

1

Introduction

1.1

Fibers—Key Functional Elements in Technology and Nature

A multitude of objects surrounding us at home, an impressive number of technical parts controlling our day to day life both privately and in technical areas, even a set of currently emerging technologies have fibers as their basic structural and functional elements or depend at least on fiber-type architectures. A fiber is of course first of all a geometric shape, a 1Dimensional object, having a certain diameter, a given axial ratio and a certain length that can often approach infinity. Figure 1.1a displays a silk fiber as one example and Figure 1.1b a synthetic polyamide fiber as another example. Such fibers may not only be straight but might also display a certain curvature, they may be bent to some extent (Figure 1.1c).

However, for real applications fibers have to be more than just geometrical elements. They have to fulfill a set of requirements, to display a selection of specific properties, of dedicated functions.

Textiles, produced, for instance, on the basis of synthetic polymer fibers not only allow us to dress up, to catch the eye of our fellow people, to display fancy dressings but they provide in many instances protection against cold temperatures, rain, strong winds, maybe in certain cases even against UV-radiation. In clothing the geometric features of the fibers enable the design, the preparation of planar textiles via weaving, knitting processes. These textiles are highly porous, as shown by the SEM image displayed in Figure 1.2a, thus controlling thermal insulation, wind resistance, passage of vapor emerging from the body such as sweat. In addition, the fibers have to be able to adsorb vapors and release them again in textile applications, they have to provide certain mechanical properties defined by particular magnitudes of fiber stiffness and strength, elasticity allowing for textile deformations that arise when using them as clothing and they should allow, for instance, to incorporate dyes, and pigments.

Transportation industries involved in building and using airplanes, rapid trains, automobiles and boats rely strongly on large-scale technical parts having an extremely low weight while displaying simultaneously a high stiffness and strength. Fibers are incorporated for this purpose into matrix materials such as polymers or ceramics, giving rise to mechanical reinforcement effects (Figure 1.2b).

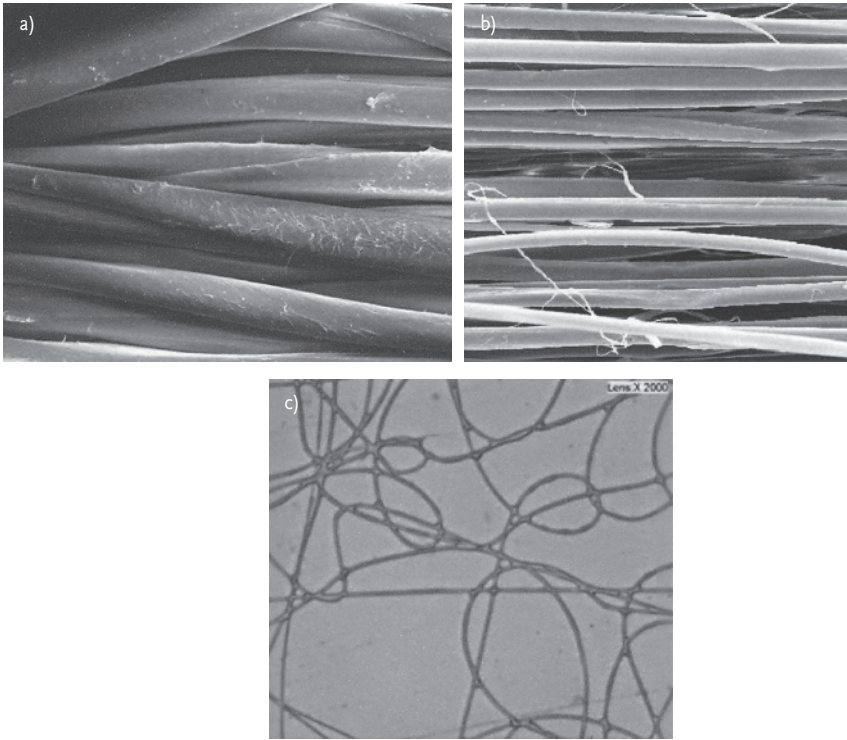


Figure 1.1 SEM images of (a) silk fibers, (b) polyamide fibers, (c) optical image of polyamide fibers displaying curvature.

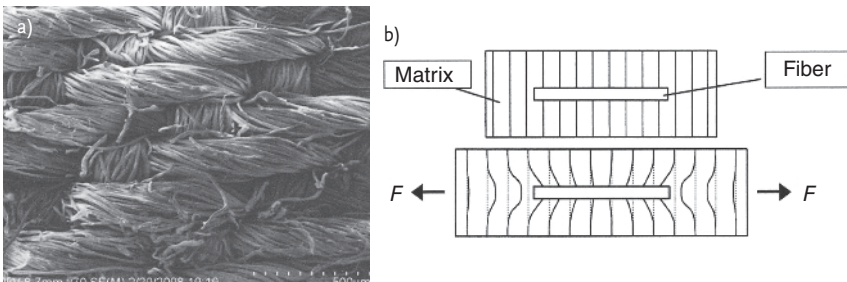


Figure 1.2 (a) SEM image of cotton textile, (b) fiber reinforcement, schematically showing fibers and stress lines; upper image: unstressed, lower image: stressed.

Optical information technology comprising the transportation, manipulation and display of information by optical means not only in local areas as in a car but also on a larger scale within buildings, all the way to covering huge distances existing between continents depend heavily on optical fibers composed of inorganic or organic glasses. It is obvious that the fibers not only have to possess in

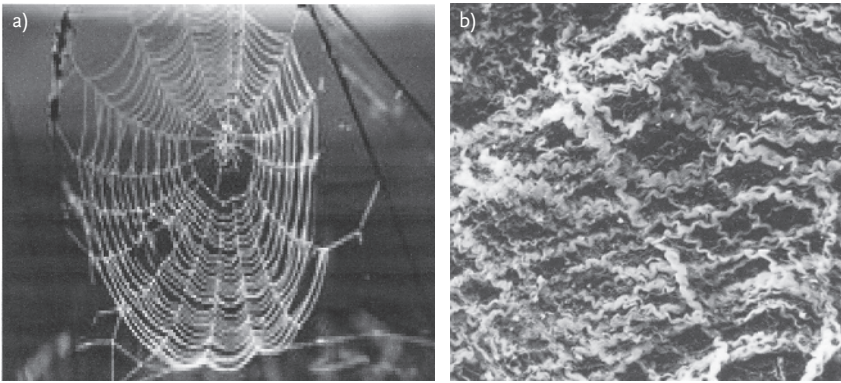


Figure 1.3 (a) Spider web constructed from fibers, (b) extracellular matrix (ECM) surrounding cells in living tissue, composed of fibrils, for details see text.

this case a very high optical clarity, that is, a very high optical transmission, that they should be flexible so that they can be subjected to bending to be integrated into technical parts, but they also should have intrinsic optical guiding properties allowing for particular optical propagation modes. Electric cables transporting electric energy, air filters or fluid filters composed of fibers and providing for clean air, water, gasoline are further technical examples of objects, devices containing and relying on fibers as key elements. Furthermore, fibers are also basic ingredients in carpets, ropes, tapestry and this list can be extended endlessly with some fantasy involved.

Fibers are, of course, not an invention of mankind, of modern techniques. Nature in fact has been using fibers as basic elements on a large scale to construct functional objects for millennia. Spider webs as displayed in Figure 1.3a obvious already to the naked eye and designed to catch insects are composed of a very loose network of intricate design to make them light, to offer a large cross-sectional area and yet to make them resistant to wind, storm, rain and to the attack of the prey trying to free itself. In terms of applications spider webs may serve as model structures for particular kinds of plant-protection devices, to be discussed later in more detail. Pheromone dispensers shaped along the architecture of spider webs and incorporating the enhanced mechanical properties of the basic fiber-like building elements offer significant advantages, as will be discussed later in some detail in Chapter 8.

A further example from nature characterized by a network of fibers in the nanometer range is the extracellular matrix (ECM), depicted in Figure 1.3b, which is an important 1D structured component of tissue. It has a broad range of tasks to accomplish. It embeds the cells of which the particular tissue is composed, it offers points of contacts to them, provides for the required mechanical properties of the tissue. Depending on the type of tissue the fibers are either tightly packed and oriented along a given direction, as in the case of muscles or are unoriented

in a plane. as for instance in skin tissues. The first types of tissues require an enhanced mechanical strength in one particular direction, whereas the second one should be able to sustain planar stresses in all directions.

Finally, fibers such as wool fibers, hairs, silk fibers protect human beings and animals in a way similar to artificial clothing. They again possess specific mechanical properties, insulation properties and are able to adsorb moisture to a significant extent. Many more examples from nature come to mind, yet the aspect of fibers coming from nature will be kept short here since this topic will be revisited.

An obvious conclusion at this stage is that fibers are highly valuable and highly functional objects in technical and life science areas. However, it is important to point out that such fibers will in general not perform well in applications if one just chooses the right geometry, if one just focuses on them as geometric 1D objects. A first important aspect is the choice of the material with a given well-known set of mechanical, optical, electrical, thermal, or perhaps also magnetic properties, from which to produce the fibers. So, depending on the kind of application in view polymers, metals, inorganic materials will be selected as basic materials for the production of fibers. Yet, the well-known and tabulated general intrinsic properties of these materials are just guidelines, merely starting points for design considerations. More important is a tailored control of the intrinsic structure of the fiber via appropriate fiber preparation techniques to come up with the required advanced properties, functions aiming at the target application.

Fiber design thus requires in any case a very fundamental understanding of the correlation between the intrinsic structure of a fiber on the one hand and its properties, functions on the other side. Fiber design requires, furthermore, also the knowledge of how particular fiber-characteristic intrinsic structures can be achieved via the selection of appropriate fiber processing techniques and via the choice of suitable processing parameters. Finally, of course, one has to have a fundamental understanding on how to construct technical elements from fibers, on how to select the best architectures for them, and how to achieve particular functions in this way.

1.2

Some Background Information

1.2.1

Structure of Crystalline and Amorphous Materials

A basic first step towards fiber design for a particular application involves, as pointed out above, the selection of the material with a given spectrum of properties from which the fiber will be produced. A macroscopic piece of matter composed, for instance, of a metal such as copper or iron, of a glass being of inorganic or organic nature, of a semiconductor such as GaAs, or of a synthetic polymer such as poly (methyl methacrylate) displays a set of characteristic

structural features and properties as controlled by the nature of the atoms/molecules of which they are composed, by the arrangement of these basic structural units in space as well as by the type of interactions existing between these units. Depending on the material under consideration various types of spatial arrangements of the atoms/molecules are experienced.

Crystalline materials are characterized by a highly regular 3D arrangement of the constituent atoms or molecules on a lattice in space displaying a translational symmetry. A so-called long-range order exists, that is, the position of the atoms/molecules far away from a reference atom/molecule is well defined as a function of the interatomic/intermolecular distances. This fact allows us to represent the crystalline structure in terms of the unit cell that is, the smallest element containing all structural features of the macroscopical crystal. As detailed in books concerned with crystallography, space-filling requirements lead to the conclusion that only certain types of lattice types—14 Bravais lattices—should exist with cubic, hexagonal or triclinic lattices being some examples, as shown in Figure 1.4. In addition to the translational

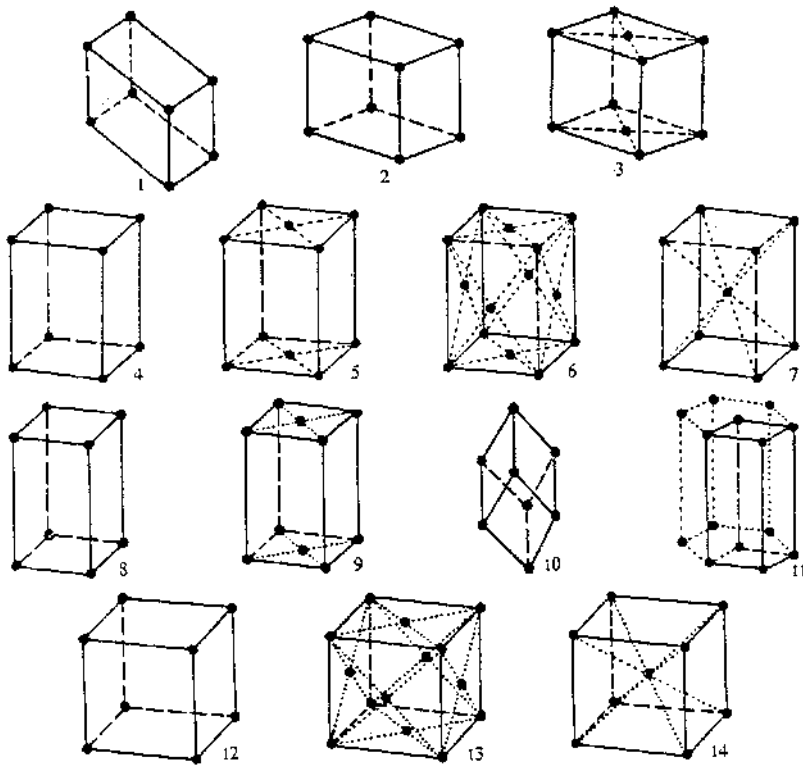


Figure 1.4 14 Bravais lattices arising from symmetry considerations and displayed by all types of materials able to crystallize including polymers.

symmetry point symmetries are used to characterize the packing of the atoms, molecules making up the crystal in space. These lattices are displayed without exception by all types of materials able to crystallize including polymers.

Based on such symmetry considerations predictions can be made on the anisotropy of properties—properties are different along different crystal axes—as well as on the presence of particular properties. Taking as an example the absence of an inversion center one can directly conclude that such a material can, in principle, display properties such as ferroelectricity, piezoelectricity or second-order nonlinear optical effects.

Considering briefly fibers one situation to be discussed later in more detail may well be that fibers prepared from one and the same material may display quite different properties, the reason being that fibers were produced in which different type of crystal modifications with different crystal unit cell occur, or in which different crystal unit-cell directions point along the fiber axis. It is also conceivable that fiber formation goes along with the introduction of specific crystals defects.

In contrast to crystalline structures, amorphous structures including glasses and melts do not display a regular packing of atoms, molecules in space, only a short-range order exists. This term represents the situation that the atoms or molecules are closely packed in an irregular manner so that one has only knowledge of the probabilities with which neighboring atoms/molecules occur as a function of the interatomic/intermolecular distance. The average distance to next and second-next neighbors is known within limits but no information is available for distances larger than these. Pair correlation functions are used to represent this situation again, as detailed in books on material science. Due to the particular kind of atomic or molecular packing amorphous materials in general display isotropic properties, that is, the properties along different directions of a piece of material will be equal. No optical birefringence is displayed by such structures, in contrast to the case of crystalline materials.

However, the situation might be quite different for fibers. Anisotropic properties may be experienced in amorphous fibers provided that orientational effects have accompanied fiber formation. Optical birefringence is one consequence and anisotropy of properties such as mechanical or electrical properties another one. Cases are known in which the tensile modulus, the refractive index or the thermal expansion coefficients along the length of the fiber differ strongly from those along a direction perpendicular to the axis.

Intermediate structures also exist for particular kinds of materials. Liquid-crystalline materials as composed of shape-anisometric molecules such as rod-shaped, disc-shaped, banana-shaped molecules, etc., have features resembling those of crystalline structures, among them lattice-type arrangements of the center of molecules along specific directions molecules that are orientationally ordered to a certain extent giving rise to optical birefringence. However, at the same time they show features resembling those of amorphous materials, fluids including viscous flow or in some cases the complete absence of a regular positional order.

1.2.2

Chain Conformation and Structures of Polymer Materials

Polymer materials, are a main topic of the book, need special considerations in this context—one reason being that a single molecule—a chain molecule—tends to be much larger than the length of unit cells, is composed of a large number of subunits, that is, repeat units and has an extremely large number of internal degrees of freedom. Even if concerned with the preparation of metal, metal oxide fibers via electrospinning the route towards such fibers will be based in the majority of cases on polymer fibers following a precursor route.

First, the macromolecular chains making up the polymer material are not geometrically highly defined, as assumed in the discussion so far, but are subjected to a large number of degrees of freedom, as already mentioned above [1–3]. Macromolecules are composed of a large number of basic molecular groups—monomers—which are all identical throughout the chain backbone—homopolymer—they can be composed of two chemically different units—copolymers—three chemically different units—terpolymers—and so on. Various chain architectures are accessible via synthetic routes, as detailed in the corresponding text books on macromolecular chemistry and physics, including linear chains, branched chains, star-like chains, random copolymers, block copolymers and many more.

Important as far as structure formation in bulk is concerned is that an individual macromolecule forms a very loose structure in solution, in the melt but also in the solid state in the shape of a coil, of a so-called Gaussian coil (Figure 1.5). The spatial extension of linear macromolecules tends to be represented by the mean square value of the chain end-to-end vector $\langle r_e^2 \rangle$, the vector pointing from one chain end to the other. In the melt and ideal solutions it is determined by the number n of monomer units within the chain as well as by the length of atomic bonds l along the chain backbone as given by

$$\langle r_e^2 \rangle = nl^2 C_n$$



Figure 1.5 Representation of the Gaussian coil conformation of a chain molecule, the monomer units being represented by dark spheres, for details see text.

where C_n is a number typically in the range between 2 and 15, representing details on the bond angles and rotational angles characteristic of the chemical structure considered. The brackets $\langle \rangle$ indicate averaging over a Gaussian distribution of the end-to-end vector originating from the large number of degrees of freedom available to the chain. A coil conformation takes place, that is, the trajectory of the chain follows in ideal cases closely that a particle would form via diffusion (Figure 1.5). For a linear chain composed of 10000 bonds, a bond length of 0.15 nm and a value of 9 for C_n the linear extension of a coil molecule as calculated from the square root of the $\langle r_e^2 \rangle$ may amount to several tens of nm.

So the intrinsic density of a single chain molecule (mass of all monomers per volume of the Gaussian coil) is very low, a single chain molecule has a lot of space within its interior. So both in the molten amorphous state and in effect also in the crystalline state the chain molecules interpenetrate each other in large numbers, chain entanglements occur in large numbers in order to form a densely packed material. The packing of segments, of monomer units within the melt or amorphous glassy state is short ranged, as detailed above.

Considering now the structures of the solid states exhibited by polymers it is obvious that strong differences should exist in comparison to the structures formed by atoms or small geometrically highly defined molecules. Polymers tend to form lamellar-type of crystals that are very thin, of the order of 10–50 nm, yet that display lateral extensions well into the micrometer range (Figure 1.6a). So in a certain sense lamellar crystals assume the geometric shape of a piece of paper. Electron scattering (Figure 1.6b) reveals that the chain molecules pass the lamellae along the lamella normal, folding back at the surfaces (Figure 1.6c).

This restriction of crystal formation to thin lamellae certainly is related to the restrictions imposed on the dynamics of the chain molecules in terms of diffusion, shape rearrangements by entanglements. The lamellae show all known types of units cells – Bravais lattices – as known from nonpolymer materials and this is not surprising in view of the general symmetry considerations leading to Bravais lattices. The chain molecules tend to pass through the lamellar oriented along the lamellar normal, they either fold back in an irregular manner after passing the lamella or they enter adjacent lamellae (Figure 1.6c).

An important feature of crystalline polymers is that they are never able to become 100% crystalline. The degree of crystallinity, as defined by the weight fraction of the material that has been transformed into the crystalline state, may assume values between about 0.05 up to 0.9, depending on the regularity of the chain molecules and the crystallization conditions. This partially crystalline state gives rise to an additional structural feature on the 10–100 nm scale in addition to the one coming from the crystalline lattice on the 1 nm scale. Crystalline lamellae form stacks in which the lamellae and amorphous layers alternate in a regular fashion giving rise to a one-dimensional regular order (Figure 1.6d).

Coming back to fiber aspects it is obvious that one expectation is that the crystals, that is, in this particular case the lamellae, may become oriented in a specific way with respect to the chain axes. However, one might also assume

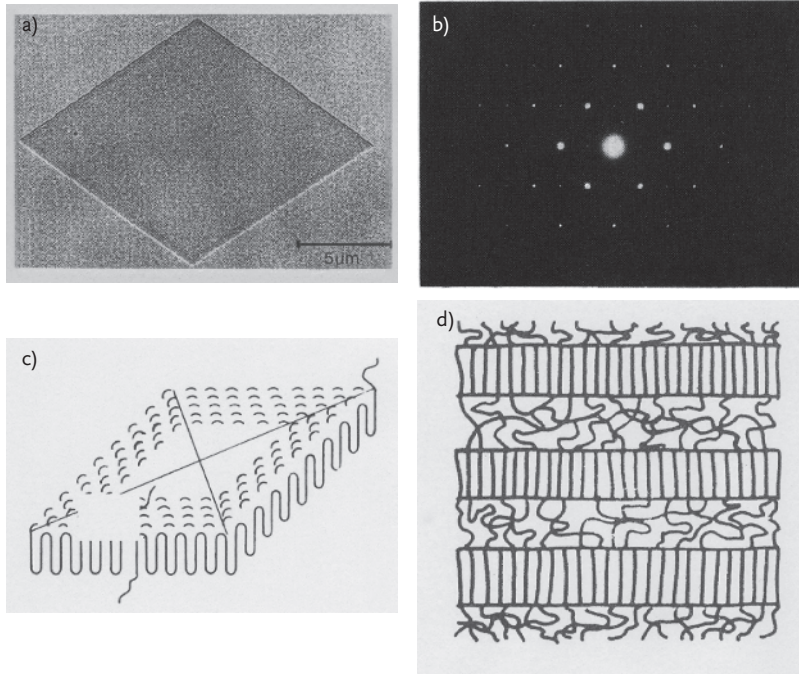


Figure 1.6 (a) Lamellar crystals composed of chain molecules, (b) electron scattering diagram showing that the chains are oriented perpendicular to the plane of the

lamella as displayed in (c, d) arrangement of amorphous layers and crystalline lamellae in partially crystalline polymers.

that fiber formation can deform, i.e. can erase the order on the 10–100 nm scale coming from the packing of lamellae and amorphous layers. In addition, the chain molecules showing so many degrees of freedom might become deformed, extended along the fiber axes both in crystalline and amorphous polymer materials. All these modifications will show up in strongly modified mechanical, thermal, optical and many more categories of properties within the fibers. In fact, it is even conceivable that deformations going with fiber formation give rise to the existence of novel types of crystal modifications, as known, for instance, from stretching poly (vinylidene fluoride) films.

With respect to properties of bulk materials composed of chain molecules it has to be pointed out that polymer materials tend to exhibit viscoelastic properties that is, a superposition of elastic properties—reversible deformation and recovery on unloading—and viscous properties—irreversible deformation on loading, plastic flow. The extent of the two contributions will depend on the temperature considered as well as on the time scale/frequency of the mechanical loading/unloading steps and again one might expect that fiber formation will also affect the nature of the viscoelastic properties.

1.3

Processing of Polymer Materials towards Fibers—Fiber Extrusion

The discussion that follows will concentrate predominantly on synthetic polymer materials, for reasons detailed above. The task is to start from the basic bulk material—melt, solid, powder—and to process it in a controlled way to fibers, hopefully in such a way that fibers with tailor-made intrinsic structures and properties result. A technically highly established large-scale industrial route is based on what we might call a top-down approach where macroscopical materials are shaped in such a way that smaller structures become available. In the case considered here this shaping of fibers, of fiber-type structures, is performed via mechanical forces in general applied to solutions or melts.

Of major importance in this respect are extrusion approaches discussed in the following with respect to polymer processing (Figure 1.7). Polymer melts or polymer solutions are pumped via screws through dies that force a fiber-like geometry on the fluid material emerging from the die. Typically, arrays of dies with a circular cross section are arranged parallel to each other so that a multitude of fibers are formed simultaneously. The still viscous jet coming out to the dies solidifies either by cooling down the melt below the respective melting temperature or glass temperature of the basic fiber material or by evaporation or coales-



Figure 1.7 Lab-type extruder with the extrusion die pointing to the reader.

cence of the solvents in the case of solution extrusion into a bath containing a nonsolvent. The fibers may in subsequent steps, in general, become subjected to strong longitudinal elongations by selecting the take-up speed to be much higher than the extrusion speed. The concept is that this deformation causes chain elongations and orientations as well as crystal orientations, with the result that the stiffness and strength of the fibers are strongly enhanced relative to the bulk material.

To introduce a few technical details, in melt extrusion pellets of the basic material are fed into a screw zone of an extruder (Figure 1.7). The screw arrangement causes the pellets to be compressed, removes residual air and water from the pellets, heats them up into the fluid state and finally transports the melt through specific dies with the desired speed as controlled, among other parameters, by the rotation speed. The choice of the die determines the geometry of the resulting products including tubes, planar structures but also fibers. Extruders may be quite small with feeding rates of just a kg/h but they can also be quite big with feeding rates of many hundreds of kg/h and more.

Man-made fibers produced via extrusion and composed of materials such as polyamides or polyethylene terephthalate obtained via synthetic routes are characterized by internal structures that are hierarchical to a certain extent yet that are by far less complex than the ones displayed by natural fibers. The extruded fibers tend to be partially crystalline for crystallizable polymers, displaying lamellar-type crystals with a thickness in the range of a few tens of nm and a lateral extension usually in the micrometer range, as discussed above. The lamellae tend to form a regular stack composed of alternating lamellar and amorphous regions. Depending on the fiber preparation the stacks may be oriented along the fiber axis with the segments being oriented and extended in the amorphous regions, as discussed above. A further feature may be the presence of microfibrils that by themselves are composed of stacks of lamellae. These features give rise to enhanced mechanical properties along the fiber axis, that is, enhanced stiffness and strength that may match the corresponding properties of natural fibers.

Compared to natural fibers these polymer fibers are cheaper to produce, it is easier to process them, to dye them or to introduce high strength and stiffness in a controlled way. Yet, they lack, to a significant extent, quite a number of functions that are beneficial for textile applications and that are displayed by natural fibers. Carrying a shirt made purely from polyamide on a hot humid day makes the difference between textiles made, for example, from cotton and from such man-made fibers very obvious. One major reason besides a chemical composition which is different from that of the natural fibers discussed above is that their internal molecular and supermolecular structures tend to be rather simple. Solid fibers with constant composition and constant structural features along the cross section are characteristic of man-made fibers. Hollow fibers have been produced and also fibers with cross-sectional shapes that differ from the circular one, yet nevertheless such architectures are far from the complex ones displayed by nature. Furthermore, specific microfibers have been prepared in various ways to enhance among others textile properties.

In fact, the application of man-made fibers is not restricted to textiles. Fibers play a major role in the reinforcement of thermoplastic or thermoset polymer matrices not only for high-end applications. Reinforcement of high-end elements of ships, trains, airplanes are well known but fiber-reinforced materials can also be found in day-to-day appliances. The important parameters as far as fiber reinforcement is concerned is the axial ratio that should be well above 100 to 1000—thus the use of fibers—and the enhanced stiffness and strength of the fiber combined with a good mechanical coupling to the matrix. Fiber reinforcement is, in the majority of cases, not done with natural fibers—although such approaches are being considered more and more for ecological reasons—but conventionally by using very specific synthetic fibers such as carbon fibers produced among others via the precursor polymer polyacrylonitrile (PAN) fibers or Kevlar fibers, produced from lyotropic polymer solutions.

1.4

Routes to More Advanced Fibers—Mimicking Nature

So, polymer fibers obtained from synthetic polymers and produced via extrusion techniques are of great technical importance and display properties which are favorable for many types of applications. However, there is a definite need for more advanced fiber designs. Fiber reinforcement, for instance, would benefit strongly from fibers much smaller in diameter than those characteristic of extruded fibers—that is, nanofibers—even at the same magnitudes of stiffness and strength. The length could thus be reduced at constant axial ratio compared to thicker fibers, thus reducing rupture during polymer processing. In addition, fibers small in diameter compared to the wavelength of light would not cause turbidity in otherwise transparent matrices and the mechanical coupling between matrix and fibers would be enhanced, as would the ductility due to the much larger internal surface areas.

A further area for the application of fibers, again predominantly of man-made fibers, concerns filters for either gas or fluid filtrations including coalescence filters (Figure 1.8) as discussed in Chapter 8 in great detail. The chemical, thermal and mechanical stability of the fibers together with the costs to produce the fibers are important features but of particular importance is the absolute magnitude of the diameter of the fibers.

The diameter determines the size of the pores provided by such filters and thus the size of the impurities to be captured. The reduction to fiber diameters well into the nanometer range will, furthermore, affect the flow pattern around the fibers significantly. Both effects taken together should strongly enhance the filter efficiency with respect to smaller-scale impurities in the air, in gasoline, etc. The specific surface area acting as adsorption site also increases strongly as the diameter is reduced. As far as textiles are concerned a reduction in fiber diameters and thus in pore sizes will cause a strong increase of wind resistivity and thermal isolation, as discussed below in more detail in Chapter 8.

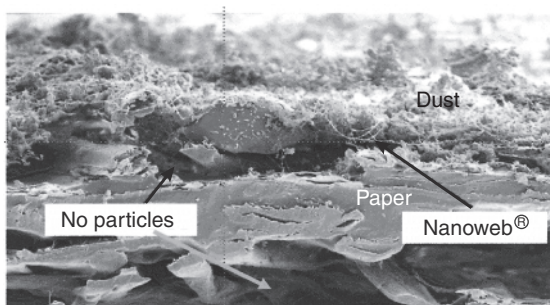


Figure 1.8 SEM image of commercial filters based on paper with nanofibers on the surface (from H.D. Hollingsworth & Vose GmbH). The nanofibers are on top of the conventional filter composed of paper inducing a surface filtration.

The discussion about fiber applications in the areas of textiles, fiber reinforcement and filters has made it apparent that these areas would definitely benefit to a great extent from a further strong reduction of the fiber diameters by several orders of magnitude well into the nanometer range. The low value of the diameter and small nonwoven pore sizes as well as the huge surface area that go along with small fiber diameters are key factors in such applications. However, it is obvious that the extremely small diameter is just one side of the coin.

Further features might be the onset of confinement effects for structural features and properties and the increasing truly 1Dimensional nature of the fibers as the diameter decreases. The potential for rapid diffusional processes into and out of the fiber characteristic of nanoscalar dimensions or the close resemblance in architecture of nanofibers and the fibrillar extracellular matrix in living systems are further specific features favorable for specific applications. It may, of course, be necessary for such fibers to carry functional units such as chromophores, catalysts, sensor molecules, quantum dots, drugs or bacteria, depending on the application in mind and they may have to be composed of organic, inorganic materials or corresponding hybrids.

It seems that in addition to trying to reduce fiber diameters down into the range of a few nm or a few tens of nm and in addition to incorporating functional compounds technical applications would benefit from fibers with highly developed hierarchical structures and consequently with higher functionalities, as often encountered in nature. Optoelectronics, sensorics, catalytics, storage are potential target areas but also drug storage and release.

Neurons may serve as a first example for highly functionalized nanoscalar fiber-type structures. Their fundamental task consists in receiving, conducting and transmitting electrochemical signals via connections with other cells called synapses. Neurons are the core components of the nervous system, which includes the brain, spinal cord, and peripheral ganglia. A number of specialized types of neurons exist: sensory neurons respond to touch, sound, light and numerous other stimuli affecting cells of the sensory organs that then send signals to the spinal

cord and brain. The central building element of the neuron is, in the majority of cases, the strongly one-dimensional that is, fiber-like axon that is surrounded in general by a plasma membrane. This kind of packaging thus providing a hierarchical architecture allows action potential to travel along the axon with enhanced speed.

The extracellular matrix already discussed above may serve as a second example for a nanoscale functional biological system. The basic building blocks of the ECM are fibers composed of collagen and other structural proteins. The collagen fibers building up the ECM have diameters ranging typically from 50 to 500 nm. ECMs characteristic of bone tissue may contain small hydroxyapatite crystals imbedded in the collagen fibers to provide an enhanced stability paired with a high elasticity. In regenerative medicine, scaffolds are used to engineer particular kinds of tissue to replace corresponding tissue destroyed partially or completely by accidents or sickness. The task of the scaffold is in this case to act as a carrier for cells, to promote their proliferation, differentiation, to guide cell growth along specific directions, to allow for the growth of blood vessels, and to deliver functional components locally such as growth factors. It has been demonstrated that scaffolds based on the architecture of the extracellular matrix are particularly effective in regenerative medicine.

Going in the direction of close to infinitely long fibers we look next at silk (Figure 1.1a). It is of importance both in nature but also for technical applications. Silk at a first glance appears to be just another fiber produced by nature. However, silk is a fiber-like material that due to its internal composition displays unusual mechanical properties but also interesting optical properties. Silk obtained from cocoons made by the larvae of the silkworm *Bombyx mori* has a shimmering appearance that originates from the triangular prism-like structure of the fibers. This allows silk cloth to refract incoming light at different angles. Silk fibers possess highly impressive mechanical properties, in particular a high ductility, related to intrinsic structural features being to a significant extent ultrafine in nature.

Cotton, wool, animal or human hairs are further examples of fiber-type structures provided by nature. These fibers are not as small in fiber diameter as those discussed above, yet they are constructed in a highly complex hierarchical way that provides them not only with unique mechanical properties but also with a set of other functions that make them of interest for various types of applications. Protection against low temperatures, rain, UV-radiation are examples of functions that are of importance both for living beings carrying such structural elements as well as for technical applications. The diameter of such natural fibers may well be in the 10–20 micrometer range and above; human hair, for example, typically has a diameter around 50 micrometer (Figure 1.9). Such fibers tend to have a hierarchical structure going down to the nm scale, as can for instance be demonstrated for wool or hairs in order to provide the functions expected from them.

The examples given above, furthermore, suggest as far as technical areas are concerned that one might try to mimic such structures to come up with novel types of technical systems for various types of advanced technologies.

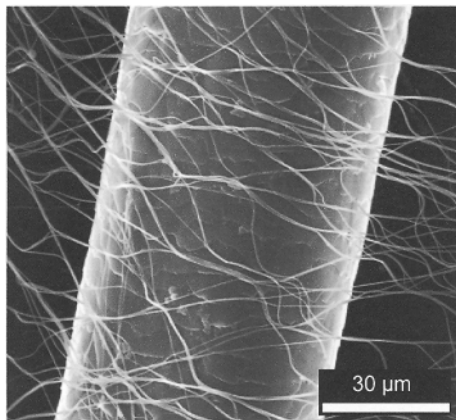


Figure 1.9 SEM images of human hair—covered by nanofibers for comparison.

To achieve this goal a very ambitious approach might be based on the mimicking not only the functional structures, building blocks suggested by nature but also the processes used by nature to construct these elements, objects. The key word is self-organization. Self-organization is a process of interplay between attractions and repulsions based among others on molecular recognition, electrostatic multipole pairing with the internal organization of a system increasing in complexity without being guided or managed by an outside source such as mechanical sources, forces as, for instance, in the case of extrusion. Phenomena that have been described as self-organizing in biology in addition to those discussed so far include the well-known spontaneous folding of proteins and other biomacromolecules or the formation of lipid bilayer membranes. In fact, strong activities exist in science on an international scale addressing shaping structures/architectures with specific functions using the self-organization approach. Among the systems constructed along this line are classical amphiphilics characterized by a polar head group and one, two or even multiple hydrophobic tails, amphiphilic rod-shaped molecules, mixtures of anionic and cationic surfactants, artificial polypeptides and, in fact, supermolecular nanofibers, nanorods have become available via self-organization in a highly controlled way displaying hierarchical structures.

These examples demonstrate that one is able to mimic nature quite successfully in various aspects. However, these examples also demonstrate that approaches based on these types of self-organization in the majority of cases have to go a long way to become of major technological impact. The self-organization process discussed above may be looked upon in terms of nanotechnological approaches as a bottom-up process: supermolecular all the way up to macroscopical structures are constructed starting on the molecular scale.

So it makes a lot of sense to look into techniques allowing preparation of fibers on a larger scale with very small diameters, complex morphology or even topology

that do not rely on mechanical means with all their restrictions in terms of fiber diameters, fiber structures, hierarchical structures. Electrospinning readily comes to ones mind in this respect. It allows for the preparation of fibers with diameters down to a few nanometers, of fibers with a high richness of fiber architectures unknown in the area of extrusion techniques and it relies to a major extent on self-organization processes, although of a different kind from those used in nature.

1.5 Electrospinning

1.5.1 A Simple Experimental Approach

Conventional processing techniques will obviously not be able to yield such extremely fine functionalized fibers, and this holds also for melt blowing and similar special techniques. The technique of choice seems to be electrospinning since it offers the unique features that fiber formation is first not based on mechanical forces but rather on electrical forces and secondly that the fiber forming takes place via a very peculiar self-organization process driven not by attractive but by repulsive electrostatic forces [4–11]. Self-assembly in electrospinning is controlled by Coulomb interactions between charged elements of the fluid body. Self-assembly follows the general Earnshaw theorem of electrostatics according to which it is impossible to prepare stable fluid structures such as, for instance, stable fluid jets in which all elements interact only by Coulomb forces. Charges located within the fluid jet, in the case considered here, move the polymer elements to which they are attached along complex pathways in such a way that the Coulomb interaction energy is minimized. The richness of fiber architectures resulting from this process and the routes along which this richness comes about will be discussed in Chapters 2 and 3 in great detail.

Prior to the year 2000 electrospinning was the domain of a few specialists; the average number of papers published per year on this topic was well below 20. This situation has changed dramatically in recent years. In 2009 significantly more than 1500 papers were published on electrospinning, it is estimated that more than 200 research groups in academia and industry work currently on this topic, the number of conferences or sessions at conferences devoted to electrospinning is continuously increasing. Electrospinning has become a widely appreciated nanostructuring technique in academia and industry and, in fact, this technique has, indeed, a lot to offer. Basically, it allows production of nanofibers with diameters down to a few nanometers from a broad range of polymers. Yet, due to the unique self-assembly processes happening in electrospinning it is a highly versatile technique in terms of the materials that can be spun to nanofibers, in terms of the control of their morphology, surface topology as well as of the properties of the fibers and nonwovens composed of them.

Electrospinning constitutes a unique technique for the production of nanofibers with diameters down to the range of a few nanometers. Electrospinning is applied predominantly to polymer-based materials including natural and synthetic polymers, but it has been extended towards the production also of metal, ceramic and glass nanofibers exploiting precursor routes. The production either of individual fibers, of random nonwovens or of orientationally highly ordered nonwovens is achieved by an appropriate selection of electrode configurations. Basic features of electrospinning—keeping in mind that the technique is a highly complex process in terms of theory and experiment—can best be introduced using a simple spinning setup and performing simple model experiments with this setup.

The setup:

To do a first electrospinning experiment it just takes

- a simple syringe with a metal tip having characteristically an inner diameter of several hundred micrometers;
- a solution of a commercially available polymer such as polyethylene oxide (PEO) in a solvent like water choosing, for instance, a concentration of 10 w% PEO in water;
- a weight that presses the shaft of the syringe down to slowly discharge the polymer solution through the syringe acting now as a die—or a container with the solution connected via flexible tubing to the syringe so that the container can be positioned well above the syringe using gravity in this case to control the discharge of the polymer solution through the die;
- an aluminum foil positioned below the tip of the syringe at a distance of a few centimeters;
- a high-voltage appliance able to deliver about 1 kV with the required current well below the microampere range;

as shown schematically in Figure 1.10a. Figure 1.10b shows an advanced laboratory setup.

The device described so far will just produce droplets falling off the tip of the syringe and impinging on the aluminum foil if no voltage is applied. However, as a sufficient voltage is applied between the tip of the syringe acting as an electrode and the aluminum foil acting as counterelectrode droplet formation is reduced and the formation of a slim fluid jet sets in that falls towards the counterelectrode. There, it is deposited as a solid fiber due to the evaporation of the solvent. Such fibers can be imaged via conventional optical microscopy if the fiber diameter achieved is well above the 1 micrometer scale. Otherwise, scanning electron microscopy has to be used. Figure 1.11 shows images of fibers produced from solutions of poly(ethylene oxide) in water as an example.

The fibers may not be uniform in diameter along the fiber length, they may contain so-called beads to start with. Yet, by modifying the polymer concentration, the applied voltage and the feeding rate one should be able to also produce fibers

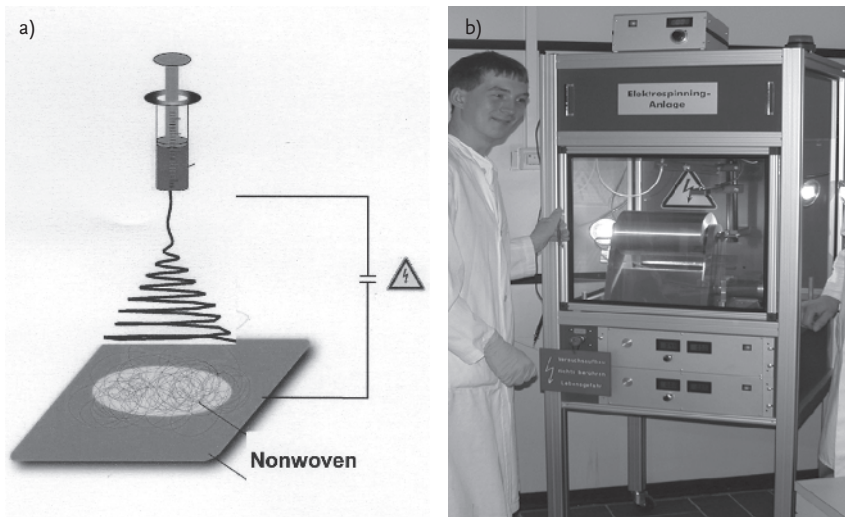


Figure 1.10 Very basic setup of an electrospinning unit allowing to perform some preliminary electrospinning experiments (a) schematic diagram, (b) experimental setup (from R. Dersch, PhD Thesis, Department of Chemistry, Philipps-Universität Marburg, Germany, 2006).

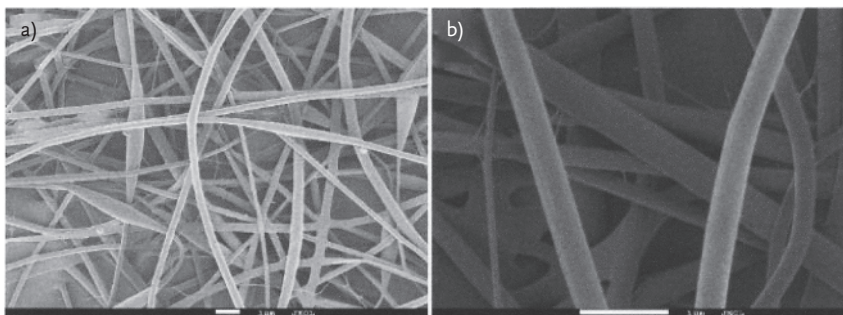


Figure 1.11 Microscopical images of fibers prepared from PEO/water solutions using the experimental setup sketched in Figure 1.10b, the displayed bars correspond to a length of 1 micrometer (from M. Rudisile, PhD Thesis, Department of Chemistry, Philipps-Universität Marburg, Germany, 2008).

with rather homogeneous diameters and one should also be able to accomplish fibers with diameters below 1 micrometer, so that the resolution of the optical microscope is no longer sufficient to give good images. In fact, one might achieve fiber diameters down to a few nanometers with enhanced electrospinning setups that have been describe as Gossamer veil invisible to the eye and optical microscopes.

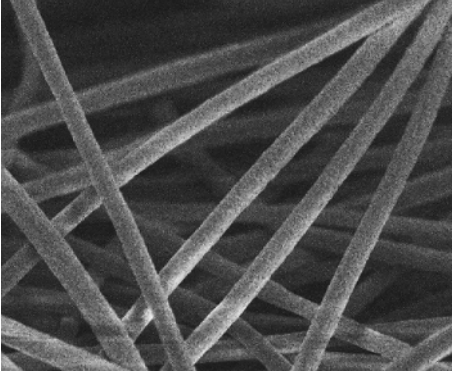


Figure 1.12 Odd-shaped pores in nonwovens as controlled by polyamide fibers crossing each other.

The fibers deposited by electrospinning, and shown in Figure 1.11, are not straight all along their length but subjected to certain curvatures, the fiber diameters are not uniform as different fibers are inspected and the fibers are more or less randomly oriented within the plane of deposition. These features are observed consistently also if advanced spinning setups are used for electrospinning.

Fibers are deposited upon the substrate/counterelectrode one on top of the other, layer by layer, as is also obvious from Figure 1.11 but shown in more detail in Figure 1.12, yielding obviously a rather porous membrane. Such an arrangement of fibers without entanglements, knots, etc., is called a nonwoven, so that electrospinning can be used to prepare nonwovens composed of fibers with diameters in the nanometer/micrometer range. The architecture of such nonwovens, that is, the orientational distribution of the fibers, can be rather easily varied. Replacing, for instance, the planar aluminum foil with two strips of aluminum arranged parallel to each other at a distance of 1–2 cm on a non-conducting substrate such as glass gives rise to the deposition of parallel fibers bridging the gap between the two electrodes. More complex electrode configurations have been proposed in the literature, these will be introduced later in some detail.

Figure 1.12 reveals, as already indicated above, that the electrospun nonwovens is characterized by the presence of odd-shaped pores as defined by the fibers crossing each other within the deposition planes and as one goes from one deposition plane to the next one.

A rough estimation based on the visual inspection of the optical images of the nonwovens leads to the conclusion that the average pore size should be about one order of magnitude larger than the fiber diameters and that the total porosity of such nonwovens that is, the volume taken by pores relative to the total volume of the nonwoven is of the order of 0.9 that is, 90% of the volume of the nonwoven

membrane consists of empty space. This yields a density of a nonwoven membrane of approximately 0.1 g/cm^3 . Further values characteristic of the nonwovens can also be estimated on this rather crude level, details will be discussed later in Chapter 4.

So the specific surface, that is surface per unit mass, can be estimated based on the fiber geometry—the specific surface scaling with the inverse of the fiber radius in this case—and the total mass of fibers present in the nonwoven. Assuming fibers with diameters in the interval from 1 micrometer down to 100 nm the specific surfaces accessible in such nonwovens cover the range from $S = 2\text{--}37 \text{ m}^2/\text{g}$. Finally, looking at the characteristic pore sizes and the total porosity the flow of gases and fluids through such nonwovens can be estimated and thus the magnitude of the permeation coefficient k as defined by Darcy's law with flux of material $u_c(x)$, permeability coefficient k , viscosity μ and pressure gradient $\nabla p(x)$

$$u_c(x) = -(k/\mu)\nabla p(x)$$

Rough estimates yield values of the order of $k = 10^{-14}\text{--}10^{-13} \text{ m}^2$ for the fiber diameters considered here, with details to be discussed later.

Looking at the structural properties discussed so far including porosity, pore sizes, internal surfaces, it becomes apparent that such nonwovens might be used as filters for fluids, gases, aerosols, yet the highly porous structure also suggests textile applications and additional advanced applications in technical and life science areas to be discussed later.

1.5.2

The Hidden Physical Complexity

So, electrospinning is a unique technique allowing production of tiny nanofibers with complex shapes, functions, topologies and corresponding nonwoven systems. The simple experimental setup introduced above that allows preliminary spinning experiments to be performed and production of fibers and nonwovens composed of them tends to mask the inherent complexity that is characteristic of the electrospinning process involving various types of physical instabilities. Figure 1.13 shows the complex hierarchical trajectory to which a fluid jet is subjected after emerging from the die/droplet as the bending instability takes over.

It is the presence of these instabilities and their superpositions that is the origin of the extreme richness of fiber-based functional structures as well as of the richness of nonwoven architectures accessible by electrospinning. Examples are given in Figure 1.14. This illustrates the broad range of fiber architectures available from electrospinning including thin smooth fibers, porous fibers and fibers with fractal surface structures, with spindle-type disturbances, bandlike fibers or odd-shaped fibers such as 'barbed' nanowires.

It is for these reasons that electrospinning has moved more and more into the focus on an international scale, particularly in the last decade both as far as basic research as well as technical oriented development activities are concerned. The

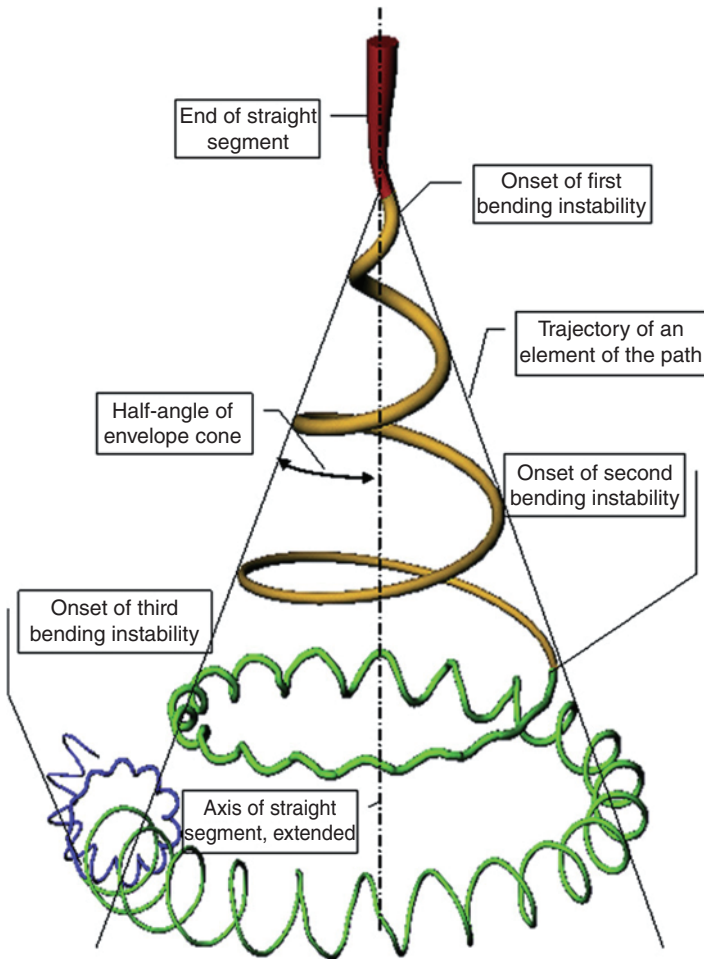


Figure 1.13 Trajectory of a fluid jet as controlled by the presence of bending instabilities (from D.H. Reneker, A.L. Yarin, *Polymer* 2008, 49, 2387). Details of the jet path are discussed in Chapter 2.

basic structural unit that is produced via electrospinning is the fiber and, in fact, fibers play a major role in functional systems both in biology and in technical areas, as will be discussed in the following chapters in great detail. A multitude of functions can be incorporated into these fibers and an extremely broad range of potential applications exists in which electrospun fibers can make major contributions.

These include obviously not only textile, filter and mechanical reinforcement applications but extend to tissue engineering, drug delivery, wound healing, sensorics, optoelectronics, catalysis and many more. The progress achieved in

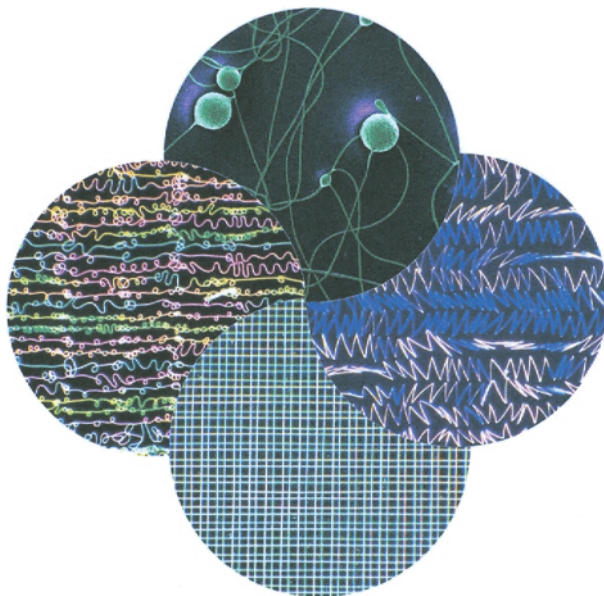


Figure 1.14 Broad range of fiber architectures available from electrospinning including buckled fibers, fibers in crossgrating arrangement and fibers with spherical beads (from A. Holzmeister, PhD Thesis, Philipps-Universität Marburg, 2009).

electrospinning in a time span covering less than one decade, the strong impact it has already made on material and life science and is continuing to do so are unique features. A set of review articles have been published recently that provide an insight into the vast opportunities offered by electrospinning.

1.5.3

Short History of Electrospinning—The Routes Go Back More Than Two Centuries

The first known experiments on electrospinning are based on previous experiments with liquids in electrical fields. In 1745 Bose described the formation of aerosols formed by electrical potentials on the surfaces of droplets [12]. The amount of charge required for the deformation of droplets was described by Lord Raleigh in 1885 [13]. In 1902 and 1903 Cooley and Moore described in patents apparatus for spraying of liquids by use of electrical charges [14–16]. The preparation of artificial silk by electrical charges was described by Hagiwaba 1929 [17] and in 1934 Formhals filed the first patent on electrospinning of plastics together with setups for electrospinning (Figure 1.15) [18].

It took a long time until others picked up on these early reports. In 1971 Baumgarten reported on electrospinning of acrylic microfibers [19] and Larrondo and

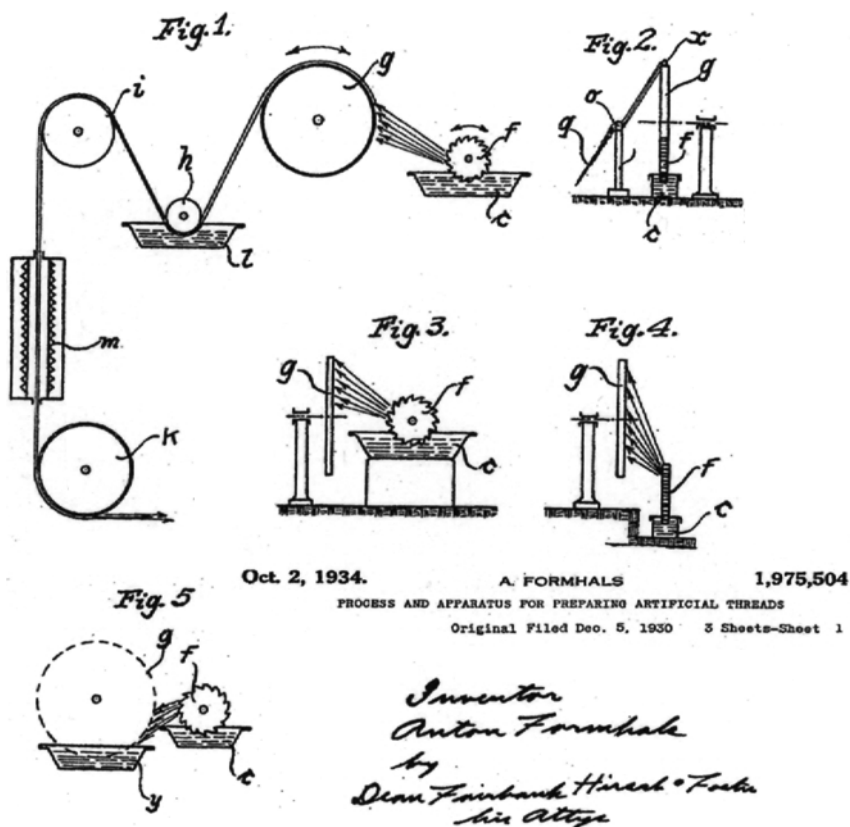


Figure 1.15 Electrospinning setups described in the patent of Formhals [18].

Manley reported in a series of papers on electrospinning of polymer melts [20–22]. In the 1970s also some attempts at commercialization were undertaken. For example Simm, from the Bayer company, submitted a series of patents on electrospinning of plastics [23]. A variety of electrospinning setups were suggested in early electrospinning setups that have some similarities to recent efforts (Figure 1.16).

The first technical application for electrospinning was suggested for the nonwoven industry. Academia picked-up electrospinning slowly in the 1990s due to the early work of Doshi *et al.* [24]. Most likely driven by the growing interest in nanomaterials more and more groups started to enter the field of electrospinning, which resulted in a dramatic increase of publications from a very few per year close to 2000 publications in 2010 (Figure 1.17). With such a huge impact electrospinning is certainly among the very hot topics in materials science.

1.6

Electrospinning – Important Facts to Remember

Fibers are key elements both in nature and for a broad range of technical applications. The transition from macroscopic fibers to fibers with diameters in the nanometer range gives rise to novel functions and applications. Such nanofibers can be produced via electrospinning.

Fiber-formation processes in electrospinning differ fundamentally from those in conventional technical approaches such as, for instance, extrusion and subsequent elongation, melt blowing or even techniques exploiting converging flow. All these involve mechanical forces and geometric boundary conditions. Fiber formation in electrospinning is dominated by self-assembly processes. The evolution of the final diameter of the nanofibers resulting from electrospinning, the intrinsic orientational order, the morphology, the cross-sectional shape, gradients along the cross section, specific phase morphologies but also the distribution of solid particles dispersed within the fiber, undulations of the fiber diameter, droplets arranged along the fibers in a regular fashion: all these features are basically governed by self-assembly processes induced by specific electrostatic interactions of elements of the original source droplet or similar geometries from which fiber formation starts.

In the case of supramolecular structure formation self-assembly is known to be controlled by specific, in general, attractive forces such as hydrogen bonding, charge-transfer interactions, etc. Self-assembly in electrospinning, on the other hand, is controlled by Coulomb interactions between charged elements of the fluid body. Self-assembly follows the general Earnshaw theorem of electrostatics, according to which it is impossible to prepare stable fluid structures such as, for instance, stable fluid jets in which all elements interact only by Coulomb forces. Charges located within the fluid jet, in the case considered here, move the polymer elements to which they are attached along complex pathways in such a way that the Coulomb interaction energy is minimized.

Droplet deformation, jet initiation and in particular the bending instabilities that determine to a major extent fiber properties as discussed in the following chapters are controlled apparently predominantly by this kind of self-assembly principle. Simple but also highly complex fiber architectures, the deposition of flat fibers, of fibers with vertical protrusions, splayed fibers to be discussed below can be considered as manifestations of the variety of self-assembly processes happening in electrospinning. Keeping this general theorem in mind it is not surprising that completely novel fiber architectures and thus novel functions become accessible.

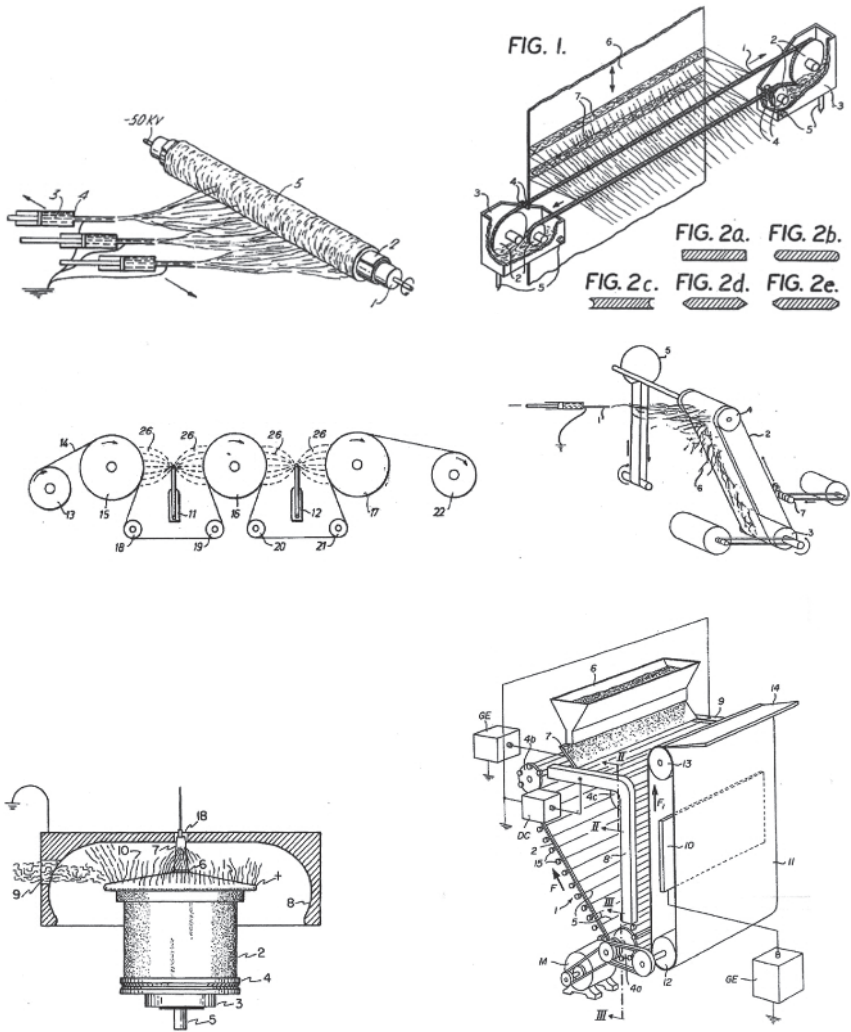


Figure 1.16 Examples of electrospinning setups in early electrospinning patents (from K. Schmidt, A. Graber, H.U. Helbeck, US patent 4 144 553).

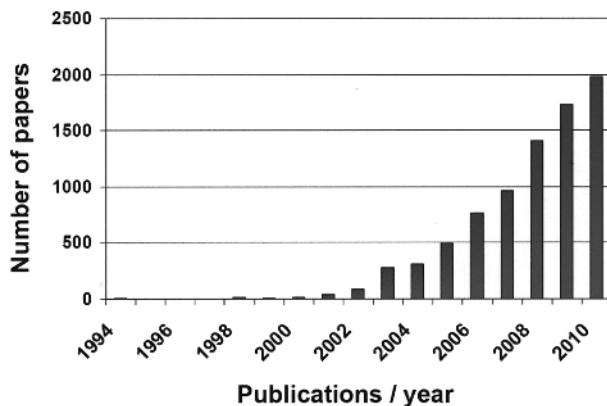


Figure 1.17 Publication containing the word 'electrospinning' (Science Finder 2011).

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