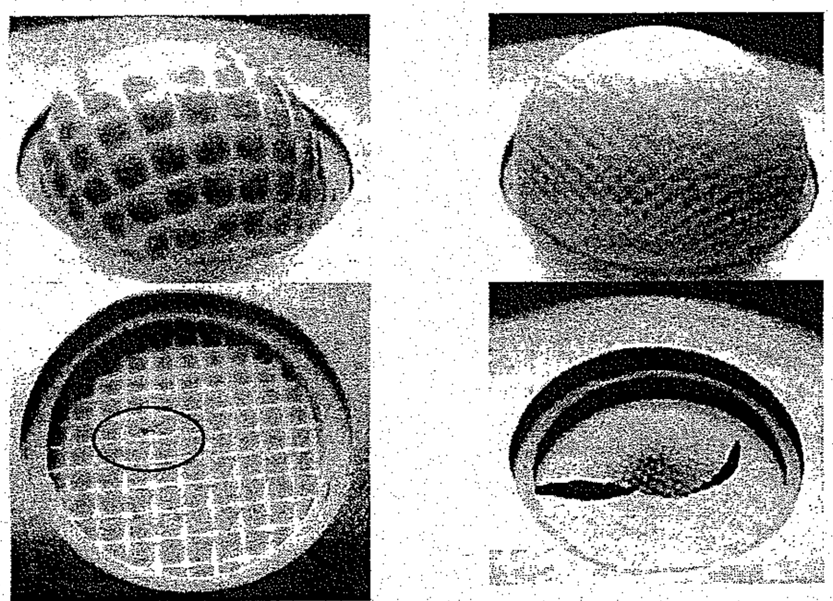


(a)

(b) (c)

Figure 8. (a) Close up image of fiber patterns in membrane produced by medium grid; (b) Fiber orientation at junctions of grid pattern and random fiber collection and (c) farther away from grid element. (Reproduced with permission from reference 48. Copyright 2003 e-Polymer.*)*

Figure 9 shows that grid size appears to affect tear propagation in bursting of the elastic membrane after inflation. Coarse and medium grid patterned electrospun elastic membranes can be inflated, as shown in figure 9 (a) and (b). After inflation and bursting, the coarse grid pattern results in a small tear (circled for clarity) in Figure 9 (a), while the medium grid pattern results in a large catastrophic tear across numerous grid junction points in Figure 9 (b).



(a) Coarse grid membrane. (b) Medium grid membrane.

Figure 9. Examples of electrospun polyurethane membranes that have been inflated in the top images, and torn after burst testing in the bottom images. (a) Membrane with coarse grid pattern. (b) Membrane with medium grid pattern. (Reproduced with permission from reference 48. Copyright 2003 e-Polymer.*)*

This recent study has shown that electrospun fibers can be collected into organized patterns that exhibit fiber alignment near grid junctions. These fiber aligned regions could lead to larger pore dimensions in patterned membranes. It has also been found that pattern size appears to result in membrane tear reinforcement. Continuing research on elastic and reinforced electrospun membranes will lead to new applications in the new future such as inflatable membranes and controlled porosity structures for medical devices.

Summary

Electrospun materials are highly porous and have high surface areas that are attractive for many applications, including filtration, biomedical materials and devices, and microporous membranes. Recent improvements of electrospinning production rates have been reported in the patent literature. Progress has also been made with respect to web strength and controlled properties such as porosity. Elastic membranes produced by electrospinning may have utility as wearable materials in applications such as protective garments in the future: they exhibit high strength and are tough and flexible. Properties of elastic fibrous membranes can be improved with crosslinking and fiber patterning to arrest tear crack propagation. Combined with woven as well as knit stretchable fabrics, elastic electrospun membranes are easily post treated for increased adhesion to substrate layers. The electrostatic fields used in electrospinning allow control of the variation of fiber deposition and orientation across the area of a web. This is an advantage over other nonwoven processes such as meltblowing, spinlacing, spunbonding, hydroentanglement, etc., which produce a fairly uniform fiber distribution across the area of the manufactured web. Controlled variations of the electric field in electrospinning or combined melt blowing/electrospinning can produce patterns across the web width that result in distict fiber pattern arrays that are useful for strength enhancements and could potentially produce porosity variations for future applications of electrospun membranes.

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