ELSEVIER

Current Opinion in Colloid and Interface Science 8 (2003) 64–75

Current Opinion in COLLOID and INTERFACE SCIENCE

www.elsevier.com/locate/cocis

Polymer nanofibers assembled by electrospinning

Audrey Frenot, Ioannis S. Chronakis*

IFP Research, Swedish Institute for Fiber and Polymer Research, P.O. Box 104, S-431 22 Mölndal, Sweden

Abstract

Electrospinning is a process by which polymer nanofibers (with diameter lower than 100 nm and lengths up to kilometres) can be produced using an electrostatically driven jet of polymer solution (or polymer melt). Simple alignment of electrospun nanofibers constructs unique functional nanostructures such as nanotubes and nanowires. Significant progress has been made in this area throughout the past few years and this technology has been exploited to a wide range of applications. Most of the recent work on electrospinning has focused either on trying to understand deeper the fundamental aspects of the process in order to gain control of nanofiber morphology, structure, surface functionality, and strategies for assembling them or on determining appropriate conditions for electrospinning of various polymers and biopolymers.

Keywords: Electrospinning; Electrospun; Nanofibers; Nanostructured material; Nanotechnology; Polymer fibers; Biopolymer fibers; Blends; Electrified fluid jet

1. Introduction

Unlike conventional fiber spinning techniques (wet spinning, dry spinning, melt spinning, gel spinning), which are capable of producing polymer fibers with diameters down to the micrometer range, electrostatic spinning, or 'electrospinning' is a process capable of producing polymer fibers in the nanometer diameter range. Electrospinning is a novel and efficient fabrication process that can be utilised to assemble fibrous polymer mats composed of fiber diameters ranging from several microns down to fibers with diameter lower than 100 nm (Fig. 1). This electrostatic processing method uses a high-voltage electric field to form solid fibers from a polymeric fluid stream (solution or melt) delivered through a millimeter-scale nozzle.

Nanofibers are the ultra-fine solid fibers notable for their very small diameters (lower than 100 nm), their large surface area per unit mass and small pore size. Due to the inherent properties of the electrospinning process, which can control the deposition of polymer fibers onto a target substrate, nanofibers with complex, and seamless three-dimensional shapes could be formed. Construction of nanoscale composite fibers by electrospinning from a mixture of rigid rod polymers and flexible polymers is also feasible. The electrospun nanofibers can even be aligned to construct unique functional nanostructures such as nanotubes and nanowires. Furthermore, depending on the specific polymer being used, a wide range of fabric properties such as strength, weight and porosity, surface functionality etc. can be achieved. This novel fiber spinning technique provides as well the capacity to lace together a variety of types of polymers, fibers, and particles to produce ultrathin layers. Small insoluble particles can be added to the polymer solution and encapsulated in the dry nanofibers. Soluble drugs or bacterial agents can be added and electrospun into nonwoven mats.

Although the process of electrospinning has been known for almost 70 years and the first patent was issued to Formhals in 1934 (US Patent, 1-975-504), polymeric nanofibers produced by electrospinning have become a topic of great interest for the past few years. Reneker and Chun, who revived interest in this technology in the early 1990s, has shown the possibility to electrospin [1] a wide range of polymer solutions in 1996. Larrondo and Manley had performed a similar work on polymer melts in 1981 [2]. Typically, electrospinning is applicable to a wide range of polymers like those used in conventional spinning, i.e. polyolefine, polyamides, polyester, aramide, acrylic as well as bio-

*Corresponding author. Tel.: +46-31-706-63-00; fax: +46-31-706-63-65.

E-mail address: ioannis.chronakis@ifp.se (I.S. Chronakis).

1359-0294/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S1359-0294(03)00004-9

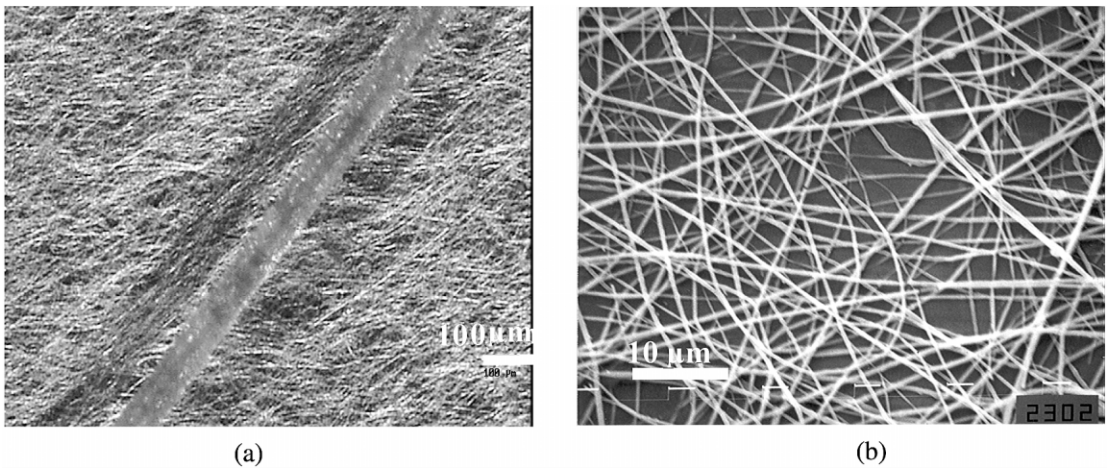

Fig. 1. (a) Electrospun PET from a solution of 13 wt.% in 1:1 dichloromethane and trifluoroacetic acid. Comparison with human hair; (b) Electrospun PEO fibers from a solution of 5 wt.% PEO in 50 wt.% H_2O and 45 wt.% ethanol. The diameter of the fibers lies between 50 and 500 nm. (Audrey Frenot, unpublished work).

polymers like proteins, DNA, polypeptides, or others like electric conducting and photonic polymers. The high specific surface area and small pore size of electrospun nanofibers make them interesting candidates for a wide variety of applications. For instance nanofibers with a diameter of 100 nm have a ratio of geometrical surface area to mass of approximately 100 m^2/g. Another interesting aspect of using electrospun fibers is that the fibers may dissipate or retain the electrostatic charges depending on the electrical properties of the polymer. The charges can be manipulated as well by electrical fields and the electrical polarity of the fibers is affected by the polarity of the applied voltage. Nanofibers provide also a connection between the nanoscale world and the macroscale world, since the diameters are in the nanometer range and the lengths are kilometres. Therefore, current emphasis of research is to exploit such properties and focus on determining appropriate conditions for electrospinning various polymers and biopolymers for eventual applications including multifunctional membranes, biomedical structural elements (scaffolding used in tissue engineering, wound dressing, drug delivery, artificial organs, vascular grafts), protective shields in speciality fabrics, filter media for submicron particles in separation industry, composite reinforcement, and structures for nano-electronic machines among others.

In this review we concentrate on current understanding of the electrospinning process and those parameters, which influence the properties of the fibers produced from it. We also address issues of nanofiber structures and characteristics and discuss models proposed for processing instabilities. Due to the growing interest on nanofibers processed with specific bulk morphologies and surface topologies, we focus on such recent advances and discuss some general considerations and remaining challenges. The current utilisation of nanofibers mainly for biomedical applications, for developing nanoelectronic machines and for designing potential structures in order to develop functional nanostructured materials, is another active research area that covered in this review. The major developments are highlighted covering the publications period from 1999 onwards.

2. The electrospinning process

The electrospinning equipment for polymer solution and melt are well presented in the papers [3–7••,8] and [2], respectively. Electrospinning is easily realised by applying a high voltage to a capillary filled with the polymer fluid to be spun with help of an electrode. The

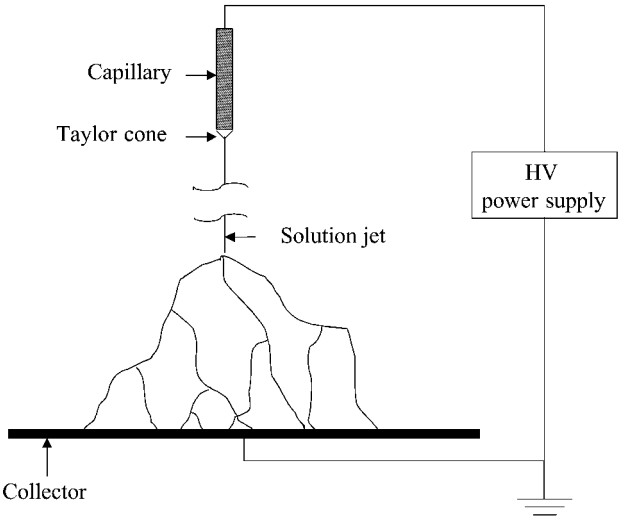

Fig. 2. Scheme of an electrospinning equipment. NB, several raw material sources can be used (i.e. several capillaries).

resulting fibers are collected on a grounded plate, which can be covered with a fabric for example. The process is schematically illustrated in Fig. 2. The groups working on electrospinning have adopted different solution for the polymer feed. Some have simply opted for placing the capillary perpendicularly, letting the polymer fluid dropping with help of gravitation and lying the collector underneath [9]. Sometimes the capillary can be tilted at a defined angle to control the flow [5,10,11]. In other cases, the capillary was horizontal [12••] and a pump was used to initiate the droplet, the pump being also used in the case of vertical feeding [3,4,6,12••]. The electrode can be inserted either in the polymer fluid or placed onto the tip of the capillary if a syringe with a metal needle is used.

The collector is usually a plane metal sheet or a grid that can be covered with a fabric. Kim and Reneker used a different set-up in a work on polybenzimidazole (PBI) [13]. Actually, they used a rotating cylinder covered with a grounded aluminium sheet. Rangpukan and Reneker have also reported the development of electrospinning from molten polymers in vacuum [14]. Electrospinning from polymer melts in vacuum is advantageous because higher electric field strength over large distances and higher temperature can be used than in air. In the work by Theron et al. an electrostatic field-assisted assembly technique was described, combined with an electrospinning process used to position and align individual nanofibers on a tapered and grounded wheel-like bobbin [15••]. The bobbin is able to wind a continuously as-spun nanofiber at its tip-like edge. The alignment approach has resulted in polyethylene oxide (PEO)-based nanofibers with diameters ranging from 100 to 300 nm and lengths of up to hundreds of microns.

The equipment developed by the University of Massachusetts Darmouth in collaboration with Massachusetts Institute of Technology had also a different configuration: parallel-plate geometry. Indeed a 'point-plate' geometry leads to curved electric field lines close to the capillary, resulting thus in a non-uniform electric field. The parallel-plate configuration allows the control of the curvature [6]. Moreover, they fed the solution to multiple spinnerets placed in a radial geometry. The collector was rotating.

Beneath, a brief description of the electrospinning process is placed (Fig. 2). Electric field is subjected to the end of a capillary tube that contains the polymer fluid held by its surface tension. This induces a charge on the surface of the liquid. Mutual charge repulsion causes a force directly opposite to the surface tension [16]. As the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone (the base region). With increasing field, a critical value is attained when the repulsive electrostatic force overcomes the surface tension and a charged jet of fluid is ejected from the tip of the Taylor cone. The discharged polymer solution jet undergoes a whipping process wherein the solvent evaporates, leaving behind a charged polymer fiber, which is highly stretched and reduced in diameter as it travels before it lays itself randomly on a grounded collecting metal screen (the jet region). The rapidly whipping jet, the fluid instability, is an essential element of the process that cause bending and stretching of the jet. In the case of the melt the discharged jet solidifies when it travels in the air and is collected on the grounded metal screen. Splaying occurs in a region in which the radical forces from the electrical charges carried by the jet, become larger than the cohesive forces within the jet, and the single jet divides into many charged jets (with approximately equal diameters and charge per unit length) before fibers 'landing' on the collector (the collection region). Although little is currently known about this splaying process of the primary jet into multiple filaments, it is thought to be responsible—together with the elongation due to the acceleration of the jet by electrical forces—for the unusually small diameter fibers which can produced by electrospinning [1].

As mentioned, electrospun fibers can be electrostatically charged and/or the charge can be manipulated. The charge can be removed, when it is not wanted, by exposure to ions carried in the air (or the charge can sometimes be neutralised during contact with the collector). If the fibers are electrically conducting, the charge can also be adjusted by conduction through the fiber [1]. Tsai and Schreuder-Gibson, discuss the effect of electrospinning material and conditions upon the residual electrostatic charge of polymer nanofibers [17]. Polymers such PEO, polycaprolactone (a polyester), polycarbonate, and polystyrene have been evaluated for their charge induction and charge retention characteristics and are ranked according to their inherent polarity.

Besides circular fibers, a variety of cross-sectional shapes and sizes can be obtained from different polymer solutions during electrospinning (Fig. 3). Actually Koombhongse, Wenxia and Reneker obtained branched fibers, flat ribbons, bent ribbons, ribbons with other shapes, and fibers that were split longitudinally from larger fibers from electrospinning a polymer solution [9]. Studies on the properties of fibers with these cross-sectional shapes from a number of different kinds of polymers and solvents indicates that fluid mechanical effects, electrical charge carried with the jet, and evaporation of the solvent all contributed to the formation of the fibers. The influence of a skin on the jets of polymer solutions accounts as well for a number of properties observed. We address the issues of the electrospinning processing variables in the next paragraph.

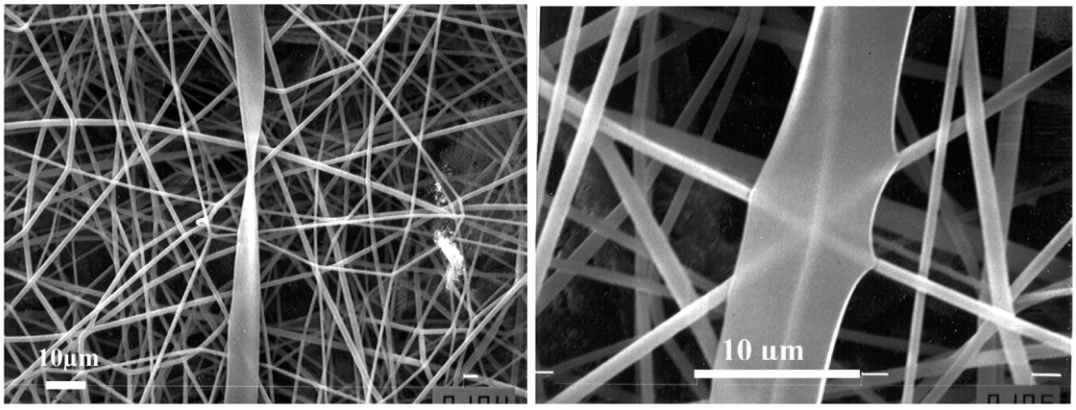

Fig. 3. Scanning electron micrographs showing flat ribbons formation during electrospinning of PET from a solution of 13 wt.% in 1:1 dichloromethane and trifluoroacetic acid. Left magnification ×1000, right: an enlarged image with magnification ×3500. (Audrey Frenot, unpublished work).

3. Electrospinning processing variables and instabilities models

The following parameters and processing variables affect the electrospinning process: (i) System parameters such as molecular weight, molecular-weight distribution and architecture (branched, linear etc.) of the polymer and solution properties (viscosity, conductivity and surface tension), and (ii) Process parameters such as electric potential, flow rate and concentration, distance between the capillary and collection screen, ambient parameters (temperature, humidity and air velocity in the chamber) and finally motion of target screen [18]. For instance, the polymer solution must have a concentration high enough to cause polymer entanglements yet not so high that the viscosity prevents polymer motion induced by the electric field. The solution must also have a surface tension low enough, a charge density high enough, and a viscosity high enough to prevent the jet from collapsing into droplets before the solvent has evaporated. Morphological changes can occur upon decreasing the distance between the syringe needle and the substrate. Increasing the distance or decreasing the electrical field decreases the bead density, regardless of the concentration of the polymer in the solution. Applied fields can, moreover, influence the morphology in periodic ways, creating a variety of new shapes on the surface.

Deitzel et al. have evaluated systematically the effects of two important processing parameters, spinning voltage and solution concentration, on the morphology of the fibers formed [19]. They found that spinning voltage is strongly correlated with the formation of bead defects in the fibers, and their measurements can be used to signal the onset of the processing voltage at which the bead defect density increases substantially. Solution concentration has also been found to most strongly affect fiber size, with fiber diameter increasing with increasing solution concentration according to a power law relationship. In addition, electrospinning from solutions of high concentration has been found to produce a bimodal distribution of fiber sizes, reminiscent of distributions observed in the similar droplet generation process of electrospray. Moreover they found evidence that electrostatic effects influence the macroscale morphology of electrospun fabrics and may result in the formation of heterogeneous or three-dimensional structures.

Meanwhile, both electrostatic and fluid dynamic instabilities can contribute to the basic operation of the process [3,7••,9,20•,21,22••,23•,24•,25•,26]. The bending instabilities that occur during electrospinning have been studied and mathematically modelled by Reneker et al. [7••,9,21]. After the jet travels straightforward, unsteadiness appears under the form of loops. The jet does not only bend but it also forms lateral excursions that grow into spiralling loop. Every loop grows larger in diameter and the jet becomes thinner [7••]. New bending instabilities arise when the jet is thin enough and enough stress relaxation of the viscoelastic stress has taken place. An envelope cone (Fig. 4) defines the region of these instabilities.

Reneker et al. [7••] chose to model the instabilities with viscoelastic dumbbells connected together (Fig. 5). The interactions between the beads forming the dumbbells were following Coulomb's law. The other parameters taken into account were the electrical forces due to the electric field, surface tension and the fact that the spring connecting the beads had a Maxwellian viscoelastic resistance to elongation, like the jet. Aerodynamic forces and gravity effect were neglected as well as solvent evaporation. This was taken into account in a later study [21]. In these articles, it is stated that electrospinning process and instabilities can be considered as particular examples of the Earnshaw theorem in

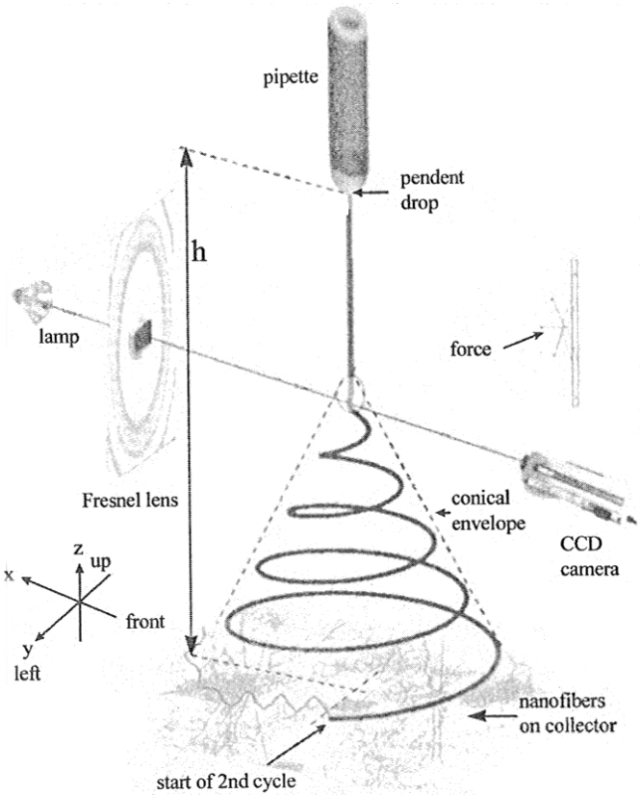

Fig. 4. Schematic of the electrospinning equipment showing the envelope cone. With courtesy of the American Institute of Physics [7••].

electrostatics. This means that one can not get a stable structure if the elements of this one interact only by Coulomb's law. There is a tendency of the charges in the polymer fluid to reduce their Coulomb interaction energy by moving the fluid in a complicated path. However, the challenges ahead lay in extending this level of fundamental knowledge to include non-linear effects arising from viscoelasticity of the fluid and additional fluid phenomena that occur downstream of the initial instability. This was attempted in a later study by the same group, where they propose that in liquids with a non-relaxing elastic force, that force also affects the shapes of the electrospun fibers [22••]. They showed that the Taylor cone does not represent a unique critical shape but half angles are much closer to this new shape.

Another group by Hohman, Shin, Rutlege and Brenner also studied electrospinning, with regard to electrically forced jet and instabilities, and proposed a stability theory for electrified fluid jets [23•,24•,25•,26]. A series of papers demonstrate that an essential mechanism of electrospinning is a rapidly whipping fluid jet. The authors analysed the mechanics of this whipping jet by studying the instability of an electrically forced fluid jet with increasing field strength. An asymptotic approximation of the equations of electrohydrodynamics was developed so that quantitative comparisons with experiments can be carried out. The approximation governs both long wavelength axisymmetric distortions of the jet, as well as long wavelength oscillations of the centerline of the jet. Three different instabilities were identified: the classical (axisymmetric) Rayleigh instability and electric field induced axisymmetric and whipping instabilities. At increasing field strengths, the electrical instabilities are enhanced whereas the Rayleigh instability is suppressed. Which instability dominates depends strongly on the surface charge density and the radius of the jet. In their later work, they have used the stability theory to develop a quantitative method for predicting when electrospinning occurs [23•]. First, a method for calculating the shape and charge density of a steady jet as it thins from the nozzle was presented and was shown to capture quantitative features of the experiments. Then, this information was combined with the stability analysis to predict scaling laws for the jet behaviour and to produce operating diagrams for when electrospinning occurs, both as a function of experimental parameters. Predictions for how the regime of electrospinning changes as a function of the fluid conductivity and viscosity were also presented.

Furthermore, Vao Soongnern, Doruker and Mattice analysed static and dynamic properties of amorphous polyethylene nanofibers by using a Monte Carlo simulation technique [27,28•]. They looked at how confinement and curvature of the surface of the nanofibers affects chain properties compared to the bulk of a thin

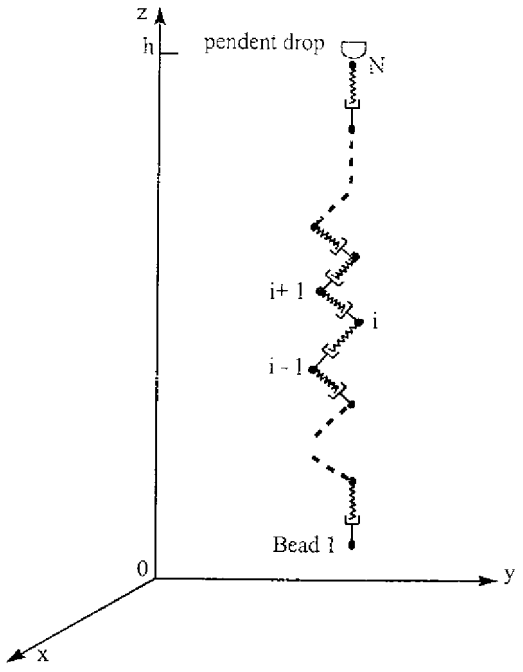

Fig. 5. Bending jet modelled by a system of beads connected by viscoelastic elements. With courtesy of the American Institute of Physics [7••].

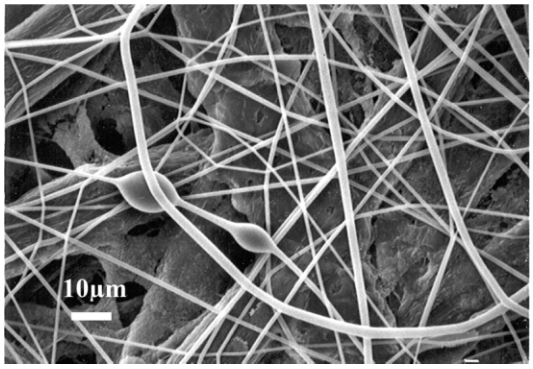

Fig. 6. Example of bead formation during electrospinning of 13 wt.% PET in 1:1 dichloromethane and trifluoroacetic acid (Audrey Frenot, unpublished work).

film. Major findings of this study were (i) fibers of different sizes, i.e. consisting of different numbers of parent chains, exhibit almost identical hyperbolic density profiles at the surfaces, (ii) the end beads are predominant and the middle beads are depleted at the free surfaces, (iii) there is an anisotropy in the orientation of bonds and chains at the surface, (iv) the centre of mass distribution of the chains exhibits oscillatory behaviour across the fibers and (v) the mobility of the chain in nanofiber increases as the diameter of the nanofiber decreases. They concluded that these nanofiber trends, with its strongly curved surface, are similar to the results seen in simulations by the same technique of free-standing thin film, where there is no curvature at the surface.

4. Polymer nanofibers with specific bulk morphologies and surface topologies

Electrospinning process is applicable to many polymers, as a melt or a solution. Reneker's group has done work on many different polymers, for example: polyethylene terephtalate [1]; PBI [13]; polystyrene [8], poly(2-hydroxyethyl methacrylate), polyvinylidene fluoride, and poly(ether imide) [9]; styrene–butadiene–styrene triblock copolymer [29] and poly(ferrocenyldimethylsilane) [30]. They have even spun DNA fibers with a diameter of approximately 30 nm [31] and silk for which there is a patent [32]. They have used PEO in order to study more deeply the electrospinning process and the influential parameters. They also studied [33] the formation of beads on the fibers (Fig. 6). The bead morphology has been well documented for electrospun fibers and is affected by processing conditions [19,33]. Beads can be considered as capillary break-up of the jets by surface tension. Thus, charge density carried by the jet, surface tension and viscoelastic properties of the solution are significant parameters. The higher the solution viscosity is, the less beads are formed. The net charge density influences in the same way. Actually, adding salt (i.e. NaCl) is a way to increase this density. Deitzel et al. investigated as well the formation of beads and found out that the spinning voltage influences mainly the formation of beads while the polymer concentration has effect on the fiber size [19]. They also noticed that at high concentration a bimodal distribution of the fiber sizes was created.

Wilkes at the Virginia Polytechnic Institute [18] has studied the effect of solution concentration, capillary–screen distance, electric potential at the tip and flow rate on electrospinning Esthane® 5720, a segmented polyether urethane. He found that bead-like structure appeared when the capillary–screen distance decreased, while the average fiber diameter was increased. When increasing the concentration, the average diameter rised and the bead-like structure turned into blobs at lower capillary–screen distance. A too high concentration leaded to failure of the fibers instead of being drawn, as the viscosity was too high. This can also be caused by a too high flow rate at lower concentration. Finally, increasing the potential decreased the fiber diameter.

Demir et al. studied the electrospinning behaviour of an elastomeric polyurethane urea copolymer in solution [34]. They observed that mainly the morphology of electrospun fibers is strongly correlated with viscosity, equivalently concentration and temperature. Actually, the morphological imperfections like formation of fibers with beads or curly fibers can be improved by increasing the solution temperature. This is also an important advantage from the aspect of industrial applications since high temperature makes the electrospinning process quick.

Biopolymers such as poly(lactic acid) (PLA) fibers have been electrospun by Bognitzki et al. [4]. The fibers had an average diameter of approximately 1 μm. They used tetraethyl benzylammonium chloride (TEBAC) to obtain fibers with lower diameter. This is due to the increased surface tension and electrical conductivity that TEBAC procures. Adding PEO to the solution resulted in the same phenomenon because of an increase of surface tension only. PLA and polyvinilpyrrolidone blends are materials that have also been used by these authors [3].

For some applications it is desirable to control not only the diameter of the fibers and their internal morphology (and thus their intrinsic properties) but also their surface structure. An interesting feature of nanofibers is that they display an internal phase morphology that is evidently controlled by rapid phase separation and rapid solidification. By selective removal of one component, fine porous fibers and functional nanofibers with specific surface topologies are accessible. Formation of such co-continuous phase morphologies was studied in a work by Bognitzki et al. where they used electrospinning of PLA to manufacture polymer/metal

hybrid nano- and mesotubes [12••]. The aim was to be able to control not only the fiber diameter but also the surface structure, which can be important for filtration applications or formation of functional nanotubes. The tubes were formed with a process they call TUbes by fiber template (TUFT) process. This process consists in coating the PLA nanofibers with first poly(*p*-xylylene) by chemical vapour deposition and then with the desired metal (aluminum in that case). Then the PLA core is removed by taking advantage of the ability to degrade of PLA. This shows a great potential for the production of novel tubular devices. Most possible TUFT process will gain significance with improvement of the control of tube diameters, structuring and functionalization of the tubes, which should be possible by adjusting the parameters for the preparation of template fibers by electrospinning. In another work by Caruso et al. poly(L-lactide) electrospun fibers were coated with amorphous titanium dioxide using a sol–gel coating technique [35]. On removal of the thermally degradable polymer, hollow titania fibers were produced. The sol–gel coating was able to mimic the finer details of the fiber, thereby forming nodules on the inner walls of the tubes. Nanotubes are also the topic treated in the presentation of Ko et al. at the ASC 16th Annual Technical Conference [36]. In that work, they have co-electrospun a mixture of carbon nanotubes and PEO solution. This process aligns the carbon nanotubes (if well dispersed in the polymer solution) in the resulting nanocomposites fibrils. According to models, the mechanical properties of carbon nanotubes composites are higher than usual composites. Nanotubes and nanowires can also be constructed by using an electrostatic field-assisted assembly technique combined with an electrospinning process to position and align individual nanofibers on a tapered and ground wheel-like bobbin [15••].

Cellulosic nanofiber membranes that present good wettability and absorbency properties as well as the ability to carry chemically reactive functionalities were reported by Liu and Hsieh [37]. In another work, Sung et al. studied the electrospinning of polycarbonates and their surface characteristic [38]. Electrospun fibers therefrom show a wrinkled structure that was found to depend on the evaporation rate of the solvent from the surface related to the rate of evaporation from the core. Indeed, as the solvent on the surface has evaporated and a 'skin' has formed, the solvent entrapped in the core diffuses to the ambient atmosphere and causes what they call the 'raisin-like structure'. They also believe that this is a reason for the formation of flat bands.

Surface functionalization of electrospun fibers has been also studied recently by Deitzel et al. [20•,39•]. This has been accomplished by electrospinning a series of random copolymers of PMMA-r-TAN (polymethyl methacrylate with varying tetrahydroperfluorooctyl acrylate concentration) from a mixed solvent of toluene and dimethyl formamide. They observed that surface segregation of fluorine in electrospun fibers is similar in magnitude to that measured for the thin film surface. Fluorinated surfaces are inherently of interest for stain resistant and water repellent materials and for coating applications.

Furthermore, chemical crosslinking method can be used to crosslink the pre-formed nanofibers. In a recent work by Ding et al., nanoscale poly(vinyl alcohol) (PVA) fiber (100–500 nm) aggregates were prepared with an electrospinning technique and then chemically crosslinked [40]. The results showed that the properly crosslinked PVA fiber aggregates had better antiwater solubility and mechanical properties than the non-crosslinked PVA fiber aggregates.

5. Molecular nano-electronic machines

Electronic polymers have been electrospun with the purpose to be able one day to create nano-electronic machines [10,11,41]. For example, these small fibers can support arrays of nanomachines, and connect integrated arrays of nanomachines to larger scale systems. Nanoscale fibers are also containing special arrangements of polymer molecules, often called crystallographic defects, which can themselves, function as nanomachines to translate and rotate polymer molecule [1].

Using electrospinning Diaz-de-Leon has prepared nanofibers of doped polyaniline (an organic conducting polymer) as itself or in blend with polystyrene or PEO and electrically characterise them [10]. The conductivity is found to be very sensitive to the morphology of the fibers (i.e. amount of defects, thickness) which is indeed related to the initial blend properties and solvent used. Therefore, better chain alignment in the polymer blends yields higher overall conductivity of the blended nanofibers. It is notable also, that the nanofibers obtained showed regions with polymer crosses; this polymer–polymer junctions are of interest in making nanoelectronic junction devices. Conductive nanofibers were obtained from electrospinning using blends of spinnable (e.g. poly(ethylene oxide)) and non-spinnable but conductive (e.g. polyaniline doped with camphorsulfonic acid) polymers, by MacDiarmid et al. [11,42•]. The rate for the vapour phase de-doping/re-doping of the electrospun fibers was at least one order of magnitude faster than to those for cast films. Again, this stresses the enormous effect of increase in the surface-to-volume ratio and selected chemical properties accomplished by electrospinning the polymer material into nanofibers. The resulting nanofibers are conductive and are of potential interest for applications in micro- and optolectronics, for example, nanowires, LEDs, photocells, etc. Moreover, the Korea Institute of Science and Technology

owns a patent on the fabrication of a lithium secondary battery comprising a fibrous film made by electrospinning [43]. Another interesting progress has been the development of a hybrid solar cell utilising electrospun conductive polymers 'doped' with photovoltaic dyes and nano-crystalline semiconductor particles [44]. Ziegler et al. have prepared a flexible photovoltaic membrane by utilising electrospun polyacrylonitrile (PAN) nanofiber dyed with copper phthalocyanine, while nano-crystalline TiO_2 semiconductor particles can be embedded as well within the nanofibers.

The feasibility of electrospinning photo-responsive polymeric materials with desirable functionalities is expected to find wide application in future electronic device fabrication. Control of the polymer solutions, blending with other polymers and electrospinning conditions can provide a variety of pathways for functionalization of interesting photo-responsive electrospun nanofibers. Drew et al. [41] have demonstrated successful engineering of polymeric membranes by electrospinning a photonic polymer system PAN blended with the light harvesting azo-dye, Congo red. The process of electrospun nanofibers can also be exploited for use in various applications in the sensor technology. A recent attempt is the one reported by Zhang et al. where a high surface area chemosensor material has been obtained, by electrospinning of fluorescent conjugated polymer [45]. Blends of PEO and fluorescent poly((*p*-phenylene ethynylene)-alt-(thienylene ethynylene)) were electrospun from a chloroform solution. Furthermore, Wang et al. have prepared fluorescent electrospun polymer film sensors valuable for the detection of explosives [46].

6. Polymer nanofibers for biomedical applications

The use of polymer nanofibers for biomedical applications is another active research area. In a recent publication, an electrospinning method was used by Zong and co-workers to fabricate bioabsorbable amorphous poly(D,L-lactic acid) and semi-crystalline poly(L-lactic acid) nanofiber non-woven membranes for biomedical applications [47]. They showed that the fiber diameter and the nanostructured morphology depended on processing parameters such as solution viscosity (e.g. concentration and polymer molecular weight), applied electric field strength, solution feeding rate and ionic salt addition. Concentration and salt addition were found to have relatively larger effects on the fiber diameter than the other parameters. The Fiber Society Spring 2001 Conference treated as well widely the electrospinning of nanofibers for biomedical applications. A study on the fabrication of a scaffold by electrospinning biomaterials such as PLA, poly(glycolic acid), poly(ethylene-co-vinyl acetate) (PEVA), and Type I collagen, was reported by Bowling et al. [48]. Fang et al. presented nano-structured electrospun poly-D,L-lactide-co-glycolide membranes for anti-adhesion applications [49]. Among them, there was also a presentation from Reneker's group on encapsulation of particles into electrospun polymeric nanofibers [50]. This was achieved by adding insoluble particles to the polymer solution. These particles were gold, pollen spore, alginate, and silver sulfadiozine for burns treatment, for example. They also added biomaterials for wound healing or other substances that functionalized the fiber, e.g. soluble drugs, antibacterial agents. Medical application of electrospinning is also the subject of a patent claimed by Reneker and co-workers [51]. They produced a skin mask by directly electrospinning fibers onto the skin surface in order to protect or heal eventual wounds. Another patent [52] claims the production of electrospun fibers containing pH-adjusting compound for use in dressing for wound treatment or protection from contamination. Electrospun fiber mats were also explored as drug delivery vehicles with promising results. Mats were made either from PLA, PEVA, or from a 50:50 blend of the two using tetracycline hydrochloride as a model drug [53].

The use of electrospinning for tissue engineering is also another interesting field of application of polymer nanofibers. Electrospun nanofibrous structures meet the essential design criteria of an ideal tissue engineered scaffold based upon its acts to support and guide cell growth. Most publications support that the electrospun nanofibrous structure is capable of supporting cell attachment and proliferation. Cells seeded on this structure tend to maintain phenotypic shape and guided growth according to nanofiber orientation. Li et al. have developed an electrospun structure for tissue-engineering applications, composed of poly(D,L-lactide-co-glycolide) PLGA fibers ranging from 500 to 800 nm in diameter [54]. The structure features a morphologic similarity to the extracellular matrix of natural tissue, which is characterised by a wide range of pore diameter distribution, high porosity, and effective mechanical properties. Matthews et al. studied how electrospinning can be adapted to produce tissue-engineering scaffolds composed of collagen nanofibers (a matrix composed of 100 nm fiber) [55•]. They found that the structural properties of electrospun collagen varied with the tissue of origin, the isotope, and the concentration of the collagen solution, which were used to spin the fibers. Moreover, blend components with collagen have been used as well for electrospinning [56]. Type I collagen-PEO fibers and non-woven fiber networks were produced by the electrospinning of a weak acid solution of purified collagen at ambient temperature and pressure. The process proposed by Huang et al. provides a convenient, non-toxic, non-denaturing approach for the generation collagen-containing nanofibers (diameter range of 100–150 nm) and nonwoven fabrics that have potential application in wound healing, tissue engineer-

ing, and as hemostatic agents. The same group has also produced elastin-mimetic fibers from peptide polymer in order to mimic protein fibers that are found in arterial wall [57•]. Electrospinning can even be used to create biocompatible thin films with useful coating design and surface structure that can be deposited on implantable devices in order to facilitate the integration of these devices with the body. Silk-like polymer with fibronectine functionality (extracellular matrix proteins) have been electrospun for making biocompatible films used on prosthetic devices aimed to be implanted in the central nervous system [58•].

7. Other functions of nanofiber structures

Non-woven textiles composed of electrospun fibers have a large specific surface area and small pore size compared to commercial textiles, making them excellent candidates for use in filtration and membrane applications. Thus, electrospinning has been exploited to produce nonwoven composites for application in filters [59]. A nanofiber web was produced from nylon 66 on a substrate made of either meltblown or spunbond polypropylene. The resulting product was then sandwiched between material of the same substrate and point bonded in a calender to form the composite structure. The filtration properties of microparticles were then measured and showed efficiency similar to the best commercial filters even if only one-fifth filtering media was used. Electrospinning can also be used to produce charged fibers for use in filtration media [17]. Obviously, the charge induction and charge retention characteristics are related to the polymer material used for electrospinning.

Kim and Reneker have investigated the use of PBI nanofibers as reinforcement in an epoxy and a rubber matrix (styrene–butadiene) [60]. They observed that the epoxy was toughened by the nanofibers and this reinforcing effect was higher than that of PBI fibroids (whiskers-like particles). Moreover, the PBI nanofibers can provide dramatic reinforcement of a rubber matrix (i.e. the Young modulus was ten times higher and the tear strength was twice as large as for the unfilled rubber). In another work, the reinforcement effect of the ultrathin fibers of nylon-4,6 with a semi-infinite length prepared by electrospinning solutions of the polymer in formic acid was clearly demonstrated by Bergshoef and Vancso [61]. These fibers can be applied to prepare transparent composites with an epoxy matrix. They noticed that at certain given process parameters, the jet of nylon-4,6 solution pulled from the capillary tip during the electrospinning process can splay into several finer jets. The potential of using polymer nanocomposites as the foundation for fabricating nanofibers structures, illustrated by the work of Fong et al. by demonstrating the dissolution and reprocessing of exfoliated montmorillonite–nylon 6 (NLS) nanocomposite [62]. They also exerted hierarchical control of morphology and form through the combination of a nanostructured material and a nanoscale fabrication technique. The electrospinning process resulted in highly aligned montmorillonite layers (layer normal perpendicular to the fiber axis) and nylon 6 crystallites (layer normal parallel to fiber axis).

Of particular interest are electrospun membranes composed of elastomeric fibers, for the development for several protective clothing applications. A lot of work is done with aim to develop garments that reduces soldiers' risks for chemical exposure [63]. The idea is to lace several type of polymers and fibers to make protective ultra-thin layers that would enhance for examples chemical reactivity and environmental resistance. The US Army presented at the Eighth International Conference on Textile Coating and Laminating its way to consider electrospinning [64,65]. They see a manner to produce membranes for laminated fabrics as well as direct sprayed-on fibrous coating structures. They prepared microporous membranes of PAN and PBI, and compared their convective airflow resistance and water vapour diffusion resistance with conventional fabrics PTFE wind barrier (like Gore-Tex). The electrospun membranes had both good water vapour transport properties and convective flow resistance, meaning that they will present remarkable 'breathing' properties, which are nowadays required in clothing applications.

8. Conclusions and future perspectives

Electrospinning is a very simple and versatile method of creating polymer-based high functional and high performance nanofibers that can revolutionise the world of structural materials. The process is versatile in that there is a wide range of polymer and biopolymer solutions or melts that can be spun. This assemble approach can be expanded even into a hierarchical assemble of produced nanofibers in other well-defined functional nanostructures, such as nanotubes and nanowires, etc. The various recent approaches that have been developed for scientific understanding, engineering control and then potential implementation in devices of electrospun nanofibers are summarised in this review.

Essential studies, nevertheless, are still required and many challenges remain to be faced. In particular, integration of nanofibers into useful devices requires nanofibers of well-controlled orientation, size, and other target characteristics as well as reproducibility locating them in specific positions and orientations. The ability to do so, however, remains a major challenge in the field. The design and construction of process equipment for controllable and reproducible electrospinning could determine the character of instabilities revealed, satisfy potential implementation and act as stimulus to provide new products. Moreover, to control over key perform-

ance parameters, the clarification of the fundamental electrodynamics of the electrospinning process and correlation to the polymer fluid characteristics must be reliably predicted and utilised. Work that address the evaluation of the fluid instabilities, postulated to be crucial for producing nanofibers, and precise characterisation of the morphology and material properties of electrospun polymer fibers themselves are in early stages and systematic studies are still emerging. With these variables under control, the challenges of fully quantitative modelling of the electrospinning process should be feasible, including both stable and unstable operating regimes, starting from the existing equations of electrodynamic theory. Productivity improvement of the electrospinning process is also an essential feature and merits more studies.

References and recommended reading

Papers of particular interest, published within the annual period of review, have been highlighted as:

- • of special interest
- •• of outstanding interest

[1] Reneker DH, Chun I. Nanometre diameter fibres of polymer produced by electrospinning. Nanotechnology 1996;7:216–23.

[2] Larrondo L, Manley RSJ. Electrostatic fiber spinning from polymer melts. I. Experimental observations on fiber formation and properties. J Polym Sci Polym Phys Ed 1981;19:909–20.

[3] Bognitzki M, Frese T, Steinhart M, Greiner A, Wendorff JH. Preparation of fibers with nanoscaled morphologies: electrospinning of polymer blends. Polym Eng Sci 2001;41:982–9.

[4] Bognitzki M, Wendorff JH, Greiner A. Submicrometer shaped polylactide fibers by electrospinning. Polym Prep (ACS, PMSE) 2000;82:115–6.

[5] Buer A, Ugbolue SC, Warner SB. Electrospinning and properties of some nanofibers. Textile Res J 2001;71:323–8.

[6] Warner SB, Buer A, Ugbolue SC, Ruteldge GC, Shin MY. M98-D01 A fundamental investigation of the formation and properties of electrospun fibers. Department of Textile Sciences, University of Massachusetts Dartmouth; Department of Chemical Engineering and Material Sciences, Massachusetts Institute of Technology Cambridge, 2000.

[7] •• Reneker DH, Yarin AL, Fong H, Koombhonge S. Bending instability of electrically charged liquid jets of polymer solutions in electrospinning. J Appl Phys 2000;87:4531–47.

In this article the reasons for the instability are analyzed and explained using a mathematical model. The theory accounts for the non-linear effects that are characteristics of finite perturbations, as well as for the rheological behaviour of viscoelastic liquids. The authors give the three-dimensional equations describing the dynamics of the bending of electrospun jets, both in the nearly straight region where the instability grew slowly and in the region where the bending dominated the path of the jet.

[8] Torres B. Ultrafine fibers of polystyrene dissolved in tetrahydrofuran prepared using electrospinning method. National Conference of Undergraduate Research, Lexington: University of Kentucky; 2001.

[9] Koombhongse S, Liu W, Reneker DH. Flat ribbons and other shapes by electrospinning. J Polym Sci, Polym Phys Ed 2001;39:2598–606.

[10] Diaz-de-Leon MJ. Electrospinning nanofibers of polyaniline and polyaniline/(polystyrene and polyethylene oxide) blends. National Conference of Undergraduate Research, Lexington: University of Kentucky; 2001.

[11] MacDiarmid AG, Jones WE, Noris ID, et al. Electrostatically-generated nanofibers of electronic polymers. Synthetic Met 2001;119:27–30.

[12] •• Bognitzki M, Hou H, Ishaque M, et al. Polymer, metal, and hybrid nano- and mesotubes by coating degradable polymer template fibers (TUFT process). Adv Mater 2000;12:637–40.

The paper introduce an efficient and simple general route, called TUFT process (tubes by fiber templates), towards nano- and mesotubes using electrospun degradable polymer fiber templates. This approach offers a great potential for the design of novel tubular devices in the sense of control of dimensions and shape and even with respect to the broad range of materials that can be manufactured.

[13] Kim J-S, Reneker DH. Polybenzimidazole nanofiber produced by electrospinning. Polym Eng Sci 1999;39:849–54.

[14] Rangpukan R, Reneker DH. Development of electrospinning from molten polymers in vacuum. J Textile Apparel, Technol Manage 2001, vol. 1. Special issue: The Fiber Society Spring 2001 Conference, Raleigh NC.

[15] •• Theron A, Zussman E, Yarin AL. Electrostatic fields-assisted alignment of electrospun nanofibres. Nanotechnology 2001;12:384–90.

A new approach was described for assembling nanofibers in parallel arrays while being able to control the average separation between the fibres using electrostatic forces during the manufacturing process.

[16] Doshi J, Reneker DH. Electrospinning process and applications of electrospun fibers. J Electrostat 1995;35:151–60.

[17] Tsai PP, Schreuder-Gibson H. Effect of electrospinning material and conditions upon residual electrostatic charge of polymer nanofibers. J Textile Apparel, Technol Manage 2001, vol. 1. Special issue: The Fiber Society Spring 2001 Conference, Raleigh NC.

[18] Wilkes GL. Available from: http://www.che.vt.edu/Wilkes/electrospinning/electrspinning.html. 2001.

[19] Deitzel JM, Kleinmeyer J, Harris D, Tan NCB. The effect of processing variables on the morphology of electrospun nanofibers and textiles. Polymer 2001;42:261–72.

[20] • Deitzel JM, Kleinmeyer D, Hirvanen JK, Tan NCB. Controlled deposition of electrospun poly(ethylene oxide) fibers. Polymers 2001;42:8163–70.

The onset of a chaotic oscillation of the electrospinning jet was controlled by the deposition of sub-micron polymer fibers on a substrate through use of an electrostatic lens element and collection target of opposite polarity.

[21] Yarin AL, Koombhongse S, Reneker DH. Bending instability in electrospinning nanofibers. J Appl Phys 2001;89:3018–26.

[22] •• Yarin AL, Reneker DH. Taylor cone and jetting from liquid droplets in electrospinning of nanofibers. J Appl Phys 2001;90:4836–46.

An interesting theory of the stable shapes of droplets as affected by an electric field is proposed in this paper. The theory compared with data acquired in experimental work on electrospinning of nanofibers from polymer solutions and melts.

[23] • Shin MY, Hohman MM, Brenner M, Ruteldge GC. Experimental characterization of electrospinning: the electrically forced jet and instabilities. Polymer 2001;42:9955–67.

The electrospinning process was described by a small set of operating parameters and summarized through the use of operating diagrams of electric field versus flow rate.

[24] • Hohman MM, Shin MY, Ruteldge GC, Brenner M. Electrospinning and electrically forced jets. I. Stability theory. Phys Fluids 2001;13:2201–20.

A complete stability analysis of a charged fluid jet in a tangential electric field as a function of all fluid parameters was performed.

[25] • Hohman MM, Shin MY, Ruteldge GC, Brenner M. Electrospinning and electrically forced jets. II. Applications. Phys Fluids 2001;13:2221–36.

The stability analysis, in conjunction with an analysis of the charge distribution and radius of the jets in electrospinning experiments, were used to derive quantitative thresholds for the onset of electrospinning as a function of all experimental parameters.

[26] Shin MY, Hohman MM, Brenner M, Ruteldge GC. Electrospinning: a whipping fluid jet generates submicron polymer fibers. Appl Phys Lett 2001;78:1149–51.

[27] Vao-Soongnern V, Mattice WL. Dynamic properties of an amorphous polyethylne nanofiber. Langmuir 2000;16:6757–8.

[28] • Vao-Soongnern V, Doruker P, Mattice WL. Simulation of an amorphous polyethylene nanofiber on a high coordination lattice. Macromol Theor Simul 2000;9:1–13.

A Monte Carlo simulation that employs a bridging technique is used to allow interconversion between a fully atomistic representation of a structure in continuous space and a coarse-grained version of the same structure in the discrete space of a high coordination lattice.

[29] Fong H, Reneker DH. Elastomeric nanofibers of styren–butadiene–styrene triblock copolymer. J Polym Sci: Part B: Polym Phys 1999;37:3488–93.

[30] Zhihao C, Foster MD, Wensheng Z, et al. Structure of poly(ferrocenyldimethylsilane) in electrospun nanofibers. Macromolecules 2001;34:6156–8.

[31] Fang X, Reneker DH. DNA fibers by electrospinning. J Macromol Sci Phys 1997;B36(2):169–73.

[32] Reneker DH, Eby RK, Ertley D, Hudson SD, Zarkoob S. Synthetically spun silk nanofibers and a process for making the same. Patent US6110590. University of Akron; 2000.

[33] Fong H, Chun I, Reneker DH. Beaded nanofibers formed during electrospinning. Polymer 1999;40:4585–92.

[34] Demir MM, Yilgor I, Yilgor E, Erman B. Electrospinning of polyurethane fibers. Polymer 2002;43:3303–9.

[35] Caruso RA, Schattka JH, Greiner A. Titanium dioxide tubes from sol–gel coating of electrospun polymer fibers. Adv Mater 2001;13:1577–9.

[36] Ko FK, Kahn S, Rahman A, Zhou O. Carbon nanotube reinforced nanocomposites by the electrospinning process. ASC 16th Annual Technical Conference, Blacksburg, VA: 2001.

[37] Liu H, Hsieh Y-L. Cellulosic nanofiber membranes for liquid wetting/absorbency and chemical reactivity. J Textile Apparel, Technol Manage 2001, vol. 1. Special issue: The Fiber Society Spring 2001 Conference, Raleigh NC.

[38] Sung C, Gibson H, Varma RNK. Electrospinning of polycarbonates and their surface characteristics. J Textile Apparel, Technol Manage 2001, vol. 1. Special issue: The Fiber Society Spring 2001 Conference, Raleigh NC.

[39] • Deitzel JM, Kosik W, McKnight SH, Tan NCB, Desimone JM, Crette S. Electrospinning of polymer nanofibers with specific surface chemistry. Polymer 2002;43:1025–9.

This paper demonstrate a pathway for surface functionalization of electrospun nanofibers which may be exploited directly in the design of fibers for various applications.

[40] Ding B, Kim H-K, Lee S-C, et al. Preparation and characterization of a nanoscale poly(vinyl alcohol) fiber aggregate produced by an electrospinning method. J Polym Sci: Part B: Polym Phys 2002;40:1261–8.

[41] Drew C, Wang X, Senecal K, et al. Electrospun nanofibers of electronic and photonic polymer systems, Orlando, FL: TANDEC; 2000.

[42] • MacDiarmid AG, Ko FK, Lec RM, Noris ID, Shaker M. Electrospinning ultrafine conductive polymeric fibers, 2001, Patent WO0151690 and Norris ID, Shaker MM, Ko FK, MacDiarmid AG. Electrostatic fabrication of ultrafine conducting fibres: polyaniline/polyethylene oxide blends. Synthetic Met 2000; 114:109–14. This paper is one of the several papers published by the authors. They have made substantial progress for fabrication of electronic polymer fibers. The group reproducibly and controllably fabricates nanofibers of pure electronic polymers (in their semiconducting and metallic regimes) and/or their blends in conventional organic polymers for the purpose of ascertaining their applicability in the fabrication of nano-electronic devices.

[43] Cho WB, Choi SW, Mu JS, Kim HS, Kim US, Cho WI. A Lithium secondary battery comprising a super fine fibrous polymer separator film and its fabrication method. Patent WO0189022 and WO0189023. Korea Institute of Science Technology; 2001.

[44] Ziegler D, Senecal KJ, Dew C, Samuelson L. Electrospun fibrous membranes of photovoltaic and conductive polymers. J Textile Apparel, Technol Manage 2001, vol. 1. Special issue: The Fiber Society Spring 2001 Conference, Raleigh NC.

[45] Zhang Y, Dong H, Norris ID, MacDiarmid AG, Jones WE. High surface area chemosensor material by electrospinning of fluorescent conjugated polymer. Abstracts of papers of the American Chemical Society 2001; 222(2) August.

[46] Wang XY, Lee SH, Drew C, Senecal KJ, Kumar J, Samuelson L. Fluorescent electrospun polymer films for the detection of explosives. Abstracts of papers of the American Chemical Society 2002; 223(2) April :D44.

[47] Xinhua Z, Kim K, Shaofeng R, Hsiao BS, Chu B. Structure and process relationship of electrospun bioabsorbable nanofiber membranes. Polymer 2002;43:4403–12.

[48] Bowling GL, Matthews JA, Simpson DG, Kenawy ER, Wnek GE. Electrospinning biomaterials. J Textile Apparel, Technol Manage 2001, vol. 1. Special issue: The Fiber Society Spring 2001 Conference, Raleigh NC.

[49] Fang D, Zong X, Chen W, Cruz S, Hsiao B, Chu B. Nanostructured electrospun poly-D,L-lactide-co-glycolide membranes for anti-adhesion applications. J Textile Apparel, Technol Manage 2001, vol. 1. Special issue: The Fiber Society Spring 2001 Conference, Raleigh NC.

[50] Kataphinan W, Dabney S, Smith D, Reneker DH. Fabrication of electrospun and encapsulation into polymer nanofibers. J Textile Apparel, Technol Manage 2001, vol. 1. Special issue: The Fiber Society Spring 2001 Conference, Raleigh NC.

[51] Kataphinan W, Dabney S, Reneker DH, Smith D, Akron UO. Electrospun skin masks and uses thereof. Patent WO0126610. University of Akron; 2001.

[52] Gibson P, McManus A, Mello C, et al. Electrospun fibers and an apparatus therefor. Patent WO0127365. University of Akron; 2001.

[53] Kenawy ER, Bowlin GL, Mansfield K, et al. Release of tetracycline hydrochloride from electrospun poly(ethylene-vo-vinylacetate), poly(lactic acid), and a blend. J Control Release 2002;81:57–64.

[54] Li WJ, Laurencin CT, Caterson EJ, Tuan RS, Ko FK. Electrospun nanofibrous structure: a novel scaffold for tissue engineering. J Biomed Mater Res 2002;60:613–21.

[55] • Matthews JA, Wnek GE, Simpson DG, Bowlin GL. Electrospinning of electrospinning of collagen nanofibers. Biomacromolecules 2002;3:232–8.

Careful experiments demonstrate that it is possible to tailor subtle mechanical properties into a matrix by controlling fiber orientation. It is highlighted that electrospun collagen promotes cell growth and the penetration of cells into the engineered matrix.

[56] Huang L, Nagapundi K, Chaikof EL. Engineered collagen-PEO nanofibers and fabrics. J Biomater Sci Polym Ed 2001;12:979–93.

[57] • Huang L, McMillan RA, Apkarian RP, Pourdeyhimi B, Conticello VP, Chaikof EL. Generation of synthetic elastin-mimetic small diameter fibers and fiber networks. Macromolecules 2000;33:2899–997.

The first report of fiber formation from an elastin-like analogue. Electrospinning techniques were employed to produce fibers in a form that mimics native elastin fiber diameter, utilising a 81 kDa synthetic elastin peptide polymer based upon the elastin-mimetic repeat sequence $(Val–Pro–Gly–Val–Gly)_4(Val–Pro–Gly–Lys–Gly)$.

[58] • Buchko CJ, Chen LC, Shen Y, Martin DC. Processing and microstructural characterization of porous biocompatible protein polymer thin films. Polymer 1999;40:7397–407.

The electrospinning process is shown to produce protein polymer coatings. Control can be exerted over the morphology and thickness of the coatings by varying process parameters (solution concentration, applied field strength, deposition distance and deposition time). The electrospinning process was shown to be a means of creating porous thin films with structural gradients and controlled morphology that could enhance biocompatibility.

[59] Doshi J. Nanofiber-based nonwoven composites: properties and applications. Nonwovens World. 2001; augusti–september:64–68.

[60] Kim J-S, Reneker DH. Mechanical properties of composites using ultrafine electrospun fibers. Polym Comp 1999;20:124–31.

[61] Bergshoef MM, Vancso GJ. Transparent nanocomposites with ultrathin electrospun nylon-4,6 fiber reinforcement. Adv Mater 1999;11:1362–5.

[62] Hao F, Weidong L, Wang C-S, Vaia RA. Generation of electrospun fibers of nylon 6 and nylon 6-montmorillonite nanocomposite. Polymer 2002;43:775–80.

[63] Ross SE. Electrospinning: the quest for nanofibers. Inter Fiber J 2001;50–3.

[64] Schreuder-Gibson H. Electrospinning technology—a novel way to apply polymers directly to a substrate, Fabrics JoC, editor. The Eighth International Conference on Textile Coating and Laminating, Frankfurt Germany: 1998.

[65] Gibson P, Schreuder-Gibson H, Rivin D. Transport properties of porous membranes based on electrospun nanofibers. Colloids Surface A: Phys. Eng. Aspects 2001;187:469–81.