

Electrospinning of Nanofibers

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ABSTRACT: Nanotechnology is the study and development of materials at nano levels. It is one of the rapidly growing scientific disciplines due to its enormous potential in creating novel materials that have advanced applications. This technology has tremendously impacted many different science and engineering disciplines, such as electronics, materials science, and polymer engineering. Nanofibers, due to their high surface area and porosity, find applications as filter medium, adsorption layers in protective clothing, etc. Electrospinning has been found to be a viable technique to produce nanofibers. An in-depth review of research activities on the development of nanofibers, fundamental understanding of the electrospinning process, and properties of

nanostructured fibrous materials and their applications is provided in this article. A detailed account on the type of fibers that have been electrospun and their characteristics is also elaborated. It is hoped that the overview article will serve as a good reference tool for nanoscience researchers in fibers, textiles, and polymer fields. Furthermore, this article will help with the planning of future research activities and better understanding of nanofiber characteristics and their applications. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 557–569, 2005

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INTRODUCTION

Production of synthetic filaments using electrostatic forces has been known for more than one hundred years. The process of spinning fibers with the help of electrostatic forces is known as electrospinning. It has been shown recently that the electrospinning process is capable of producing fibers in the submicron range.¹ Electrospinning has gained much attention in the last decade 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 submicron range. In fiber science related literature, fibers with diameters below 100 nm are generally classified as nanofibers.² These fibers, with smaller pores and higher surface area than regular fibers, have enormous applications in nanocatalysis, tissue scaffolds, protective clothing, filtration, and optical electronics.

The electrospinning process uses a high voltage electric field to produce electrically charged jets from polymer solution or melts, which on drying by means of evaporation of the solvent produce nanofibers. The highly charged fibers are field directed towards the oppositely charged collector, which can be a flat

surface or a rotating drum, to collect the fibers. In normal conventional spinning techniques, the fiber is subjected to a group of tensile, gravitational, aerodynamic, rheological, and inertial forces.³ In electrospinning, the spinning of fibers is achieved primarily by the tensile forces created in the axial direction of the flow of the polymer by the induced charges in the presence of an electric field.

With enormous research interests and both fundamental and applied research opportunities in nanofibers, there is a need for a comprehensive review of the subject in a systematic fashion. The aim of this overview article is to understand the history of electrospinning and examine earlier research works on the electrospinning of nanofibers, influence of processing variables on the structural morphology, and characteristics of electrospun fibers. In addition, the article will also elaborate on the potential applications of electrospun nanofibers in many different fields.

HISTORY OF ELECTROSPINNING

The origin of electrospinning as a viable fiber spinning technique can be traced back to the early 1930s. In 1934, Formhals patented his first invention relating to the process and the apparatus for producing artificial filaments using electric charges.⁴ Though the method of producing artificial threads using an electric field had been experimented with for a long time, it had not

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gained importance until Formhals's invention due to some technical difficulties in earlier spinning methods, such as fiber drying and collection. Formhals's spinning process consists of a movable thread collecting device to collect the threads in a stretched condition, like that of a spinning drum in the conventional spinning. Formhals's process was capable of producing threads aligned parallel on to the receiving device in such a way that it can be unwound continuously. In his first patent, Formhals reported the spinning of cellulose acetate fibers using acetone as the solvent.⁴

The first spinning method adopted by Formhals had some technical disadvantages. It was difficult to completely dry the fibers after spinning due to the short distance between the spinning and collection zones, which resulted in a less aggregated web structure. In a subsequent patent, Formhals refined his earlier approach to overcome the aforementioned drawbacks.⁵ In the refined process, the distance between the feeding nozzle and the fiber collecting device was altered to give more drying time for the electrospun fibers. Subsequently in 1940, Formhals patented another method for producing composite fiber webs from multiple polymer and fiber substrates by electrostatically spinning polymer fibers on a moving base substrate.⁶

In the 1960s, fundamental studies on the jet forming process were initiated by Taylor.⁷ In 1969, Taylor studied the shape of the polymer droplet produced at the tip of the needle when an electric field is applied and showed that it is a cone and the jets are ejected from the vertices of the cone.⁷ This conical shape of the jet was later referred to by other researchers as the "Taylor Cone" in subsequent literature. By a detailed examination of different viscous fluids, Taylor determined that an angle of 49.3 degrees is required to balance the surface tension of the polymer with the electrostatic forces. The conical shape of the jet is important because it defines the onset of the extensional velocity gradients in the fiber forming process.⁸

In subsequent years, focus shifted to studying the structural morphology of nanofibers. Researchers were occupied with the structural characterization of fibers and the understanding of the relationships between the structural features and process parameters. Wide-angle X-ray diffraction (WAXD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and differential scanning calorimetry (DSC) have been used by researchers to characterize electrospun nanofibers. In 1971, Baumgarten reported the electrospinning of acrylic microfibers whose diameters ranged from 500 to 1100 nm.⁹ Baumgarten determined the spinability limits of a polyacrylonitrile/dimethylformamide (PAN/DMF) solution and observed a specific dependence of fiber diameter on the viscosity of the solution. He showed that the diameter of the jet reached a minimum value after an initial increase in the applied field and then became larger

with increasing electric fields. Larrondo and Mandley produced polyethylene and polypropylene fibers from the melt, which were found to be relatively larger in diameter than solvent spun fibers.^{10,11} They studied the relationship between the fiber diameter and melt temperature and showed that the diameter decreased with the increasing melt temperature. According to them, fiber diameter reduced by 50% when the applied voltage doubled, showing the significance of applied voltage on fiber characteristics.

In 1987, Hayati et al. studied the effects of electric field, experimental conditions, and the factors affecting the fiber stability and atomization. They concluded that liquid conductivity plays a major role in the electrostatic disruption of liquid surfaces. Results showed that highly conducting fluids with increasing applied voltage produced highly unstable streams that whipped around in different directions. Relatively stable jets were produced with semi conducting and insulating liquids, such as paraffinic oil.¹² Results also showed that unstable jets produce fibers with broader diameter distribution.

After a hiatus of a decade or so, a major upsurge in research on electrospinning took place due to increased knowledge on the application potential of nanofibers in different areas, such as high efficiency filter media, protective clothing, catalyst substrates, and adsorbent materials. Research on nanofibers gained momentum due to the work of Doshi and Reneker.¹ Doshi and Reneker studied the characteristics of polyethylene oxide (PEO) nanofibers by varying the solution concentration and applied electric potential.¹ Jet diameters were measured as a function of distance from the apex of the cone, and they observed that the jet diameter decreases with the increase in distance. They found that the PEO solution with viscosity less than 800 centipoise (cP) was too dilute to form a stable jet and solutions with viscosity more than 4000 cP were too thick to form fibers.

Jaeger et al. studied the thinning of fibers as the extrusion progressed in PEO/water electrospun fibers and observed that the diameter of the flowing jet decreased to 19 μm in traveling 1 cm from the orifice, 11 μm after traveling 2 cm, and 9 μm after 3.5 cm.¹³ Their experiment showed that solutions with conductivities in the range of 1000–1500 $\mu\text{s}\cdot\text{cm}^{-1}$ heated up the jet due to the electric current in the order of 1–3 μA . Deitzel et al. showed that an increase in the applied voltage changes the shape of the surface from which the jet originates and the shape change has been correlated to the increase in the bead defects.¹⁴ They tried to control the deposition of fibers by using a multiple field electrospinning apparatus that provided an additional field of similar polarity on the jets.¹⁵

Warner et al.¹⁶ and Moses et al.^{17,18} pursued a rigorous work on the experimental characterization and evaluation of fluid instabilities, which are crucial for

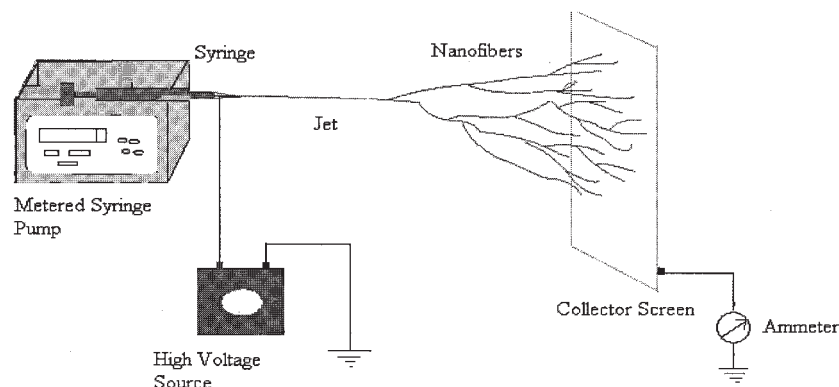


Figure 1 Schematic of electrospinning process.

the understanding of the electrospinning process. Shin et al. designed a new apparatus that could give enough control over the experimental parameters to quantify the electrohydrodynamics of the process.¹⁹ Spivak and Dzenis showed that the Ostwald–deWaele power law could be applied to the electrospinning process.²⁰ Gibson et al. studied the transport properties of electrospun fiber mats, and they concluded that nanofiber layers give very less resistance to the moisture vapor diffusional transport.²¹

ELECTROSPINNING THEORY AND PROCESS

Electrospinning is a unique approach using electrostatic forces to produce fine fibers. Electrostatic precipitators and pesticide sprayers are some of the well known applications that work similarly to the electrospinning technique. Fiber production using electrostatic forces has invoked glare and attention due to its potential to form fine fibers. Electrospun fibers have small pore size and high surface area. There is also evidence of sizable static charges in electrospun fibers that could be effectively handled to produce three-dimensional structures.²²

According to the authors of this article, electrospinning is a process by which a polymer solution or melt can be spun into smaller diameter fibers using a high potential electric field. This generic description is appropriate as it covers a wide range of fibers with submicron diameters that are normally produced by electrospinning. Based on earlier research results, it is evident that the average diameter of electrospun fibers ranges from 100 nm–500 nm. In textile and fiber science related scientific literature, fibers with diameters in the range 100 nm–500 nm are generally referred to as nanofibers. The advantages of the electrospinning process are its technical simplicity and its easy adaptability. The apparatus used for electrospinning is simple in construction, which consists of a high voltage electric source with positive or negative polarity, a syringe pump with capillaries or tubes to carry the

solution from the syringe or pipette to the spinnerette, and a conducting collector like aluminum. The collector can be made of any shape according to the requirements, like a flat plate, rotating drum, etc. A schematic of the electrospinning process is shown in Figure 1. Many previous researchers have used an apparatus similar to the one given in Figure 1 with modifications depending on process conditions to spin a wide variety of fine fibers.

Polymer solution or the melt that has to be spun is forced through a syringe pump to form a pendant drop of the polymer at the tip of the capillary. High voltage potential is applied to the polymer solution inside the syringe through an immersed electrode, thereby inducing free charges into the polymer solution. These charged ions move in response to the applied electric field towards the electrode of opposite polarity, thereby transferring tensile forces to the polymer liquid.³ At the tip of the capillary, the pendant hemispherical polymer drop takes a cone like projection in the presence of an electric field. And, when the applied potential reaches a critical value required to overcome the surface tension of the liquid, a jet of liquid is ejected from the cone tip.⁷

Most charge carriers in organic solvents and polymers have lower mobilities, and hence the charge is expected to move through the liquid for larger distances only if given enough time. After the initiation from the cone, the jet undergoes a chaotic motion or bending instability and is field directed towards the oppositely charged collector, which collects the charged fibers.²³ As the jet travels through the atmosphere, the solvent evaporates, leaving behind a dry fiber on the collecting device. For low viscosity solutions, the jet breaks up into droplets, while for high viscosity solutions it travels to the collector as fiber jets.¹⁴

Electrospinning: Jet initiation

The behavior of electrically driven jets, the shape of the jet originating surface, and the jet instability are

some of the critical areas in the electrospinning process that require further research. Rayleigh²⁴ and Zeleny²⁵ gave initial insight into the study of the behavior of liquid jets, later followed by Taylor.⁷ Taylor showed that a conical shaped surface referred to as the Taylor cone with an angle of 49.3° is formed when a critical potential is reached to disturb the equilibrium of the droplet at the tip of the capillary, that is, the initiating surface. When a high potential is applied to the solution, electrical forces and the surface tension help in creating a protrusion wherein the charges accumulate. The high charge per unit area at the protrusion pulls the solution further to form a conical shape, which on further increase in the potential initiates the electrospinning process by jetting.³ In a recent study, Yarin et al. have shown that the Taylor cone corresponds only to a specific self-similar solution and there exists another shape corresponding to nonself-similar solutions.²⁶ Taylor's work proposed a spheroidal approximation of the initiating droplet shape, while Yarin et al. considered a family of nonself-similar solutions for the hyperboloidal shapes of electrified liquid bodies and concluded that a cone sharper than that of the Taylor can precede the initiation of the jet. It has been shown both experimentally and theoretically that a liquid surface on application of a critical electric potential forms a conical shape with an angle of 33.5° , that is, less than the typical Taylor cone angle of 49.3° .²⁶ The importance of the jet originating surface has been discussed by Cloupeau and Prunet-Foch²⁷ and Grace and Marijnissen.²⁸ Different shapes of the jet initiation have been associated with varying degrees of instability along the path of the jet.²⁷

Bending instability

The jet ejected from the apex of the cone continues to thin down along the path of its travel towards the collector, and the jetting mode has been termed as electrohydrodynamic cone-jet.²⁷ The charges in the jet accelerate the polymer solution in the direction of the electric field towards the collector, thereby closing the electrical circuit. The jet while moving towards the collector undergoes a chaotic motion or bending instability as suggested by Yarin et al. due to the repulsive forces originating from the charged ions within the electrospinning jet.²⁶ The bending instability was originally thought to be occurring by a single jet splitting into multiple thin fiber filaments due to radial charge repulsion, which was termed as splaying.¹ Doshi and Reneker argued that as the fiber diameter decreases due to the simultaneous stretching of the jet and the evaporation of the solvent, the increased charge density splits the jet into smaller jets. This splitting is expected to occur repeatedly, resulting in smaller diameter fibers.¹

However, recent observations suggest that the rapid growth of a nonaxisymmetric or whipping instability causes the stretching and bending of the jets.²⁹ Warner et al. and Shin et al. have used high-speed photography (with exposure times down to 1 ms) to confirm that the unstable region of the jet, which appears as an inverted cone suggesting multiple splitting, is in reality a single rapidly whipping jet.^{16,29} They suggest that the whipping phenomena occur so fast that the jet appears to be splitting into smaller fiber jets, resulting in ultra fine fibers.

A steady state model of the jets using nonlinear power law constitutive equations (Oswald-de Waele model^{30,31}) was developed by Spivak et al.³² Reneker and his coworkers have contributed significantly for reasoning the instability behavior and developed a mathematical viscoelastic model for the rectilinear electrified jet. In their work they have mathematically modeled the jet path, trajectory and velocity of jet, area reduction ratio, and the longitudinal strain of the jets.³³ They have observed the onset of jetting instability from the vertex of the envelope cone by imaging with a lens of focal length 86 mm and an "f" number of 1.0. The image produced by this lens was observed on an electronic camera with exposure time of 0.0125 ms and recording speed of 2000 frames/s.³³ According to Reneker et al., a smooth surface with a slight curvature suddenly develops an array of bends, on elongation the array of bends becomes a series of spiraling loops with growing diameters, and as the perimeter of the loop increases, the jets forming the loop start thinning. They inferred that many cycles of instability repeat to form nanofibers.³³

Shin et al.²⁹ in their attempt to model the instability behavior of electrically forced jets stressed the competition between different types of instabilities that could occur due to the interactions between the charged ions and the electric field. These instabilities were shown to vary along the path depending upon the fluid parameters and the operating conditions.²⁹ The work showcased the possibility of three types of instabilities: (1) the classical Rayleigh mode (axisymmetric) instability, (2) electric field induced axisymmetric conducting mode, and (3) whipping conducting mode instabilities. To have a better understanding of the different instability modes, it is necessary to precisely model the process. Shin et al. have presented an approach to model the stability of jets as a function of fluid properties like viscosity and conductivity and process variables like applied electric field and flow rate. They observed that the whipping mode instability is dominant with high charge density in the jets, while the axisymmetric instability dominates at lower charge density. The physical mechanisms of the instability and the development of asymptotic approximations for modeling the instability behavior were discussed elsewhere in detail.^{17,18} Fridrikh et al. re-exam-

ined the equations of motion derived earlier^{17,18} for creating a model to derive the ultimate diameter of the jets by accounting for the nonlinear instability of the jets at the final stage of whipping.³⁴ Their model assumes the charged fluid jet as Newtonian fluid, and an empirical model of the terminal diameter of the whipping jet has been derived as a function of flow rate, electric current, and surface tension of the fluid. The model predicted $10^{2/3}$ fold variations in fiber diameter for varying flow rate, and this $2/3$ scaling was experimentally verified for varying concentrations of polycaprolactone (PCL) solution.³⁴

ELECTROSPINNING TECHNOLOGY AND EQUIPMENT: CURRENT SCENARIO

There has been a substantial amount of research carried out on the fundamental aspects of electrospinning. The major issue that is yet to be resolved is the scaling-up of the process for commercialization. Academic and research communities should join hands in taking the lab-scale technology to the commercial level. A succinct summary on nanofiber research that is of use to the fiber and textile industry has been provided by Shastri and Ramkumar.³⁵ Electrospinning apparatus is simple in construction, and there have been no significant developments in the equipment design in the last decade. Research groups have improvised the basic electrospinning setup to suit their experimental needs and conditions. Warner et al. have designed a new parallel plate setup for effectively controlling the operating variables to quantify the electrohydrodynamics of the process.¹⁶ The parallel plate design is expected to overcome the problem of a nonuniform electric field experienced in the point-plate configuration. Jaeger et al. have used a two electrode setup by placing an additional ring electrode in front of the capillary to reduce the effect of the electrostatic field at the tip and to avoid corona discharges.¹³ It has been stipulated that by using the two electrode setup, a more stable field can be established between the ring electrode and the collector, thereby avoiding the effect of changing shape at the capillary tip over the electric field.

Productivity enhancement for commercializing the electrospinning process is under active research, with emphasis on multiple spinneret designs and alternative experimental setup for feed charging. However, there is still a debate on the potential of scaling up this technology for commercialization. This is an important issue, which government agencies, academia, and industry should pay attention to for further growth and development of the field. There are only a few technology companies engaged in research and development on nanofibers. There is hardly any information available in the public domain on the mass production of nanofibers for different applications. Espin

Technologies, a nanofiber technology company, is involved in developing a proprietary high speed device that could effectively overcome the traditional drawbacks of low output and high production cost.³⁶ Donaldson filtration has its own patented process setup for making tens of thousands of square meters of electrospun nanofiber filter media.³⁷ From the available published literature and the current state of understanding of the electrospinning process, it is likely that commercial scaling up of the electrospinning process can only be achieved by more fundamental understanding of the process and better control of the instability behavior of the jets that determine the diameter of the fibers. In addition, there needs to be an active participation between government agencies, industry, and academia for scaling-up the process. With greater enthusiasm among the interested parties, programs that are in place, such as Grants Opportunities for Academic Liaison with Industry of the NSF and SBIR programs, can be of assistance for technology transfer and commercialization.

SPINNING OF POLYMERIC NANOFIBERS

Research activity on the electrospinning of nanofibers has been successful in spinning submicron range fibers from different polymeric solutions and melts. Although a plethora of literature is available on the structure and morphological properties of polymeric nanofibers, there is very little information in the public domain on the electrohydrodynamics of the electrospinning process. Polymers with attractive chemical, mechanical, and electrical properties like high conductivity, high chemical resistance, and high tensile strength have been spun into ultrafine fibers by the electrospinning process, and their application potential in areas like filtration, optical fibers, drug delivery system, tissue scaffolds, and protective textiles have been examined.^{14,21} Some of the polymers attempted to-date for electrospinning and their corresponding literature are tabulated in Table I for a quick and cursory review.

Structure and morphology of polymeric nanofibers

In recent times, nanofibers have attracted the attention of researchers due to their pronounced micro and nano structural characteristics that enable the development of advanced materials that have sophisticated applications. More importantly, high surface area, small pore size, and the possibility of producing three-dimensional structures have increased the interest in nanofibers. As theoretical studies on the electrospinning process have been conducted by various groups^{17-19,23,26,29,33,34} for a while to understand the electrospinning process, there have been some simultaneous efforts to characterize the structure and mor-

TABLE I
Electrospun Polymers and Corresponding Literature

S. No	Polymer	Solvent	Comments
1	Cellulose acetate	Acetone	Formhals attempted the electrospinning of cellulose acetate fibers in 1934. ⁴
2	Acrylic resin (96% acrylonitrile)	DMF	Baumgarten spun acrylic fibers and studied the effect of polymer flow rate and viscosity on fiber diameter in 1971. ⁹ The fibers were less than 1 μm in diameter.
3	a) Polyethylene oxide b) Polyvinyl alcohol c) Cellulose acetate	a) Water/chloroform b) Water c) Acetone	Jaeger et al. studied the morphological characteristics of electrospun polymeric fibers in the diameter range of 200–800 nm. ¹³
4	a) Poly (2-hydroxy ethyl methacrylate) b) Polystyrene c) Poly (ether amide)	a) Formic acid and Ethanol b) Dimethyl Formamide and Diethyl Formamide c) Hexa fluoro 2- propanol	Koomphongse et al. spun different fibers and reported flat ribbon like structures and branched fibers. ³⁸ The electrospun fibers were between 1–3 μm in diameter
5	Polyethylene oxide (PEO)	Water	Doshi and Reneker have experimented with the spinning of PEO fibers from aqueous solutions and studied the relationship between process and solution parameters on fiber characteristics. ¹ Electrospun fibers were about 0.05 to 5 microns in diameter.
6	Polyethylene terephthalate	Mixture of dichloromethane and trifluoroacetic acid	Reneker and Chun demonstrated the spinning of polyethylene terephthalate fibers of 300 nm in diameter with cylindrical structures. ³
7	Polyaniline/PEO blends	Chloroform	Norris et al. produced fine fibers with desired conductivity by using Polyaniline/PEO polymeric blends. ³⁹ The fiber diameters were in the range of 950 nm to 2.1 μm .
8	Polyether urethane	Dimethyl acetamide	Wilkes observed the dependence of fiber diameter distribution and the occurrence of beaded structures on the flow rate and applied electric potential. ⁴⁰ Fibers from 148 nm to 5 μm were obtained by Wilkes.
9	Poly-L-lactide (PLLA), Polycarbonate (PC), Polyvinylcarbazole	Dichloromethane	Bognitzki et al. examined the relationship between the volatility of solvents used and the pore structure of fibers. They inferred that the solidification of fibers is controlled by the onset of glass transition or by the onset of crystallization. ⁴¹
10	Polystyrene	Tetrahydrofuran (THF)	MacDiarmid et al. have electrospun polystyrene using THF as a solvent to produce nanofibers with a minimum diameter of 16 nm and an average diameter of 30.5 nm. They observed higher temperature in fibers due to higher conductivity. ²
11	Polybenzimidazole (PBI)	N,N-Dimethyl Acetamide (DMAc)	Kim and Reneker electrospun aromatic heterocyclic PBI polymer by electrospinning and produced birefringent fibers of approximately 300 nm in diameter. ⁴²
12	Nylon 6 and Nylon 6 +montmorillonite (NLS)	1,1,1,3,3,3-hexa fluoro-2-Propanol (HFIP) and DMF	Fong et al. experimented with the spinning of NLS with HFIP and DMF and observed cylindrical fibers along with some ribbon shaped fibers with thickness of 100–200 nm and width of $\sim 10\mu\text{m}$. ⁴³ They concluded that even though electrospinning should produce great chain alignment, rapid solvent removal inhibits perfect crystallites in the electrospun fibers. ⁴³
13	a) Polyethylene oxide (PE) b) Polycarbonate (PC) c) Polyurethane (PU)	a) Isopropyl alcohol (IPA) b) DMF and THF c) DMF	Tsai et al. developed nonwoven fibers of PEO, PC, and PU by different fiber charging methods like electrostatic spinning, corona charging, and tribocharging, and inferred that electrospun fibers have higher filtration efficiency than other nonwoven webs. PU and PC were found to have higher charge retention capacities than electrospun PEO fibers. ⁴⁴ Fibers with diameter of 0.1 to 0.5 μm were produced.

TABLE I Continued

S. No	Polymer	Solvent	Comments
14	Polyvinyl chloride	THF, DMF	Lee et al. studied the effect of volume ratio of mixed solvents on the structure and morphology of electrospun fibers. ⁴⁵
15	Polyurethane	DMF	Demir et al. prepared polyurethane urea copolymer solution in DMF and observed that the average fiber diameter (AFD) increases with the solution concentration as given by $AFD = (Conc.)^{346}$. A trimodal distribution of the fiber diameter has been observed with fiber diameter varying from 7 nm to 1.5 μm . ⁴⁶
16	Polycaprolactone	Acetone	Reneker et al. studied the onset of the bending instability during spinning and observed the formation of a closed single and double loop fiber structure called "Garland". ⁴⁷ This garland structure has been observed in other copolymers like vinylidene fluoride, tetra fluoroethylene, and polyethyloazoline. ⁴⁷ The fiber diameter varied from 1 μm to 1.5 μm .
17	Styrene-Butadiene-Styrene (SBS) triblock copolymer	75% THF and 25% DMF	Fong and Reneker examined the morphology of fibers with respect to micro phase separation and experimented with annealing for accelerating the ordering process and stress relaxation. ⁴⁸ The electrospun fibers were around 100 nm in diameter.
18	Poly-L-Lactide	Dichloromethane	Zeng Jun et al. electrospun PLA fibers and observed the cylindrical morphology of fibers with diameters ranging from 800 nm–2400 nm. ⁴⁹
19	Poly (methyl methacrylate-random) PMMA-r-TAN	Mixed solvent of Toluene and DMF	Dietzel et al. produced electrospun fiber mats with specific surface chemistry from random copolymers of PMMA-r-TAN. They have demonstrated that the atomic concentration of fluorine at the surface of electrospun fibers was twice the amount seen in bulk materials. ⁵⁰ The fiber diameter was in the range of 2 μm to 300 nm.
20	Polyethylene-co-vinyl acetate (PEVA), Poly lactic acid (PLA) and blend of PEVA and PLA.	Chloroform	Kenawy et al. studied the potential of electrospun fiber mats as a drug delivery system for the release of tetracycline hydrochloride. ⁵¹ Electrospun PEVA + PLA blended fibers were 1–3 μm in diameter, while the PLA fibers were around 3–6 μm .
21	Poly (p-phenylene terephthalamide) (PPTA) (Kevlar 49® from Dupont)	95–98 wt % Sulphuric acid	Srinivasan and Reneker examined the crystal structure and morphology of electrospun Kevlar fibers. ⁵² Fibers from 40 nm to a few hundreds of nanometers were produced.
22	Polyethylene terephthalate (PET) and Polyethylene naphthalate (PEN)		Kim and Lee investigated the thermal properties of electrospun PET and PEN fibers made from melts. ⁵³
23	Silk like polymer with fibronectin functionality (SLPF)	Formic acid/hexafluoro isopropanol	Buchko et al. used the electrospinning technique to create biocompatible thin films for their use in implantable devices. They studied the morphological characteristics with regard to the changes in process and solution parameters. ⁸
24	Polyurethane and PEO	Tetrahydrofuran and Dimethylformamide	Subbiah and Ramkumar studied the structure and morphology of polyurethane nanofibers. Fiber diameter as low as 30nm was prepared. ⁵⁴

phology of nanofibers as a function of process parameters and material characteristics.

The production of nanofibers by the electrospinning process is influenced both by the electrostatic forces and the viscoelastic behavior of the polymer. Process parameters, like solution feed rate, applied voltage, nozzle-collector distance, and spinning environment, and material properties, like solution concentration, viscosity, surface tension, conductivity, and solvent vapor pressure, influence the structure and properties of electrospun nanofibers. Significant work has been done to characterize the properties of fibers as a function of process and material parameters. A detailed account on the influence of process and material characteristics on the structure and properties of nanofibers is provided in the following sections of this paper.

Process parameters and fiber morphology

Applied voltage

Various instability modes that occur during the fiber forming process are expected to occur by the combined effect of both the electrostatic field and the material properties of the polymer. It has been suggested that the onset of different modes of instabilities in the electrospinning process depend on the shape of the jet initiating surface and the degree of instability, which effectively produces changes in the fiber morphology.¹⁴ In electrospinning, the charge transport due to the applied voltage is mainly due to the flow of the polymer jet towards the collector, and the increase or decrease in the current is attributed to the mass flow of the polymer from the nozzle tip. Deitzel et al. have inferred that the change in the spinning current is related to the change in the instability mode.¹⁴ They experimentally showed that an increase in applied voltage causes a change in the shape of the jet initiating point, and hence the structure and morphology of fibers. Experimentation on a PEO/water system has shown an increase in the spinning current with an increase in the voltage.¹⁴ It was also observed that for the PEO/water system, the fiber morphology changed from a defect free fiber at an initiating voltage of 5.5KV to a highly beaded structure at a voltage of 9.0KV.¹⁴ The occurrence of beaded morphology has been correlated to a steep increase in the spinning current, which controls the bead formation in the electrospinning process. Beaded structure reduces the surface area, which ultimately influences the filtration abilities of nanofibers.

Earlier in 1971, Baumgarten while carrying out experiments with acrylic fibers observed an increase in fiber length of approximately twice with small changes in fiber diameter with an increase in applied voltage.⁹ Megelski et al. investigated the voltage de-

pendence on the fiber diameter using polystyrene (PS). The PS fiber size decreased from about 20 μm to 10 μm with an increase in voltage from 5KV to 12KV, while there was no significant change observed in the pore size distribution.⁵⁵ These results concur with the interpretation of Buchko et al.,⁸ who observed a decrease in the fiber diameter with an increase in the applied field while spinning silk like polymer fiber with fibronectin functionality (SLPF). Generally, it has been accepted that an increase in the applied voltage increases the deposition rate due to higher mass flow from the needle tip.

Jaeger et al. used a two-electrode setup for electrospinning by introducing a ring electrode in between the nozzle and the collector.¹³ The ring electrode was set at the same potential as the electrode immersed in the polymer solution. This setup was thought to produce a field-free space at the nozzle tip to avoid changes in the shape of the jet initiating surface due to varied potential.¹³ Though this setup reduces the unstable jet behavior at the initiation stage, bending instability is still dominant at later stages of the process, causing an uneven chaotic motion of the jet before depositing itself as a nonwoven matrix on the collector. Deitzel et al. experimented with a new electrospinning apparatus by introducing eight copper rings in series in between the nozzle and the collector for dampening the bending instability.¹⁵ The nozzle and the ring set were subjected to different potentials (ring set at a lower potential) of positive polarity, while the collector was subjected to a negative polarity. The idea behind this setup was to change the shape of the macroscopic electric field from the jet initiation to the collection target in such a way that the field lines converge to a center line above the collection target by the applied potential to the ring electrodes. The authors have suggested that the bending instability of fibers was dampened by the effect of the converging field lines producing straight jets.¹⁵ Controlled deposition helps to produce specific deposition patterns and also yarn like fibers. Deitzel et al. investigated the spinning of PEO in aqueous solution using multiple electric fields, which resulted in fibers depositing over a reduced area due to the dampening of bending instability. The multiple field technique was also shown to produce fibers of lesser diameter than the conventional electrospinning method.¹⁵

Nozzle collector distance

The structure and morphology of electrospun fibers is easily affected by the nozzle to collector distance because of their dependence on the deposition time, evaporation rate, and whipping or instability interval. Buchko et al. examined the morphological changes in SLPF and nylon electrospun fibers with variations in the distance between the nozzle and the collector

screen. They showed that regardless of the concentration of the solution, lesser nozzle-collector distance produces wet fibers and beaded structures. SLPF fiber morphology changed from round to flat shape with a decrease in the nozzle collector distance from 2cm to 0.5cm.⁸ This result shows the effect of the nozzle collector distance on fiber morphology. The work also showed that aqueous polymer solutions require more distance for dry fiber formation than systems that use highly volatile organic solvents.⁸ Megelski et al. observed bead formation in electrospun PS fibers on reducing the nozzle to collector distance, while preserving the ribbon shaped morphology with a decrease in the nozzle to collector distance.⁵⁵

Polymer flow rate

The flow rate of the polymer from the syringe is an important process parameter as it influences the jet velocity and the material transfer rate. In the case of PS fibers, Megelski et al. observed that the fiber diameter and the pore diameter increased with an increase in the polymer flow rate.⁵⁵ As the flow rate increased, fibers had pronounced beaded morphologies and the mean pore size increased from 90 to 150 nm.⁵⁵

Spinning environment

Environmental conditions around the spinneret, like the surrounding air, its relative humidity (RH), vacuum conditions, surrounding gas, etc., influence the fiber structure and morphology of electrospun fibers. Baumgarden observed that acrylic fibers spun in an atmosphere of relative humidity more than 60% do not dry properly and get entangled on the surface of the collector.⁹ The breakdown voltage of the atmospheric gases is said to influence the charge retaining capacity of the fibers.⁹ Srinivasarao et al. proposed a new mechanism for pore formation by evaporative cooling called "breathe figures."⁵⁶ Breathe figures occur on the fiber surfaces due to the imprints of condensed moisture droplets caused by the evaporative cooling of moisture in the air surrounding the spinneret. Megelski et al. investigated the pore characteristics of PS fibers at varied RH and emphasized the importance of phase separation mechanisms in explaining the pore formation of electrospun fibers.⁵⁵

Solution parameters and fiber morphology

Solution concentration

Solution concentration decides the limiting boundaries for the formation of electrospun fibers due to variations in the viscosity and surface tension.¹⁴ Low concentration solution forms droplets due to the influence of surface tension, while higher concentration

prohibits fiber formation due to higher viscosity. Previously published literature has documented the difficulties in the electrospinning of polymers like PEO,¹⁴ PAN,³⁴ and PDLA⁵⁷ in certain concentration levels. By increasing the concentration of polystyrene solution, the fiber diameter increased and the pore size reduced to a narrow distribution.⁵⁵ In the case of a PEO/water system, a bimodal distribution in fiber diameter was observed at higher concentrations.¹⁴ In the PEO system, Dietzel et al. related the average fiber diameter and the solution concentration by a power law relationship.¹⁵ Dietzel et al. interpreted the variations in the fiber diameter and morphology to the shape of the jet-originating surface, which concurred with the observations of Zong et al.⁵⁷ Undulating morphologies in fibers were attributed to the delayed drying and the stress relaxation behavior of the fibers at lower concentrations.⁵⁷ As is evident from the discussions, the concentration of the polymer solution influences the spinning of fibers and controls the fiber structure and morphology.

Solution conductivity

Polymers are mostly conductive, with a few exceptions of dielectric materials, and the charged ions in the polymer solution are highly influential in jet formation. The ions increase the charge carrying capacity of the jet, thereby subjecting it to higher tension with the applied electric field. Baumgarden showed that the jet radius varied inversely as the cube root of the electrical conductivity of the solution.⁹ Zong et al. demonstrated the effect of ions by adding ionic salt on the morphology and diameter of electrospun fibers.⁵⁷ They found that PDLA fibers with the addition of ionic salts like KH_2PO_4 , NaH_2PO_4 , and NaCl produced beadless fibers with relatively smaller diameters ranging from 200 to 1000 nm.⁵⁷

Volatility of solvent

As electrospinning involves rapid solvent evaporation and phase separations due to jet thinning, solvent vapor pressure critically determines the evaporation rate and the drying time. Solvent volatility plays a major role in the formation of nanostructures by influencing the phase separation process. Bognitzki et al. found that the use of highly volatile solvents like dichloromethane yielded PLLA fibers with pore sizes of 100 nm in width and 250 nm in length along the fiber axis.⁴¹ Lee et al. evaluated the effect of volume ratio of the solvent on the fiber diameter and morphology of electrospun PVC fibers.⁴⁵ Average fiber diameters decreased with an increase in the amount of DMF in the THF/DMF mixed solvent. Lee et al. found the electrolytic nature of the solvent to be an important parameter in electrospinning.⁴⁵ Megelski et al.

studied the characteristics of electrospun fibers with respect to the physical properties of solvents. The influence of vapor pressure was evident when PS fibers spun with different THF/DMF combinations resulted in micro and nanostructure morphologies at higher solvent volatility and a much-diminished microstructure at lower solvent volatility.⁵⁵

Properties of nanofibers

As briefly discussed in the introductory section of the article, a major upsurge in research on nanofibers has taken place most recently due to its high surface area and nanostructure surface morphologies that enable a myriad of advanced applications. Nanofibers have been reported to have marked differences in their thermal and mechanical properties compared to regular fibers and bulk polymers.

Thermal properties

There are a few published reports on the thermal properties of nanostructured materials. Thermal analysis has been carried out on a number of electrospun polymeric materials to understand the relationship between nanostructure and thermal properties. DSC studies have indicated that electrospun PLLA fibers have lower crystallinity, glass transition temperature (T_g), and melting temperature (T_m) than semicrystalline PLLA resins.⁵⁷ Zong et al. attributed the decrease in the T_g to the large surface to volume ratio of nanofibers with air as the plasticizer. The high evaporation rate followed by rapid solidification at the final stages of electrospinning is expected to be the reason for the low crystallinity. The T_g and the peak crystallization temperature (T_c) of the electrospun polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) decreased significantly, while the heat of crystalline melting increased.⁵³ The decrease in T_g and T_m , and the increase in the heat of melting were attributed to the increase in the segmental mobility. The melting temperature of the PET and PEN electrospun fibers remained almost constant, without any significant variations compared to that of regular fiber forms. PEO nanofibers have shown a lower melting temperature and heat of fusion than the PEO powder, which is attributed to the poor crystallinity of the electrospun fibers.¹⁴ The crystallinity of the PLLA fibers was observed to be completely retarded by electrospinning, and the WAXD patterns of the electrospun PLLA fibers confirmed highly oriented fibers.⁵⁷ This decrease in crystallinity has been shown to be a general phenomenon and has been observed in poly (*meta*-phenylene isophthalamide), poly (glycolide), and polyacrylonitrile. Deitzel et al. inferred that PEO nanofibers retained the same crystal structure as PEO powders, while there is a clear indication of reduced crystalline

order in nanofibers.¹⁴ Bognitzki et al. concluded with the help of a DSC thermogram that the degree of crystallinity of electrospun PLLA fibers was in the order of 40%.⁵⁸

Thermal degradation of PET and PEN before and after electrospinning was analyzed by Kim and Lee using the TGA thermogram, and they found that on electrospinning the intrinsic viscosities of both PET and PEN reduced significantly.⁵³ The thermal degradation and hence the decrease in intrinsic viscosities (i.e., decrease of molecular weight) were postulated to be the reasons for the decrease in T_g and T_c caused by reduced entanglements.⁵³

Mechanical properties

Electrospun fibers have nanostructured surface morphologies with tiny pores that influence mechanical properties like tensile strength, Young's modulus, etc. Gibson et al. have found that there is no significant change in the Young's modulus of electrospun Pellethane thermoplastic elastomers. When compared with cast films, electrospun elastomers have shown a 40% reduction in the peak tensile strength and 60% reduction in elongation at maximum applied stress.⁵⁹ The decrease in the tensile strength has also been reported by Buchko et al. with SLPF fibers.⁸ Nanofiber reinforced polymer composites have shown more highly enhanced mechanical properties than the unfilled or carbon/glass fiber filled composites. Young's modulus of a nanofiber composite has been found to be 10-fold greater than the pure Styrene-Butadiene rubber.⁶⁰ As is evident, there is less information available on the mechanical properties of nanofibers and nanofiber composites. Research on the mechanical properties of nanofibers and their composites from a variety of polymers is essential for a greater understanding on the contributions of nanofibers to the mechanical and performance related characteristics of nanofiber composites.

Applications of nanofibers

Nanomaterials have been attracting the attention of global materials research these days primarily due to their enhanced properties required for application in specific areas like catalysis, filtration, NEMS, nanocomposites, nanofibrous structures, tissue scaffolds, drug delivery systems, protective textiles, storage cells for hydrogen fuel cells, etc. A brief discussion on some of the applications of nanofibers and related nanomaterials is given in this section.

Carbon and graphitic nanofibers

Carbon nanofibers are finding enormous applications in unconventional energy sources and storage cells

due to their enhanced conductivity and high aspect ratio. Their mechanical properties enable them to be used as fillers in composites that find applications in synthetic and rubber industries.⁶¹ Carbon nanofiber reinforced composites offer increased stiffness, high strength and low electrical resistivity. Also, aligned nanofiber composites provide enhanced mechanical properties than the randomly aligned nanofiber composite structure.⁶² Ma et al. studied the morphology and mechanical properties of polyethylene terephthalate (PET) resins compounded with carbon nanofibers (CNF).⁶³ The compressive and torsional properties of the composites increased up to 50% compared to the normal PET fiber, while its tensile modulus showed only moderate improvement.⁶³

Tissue scaffolds and drug delivery

Nanofibers with high surface area and porosity have enormous scope for applications in engineering mechanically stable and biologically functional tissue scaffolds. The tissue scaffolding material must be selected carefully to ensure its biocompatibility with the body cells. The biocompatibility depends on the surface chemistry of the scaffolds, which is influenced by the material properties.⁶⁴ Biological signals from growth factors, extracellular matrix (ECM), and the surrounding cells regulate the biological functions, and the ECM molecules surround the cells to give the necessary mechanical support.⁶⁴ Natural polymers of type I and type III collagen are the primary structural elements of the ECM that supports tissue reconstruction.⁶⁵ The high surface to volume ratio of the nanofiber provides more room for the cell attachment than the regular fibers.⁶⁴ The dimensions of these engineered scaffolds were in the same scale with those of the natural ECM. Poly (D, L-lactide-co-glycolide) (PLGA), the commonly used biodegradable polymer in tissue engineering while electrospinning, produced highly suitable tissue scaffolds that have high porosity, pore diameter, and pore volume.⁶⁴ The high porosity of the electrospun nanofiber scaffolds provides enough space for the cell accommodation and an easy passage for the nutrient intake and metabolic waste exchange. Mechanical properties like the modulus of elasticity and strain at failure are important for the application of electrospun nanofibers as tissue scaffolds.⁶⁶ The material properties can be suitably tailored by varying the fiber orientation and solution concentration.⁶⁶ Matthews et al. used type I collagen from calfskin and type I and type III collagen from human placenta for spinning collagen nanofibers.⁶⁷ These electrospun collagen fibrils closely resembled the structural and biological properties of natural polymer tissues. Culturing aortic muscle cells on these electrospun collagen microfibrils produced scaffolds with densely populated smooth muscle cells. The

muscle cells were seen deeply meshed within the electrospun collagen.⁶⁷ Huang et al. electrospun collagen/PEO nanofiber mats and studied its potential for applications in wound healing and tissue engineering.^{68,69} Uniform fibers with diameter ranging from 100 to 150 nm were produced. The superior mechanical properties of the collagen nanofibers were attributed to the high intermolecular interaction between the PEO and collagen component.⁶⁹

Nanofiber mats due to their high functional characteristics find application as drug carriers for the drug delivery system.⁵¹ Controlled delivery of drugs at a defined rate over a definite period of treatment is possible with biocompatible delivery matrices of either biodegradable or nonbiodegradable polymers. Kenawy et al. investigated the drug delivery potential of electrospun polymers by spinning poly (ethylene-co-vinyl acetate) (PEVA) and poly lactic acid with ethanol and tetracycline hydrochloride as the model drug.⁵¹ The release of tetracycline from the electrospun mats was found much greater than from the cast films. They observed that the electrospun PEVA and 50/50 PLA/PEVA mats gave very smooth release of tetracycline over a period of five days.⁵¹ These observations stress the importance and application of electrospun fiber mats in controlled drug delivery systems and other biomedical applications.

Catalytic nanofibers

Chemical reactions employing enzyme catalysts are important in chemical processes due to their high selectivity and mild reaction conditions.⁷⁰ Immobilized enzymes are used largely due to easiness of catalyst separation, enzyme stability, and their availability for continuous operations. The efficiency of these immobilized enzymes depends mainly on the pore structure and diffusion limitations of the substrate material. Nanomaterials are of recent interest as catalyst substrates due to their large surface area per unit mass and the feasibility for high catalyst loading.⁷⁰ Nanofibrous catalysts could substitute catalytic nanoparticles in order to overcome the limitations of catalyst recovery.⁶⁸ Jia et al. prepared bioactive polystyrene (PS) nanofibers by chemical attachment of α -chymotrypsin on PS and observed a high catalytic activity with improved enzyme stability over other forms of immobilized enzymes.⁷⁰

Fibrous catalysts offer advantages, such as feasibility of adapting to any geometry and low resistance to the flow of liquids and gases.⁷¹ Though catalyst loading and mechanical properties limit the usage of fibrous catalysts, the advent of nanofibrous materials as catalytic substrates alters the scope of its application. The activity of the catalyst supported on a substrate depends on its large active surface area. Nonporous substrates can be coated with a high surface area

material like nanofibers to increase the surface area, thereby enhancing reactivity.⁷¹ Carbon nanofiber supports loaded with iron particles have shown high conversion of hydrocarbons in comparison with active carbon and γ -alumina.⁷² It has been shown that the intrinsic catalyst effect is more pronounced when loaded in smaller diameter fibers such as nanofibers.⁷²

Filtration

Polymeric nanofibers have been used in air filtration applications for more than a decade.⁷¹ Due to poor mechanical properties of thin nanowebs, they were laid over a substrate suitable enough to be made into a filtration medium. The small fiber diameters cause slip flows at fiber surfaces, causing an increase in the interception and inertial impaction efficiencies of these composite filter media.⁷³ The enhanced filtration efficiency at the same pressure drop is possible with fibers having diameters less than 0.5 micron.⁷³

The potential for using nanofiber webs as a filtering medium is highly promising. Knowing that the essential properties of protective clothing are high moisture vapor transport, increased fabric breathability, and enhanced toxic chemical resistance, electrospun nanofiber membranes have been found to be good candidates for these applications.⁶⁵ The highly porous electrospun membrane surfaces help in moisture vapor transmission. Gibson et al. have analyzed the possibility of using thin nanofiber layers over the conventionally used nonwoven filtration media for protective clothing.⁷⁴ Polyurethane and nylon 6 nanowebs were applied over open cell foams and carbon beads and tested for air flow resistance. They concluded that the airflow resistance, filtration efficiency, and pore sizes of nonwoven filter media could be easily altered by coating with the lightweight electrospun nanofibers.⁷⁴ Doshi et al. have evaluated composites of nanofibers with spunbond and meltblown fabrics for filtration characteristics.⁷⁵ The nanofiber composite membranes have shown very high increase in the filtration efficiencies.⁷⁵ Researchers at General Motors Company are working on nanofibers for different composite applications because of its scratch/wear resistance, low temperature ductility, low flammability, and recyclability.⁷⁶

Nanofibers also find applications in aerospace and semiconductor industries. Piezoelectric polymers were electrospun and investigated for applicability as a component on the wings of micro-air vehicles.⁷⁷ Poly(vinylidene fluoride) (PVDF) and (β -CN) APB-ODPA, a piezoelectric polyamide, were electrospun at NASA Langley Research Center, and their morphologies were evaluated for various experimental conditions.⁷⁷ Gibson et al. prepared conductive membrane coatings using carbon nanotubes by an electrospinning process. Carbon nanotubes (CNT) were dispersed in the polymer solution and electrospun to form nanotube

encapsulated conductive polymer fiber. CNTs boost the conductivity of dielectric materials like polyurethane to form organic nanofiber electrodes, with applications in conductive coatings, flexible photovoltaic cells, and wearable solar power cells.⁷⁸

As is evident from the aforementioned brief discussion on the applications of nanomaterials, the potential of nanostructured materials in advanced applications is unlimited. Researchers are making constant efforts to exploit the high surface area and porosity properties to develop value added and sophisticated high tech materials.

CONCLUSIONS

Nanoscience is one of the few growing scientific fields of this decade that is enjoying broad based support from the government and industries. The ability to manipulate individual molecules and understand their characteristics at atomic levels has made this field very promising. Electronics and semiconductor industries have been harnessing the potential of nanotechnology to a major extent. Other fields, such as biomedical, polymer, and fiber science, are yet to realize the full potential of nanotechnology. To enable the fullest exploitation of nanotechnology in fiber and polymer science disciplines, a timely and in-depth review of research on nanofibers is essential. Government agencies and nongovernmental agencies have given high priority to both fundamental and applied nanoscience research activities. The support for research activities in nanotechnology is growing internationally. As elaborated in this overview article, nanofibers have applications in many different fields, such as protective textiles, filtration, drug delivery, etc. The production of nanofibers is still in the laboratory level, and it is extremely important to make efforts for scaled-up commercialization. A thorough investigation on the scaling up of nanofiber technology is necessary for the growth and development of this field. The overview presented in this article has focused on nanofibers, experimental methods to produce them, and their applications in important fields. A succinct listing of previous research activities has been provided for a quick and knowledgeable understanding of the state-of-the-art in the field. It is hoped that this article will be of immense use to researchers for future research and planning in nanofiber research.

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