Electrospun composite nanofibers and polymer composites

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Nanofibers  
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14.1 Introduction

Nowadays the field of synthetic polymer-polymer composites (PPCs) is characterized by very rapid progress. It is because new ideas forming the basis of new technologies often require new materials to be developed. Thus new materials such as nanofibers and nanofiber reinforced composites can lead to newer ideas and further applications and these further applications in turn can lead to the development of more specialized materials. PPC industry requires advanced matrices, advanced reinforcements, advanced additives and advanced technologies and also the application fields are still widening.

This chapter tries to interpret electrospun materials and their applications from the materials aspect although we try to reflect on future applications as well as on the need for functionalized materials which led to the development of the existing ones.

The demand for special synthetic fibers for the composites industry has been continuously growing. In this context special means that these fibers have some unique properties making them applicable to build high strength, highly functional or smart materials and composites or they can modify the mechanical properties of composites even by applying only a small amount of them. In the last two decades the research on fibers basically branched into three different sub-directions.

The first one is microfibers with unique mechanical properties [1]. It has always been a challenge for scientists and for companies to develop stronger fibers, new fibers with higher modulus or even to advance their former products in order to increase strength. If we have a look at this from the application side, for example in case of automotive and aeronautical applications fuel can be saved by decreasing weight. It can be made by exchanging existing composite parts in the design construction for advanced composites which have more efficient reinforcement.

The second way is to create specially functionalized fibers [3]. There may be different reasons for doing this such as better adhesion between fiber and matrix, conductive fibers against lightning strikes or for microelectronics, self-healing composites, quality insurance, damage analysis, sensing, etc. This field is quite interdisciplinary, because these innovations are advantageous not only for the composite industry but also for many others. Just to mention a few: textile industry and clothing (e.g. photo luminescent fibers), biomedical applications (e.g. drug delivery),
filtration (e.g. functionalized filters to remove toxic or hazardous materials from water), sensors (e.g. more efficient and sensitive ones), etc.

The third direction which was the concept of diameter reduction has led to the group of ‘nano’fibers, although such fibers can also be built up in a bottom-up way [1]. This group is somehow the combination of the two former groups because the aim in this case is both increased strength and functionalization. The decrease of the fiber diameter generally leads to an increased strength because of the so-called size-effect [2]. This phenomenon revived the development of nanocomposites and nano-reinforcements where the typical size of reinforcement is in the nanometer or submicron scale.

Nano-additives are able to further functionalize the materials or can even be used to produce hybrid composites [5-6]. Even the fibers can be composites themselves where for example microfibers or even nanofibers are reinforced with carbon nanotubes (CNTs) [7-8] or with nanoclay [9-10], etc. In these cases nano-reinforcement is typically embedded into a fiber which becomes a kind of matrix itself. These composite fibers can have excellent tensile properties [7] or can be used for detecting damage in composite structures [11] or can be precursors of carbon fibers [12].

Fiber diameters can be decreased to the submicron-scale in several ways in order to get nano-reinforcement. Nanofibers can have unique properties which primarily originate from their small diameter. They are very flexible and have a very high surface to mass ratio. Self-crystalline polymer nanofibers can have different crystallinity compared with microfibers [13-14]. They can have very high aspect ratios which is preferable to establish a good adhesion with the matrix. These continuous fibers can mostly be used in hybrid composites in combination with microfibers. In principle it is possible to reinforce composites with nanofibers alone but nowadays our knowledge is very limited in this field.

Nanofibers include many types depending on their material and manufacturing processes, for example: electrospun nanofibers, various titania (TiO₂) nanofibers [15], special ceramic-based nanofibers [16], supersonic laser drawn nanofibers [17-18], sea-island-type conjugated melt spun nanofibers [19], technologies include formation of nanofibrils from polymer blends [20], jet blowing [21] and there are CNTs [22] and other special forms of carbon nanofibers [23].

As one can see, there are several types of nanofiber preparation, but for now it seems that electrospinning is the most popular and emerging technique in case of continuous nanofiber
production [24]. There are many reasons for this, such as easy processability of a wide variety of polymers [25] and ceramics [26], feasibility [27], etc. Unlike many nano-structures which are produced in a bottom-up way, electrospinning offers a top-down process resulting in cost-effectiveness and easy processing. Scanning electron micrograph of a typical electrospun material can be seen in Figure 1.

![Scanning electron micrograph (SEM) of electrospun poly(vinyl alcohol) (PVA) nanofibrous mat](image)

Figure 1 Scanning electron micrograph (SEM) of electrospun poly(vinyl alcohol) (PVA) nanofibrous mat

This subsection introduces electrospun nanofibers and their typical behavior and moreover it tries to give a short introduction why and how it can be a feasible way to reinforce or even toughen PPCs with nanofibers. The general benefits of nanofibers can also be emphasized. Nanofibers are usually form a cross-linked fiber net, which is not harmful to human and animal health, in the sense that it does not cause silicosis nor is carcinogenic, etc. as other nanomaterials [28]. On the other hand there are several feasible and cost-effective and simple ways to produce these nanofibrous materials. These can have different formats, such as yarns [29-32], nonwovens, mats with oriented structure [33], unidirectional fabrics [34], and 3D structures as well [35]. These different formats can lead to different application fields or stated otherwise for a wide spectrum of applications the appropriate format of these nanomaterials can be produced. These nanomaterials have very high surface to weight ratio which is their main advantage for example
in drug delivery, filtration or in case of PPCs a better adhesion of fibers with the matrix material can be achieved by simply increasing the contact surface [35-37].

This chapter deals with nanofibers processed by electrospinning method, their applications in the composites industry, academic researches and with further developments in detail.

14.2 Electrospinning of nanofibers

Nanotechnology literally means any technology performed on a nanoscale that has applications in the real world [1] Electrospinning (*electrostatic spinning*) method and its products are principally related to nanotechnology. The electrospun fiber’s diameters are usually from several nanometers up to a few microns but they are typically in the submicron range. These fibers are called nanofibers in the literature [38], because they have unique properties compared to microfibers.

Electrospinning was developed from the elecrospraying method which was first patented in 1902 by Morton [39] and Cooley [40] who both invented methods which were able to disperse fluids by using electrostatic forces. The other important step which led to the electrospinning technique as known today was the workmanship of Zeleny [41]. In 1934, Formhals developed a feasible method [42] to obtain yarns via electrospinning. Somehow the technology was less appreciated and did not have either scientific or industrial importance. As nanotechnology became a well-researched field, many scientists began to focus on electrospinning in the 1990’s.

The potential applications of electrospun nanofibers, which still a steadfastly extending field are summarized in Figure 2 by Huang et al. [43].

Inasmuch as we focus on the composite applications of nanofibers only the most important fields are introduced here and even these only briefly. The first one is filtration, which is nowadays the primary utilization of electrospun nanofibers. Nanofibrous mats can be bought in the market and can be applied in industrial filters, air and water cleaning systems. It is also an example for functionalized nanofibers because these nanomaterials contain activated carbon particles and therefore can filter out different chemicals in addition to submicron particles [44].
Nanofibrous mats can also act as ion exchangers [45-46] which have faster kinetics compared to the classical, granular systems. SEM image of pollens of *Aesculus hippocastanum* filtered by electrospun media can be seen in Figure 3. It is worth mentioning that nanofibers have approximately two orders of magnitude lower pore size than the size of the pollens, therefore even smaller things can be filtered such as bacteria, etc. which points to the biomedical applications of electrospun nanofibers.

The biomedical field is very wide but can principally be divided into three different groups:

1. Wound and burn healing [47, 48].
2. Synthetic prosthesis, transplant surgery, and dental applications [49-54].
3. Drug, vitamin, other organic materials delivery [55, 56].

There are many good reviews on this topic [52, 57, 58] which are suggested to be read for further details.
The application field of nanofibers is still growing and there are researches on functionalized nanofibrous materials, energy-related applications, such as fuel cells, dye-sensitized solar cells, Li-ion batteries, supercapacitors, catalyst support for rechargeable batteries [59], sensors and optoelectronics [3-60], building and aeronautical acoustics [61] and composites industry [43].

**14.2.1 The principles of electrospinning**

Electrospinning is a method which gives the opportunity to produce nanofibers in a quite simple and cost-effective way. It has many advantages, and some disadvantages as well. The base material is a polymer solution or a melt, which may contain various admixed additives or particles. Generally electrospinning operates with solutions, if the material is melt it is emphasized and called melt-electrospinning [62-63]. The fibers are usually round-shaped and their diameter can be set easily by adjusting the process parameters [25]. It is a single-step technology which means that fiber formation, drawing and the deposition of fibers (formation of the textile structure) occur simultaneously and almost in the
same place. Fibers are deposited randomly because of the stochastic nature of the fiber formation. If the aim is to produce nanofibrous nonwoven mats the method has a benefit of saving cost and time and requires only a simple apparatus. The resulting nanofibers have some kind of mechanical connections and interactions between themselves as they traverse or overlap each other. The fiber length is potentially infinite because no fiber endings can be seen in scanning electron micrographs (SEM), for instance in Figure 1. The material destined for electrospinning is preferably a polymer solution which has an adequate conductivity, although polymer melts can also be used [63]. In the basic electrospinning setup (Figure 4) the material is located on a tip of a capillary spinneret which is exposed to high voltage [64]. The high voltage is generated by a power supply. Commonly direct current output is used but there is an opportunity to use alternating current too [65]. A collector electrode which is usually grounded collects nanofibers after the spinning process.

![Diagram of basic electrostatic spinning apparatus](image)

Figure 4 Scheme of basic electrostatic spinning apparatus [64]

The electrostatic forces generated by the high electrostatic field can easily interact with electrically conductive liquids. In case of classical electrospinning a droplet of solution is applied. If the interaction is adequate than the droplet forms a conical shape. This shape is called Taylor-cone in honour of Taylor [59] who gained significant results in the mathematical description of the forming liquid surface.
This deformation is caused by volumetric forces such as gravitational force and Stokes-friction, and surface tensions (normal and tangential ones). The equilibrium of forces and surface tensions can be calculated although there is no generic analytical method solving these equations [60].

If the electrostatic field exceeds a critical limit one or more thin solution jets emerge from the tip of the Taylor-cone depending on the solution parameters and on the charge density within the droplet. The jet has a diameter of less than say 100 µm, so it is not yet in the nano-range. The electric charges are carried along with the conductive jet and due to the Coulomb-repulsion they are moving to the surface because the electrostatic field tends to be zero within the liquid. The time required for this charge-arrangement depends on the conductivity and dielectric properties of the solution. The jet begins to elongate as it travels to the collector due to the repulsive forces induced by electric surface-charges. It must be noted that here the surface tension, viscosity and interacting electrostatic forces of the liquid play a very important role. The destiny of the charged jet is mainly determined by the dominating factor [68-69]. This phenomenon was even known before the invention of electrospinning, because Rayleigh had unfolded this problem back in 1882 [70], through fluids placed in electrostatic and magnetic fields. He experienced that the liquid droplets can break into smaller ones if the interaction forces (electrostatic or magnetic ones) dominate over surface tension of the liquid and suggested to use fissility index which is some kind of a ratio of them. On the other hand if the surface tension is high, higher forces are required to break the droplet into smaller ones.

In our case if the liquid jet breaks up and small droplets are formed we can talk about electrospraying which is a generally used spraying method in for instance the ink industry. If the jet can elongate without defections it is definitely electrospinning.

According to this, two different modes can be distinguished when talking about polymer solutions or melts in electrostatic fields, which are: spraying and spinning jet [68]. Cloupeau and Prunet-Foch [71-72] were dealing with these modes in detail and distinguished 2 times 4 sub-modes which can be seen in Figure 5 and where a-d refer to spraying and the latter ones for spinning fibers [67].
A typical multi-jet mode spinning with forming Taylor-cones can be seen in Figure 6. It can be seen that jets are straight until a specific distance.

During drawing and traveling to the collector screen the solvent evaporates [73]. In higher output devices the harmful solvents should be properly managed in order to avoid health risks. There can be residual solvent in the fibrous product after electrospinning process which can be eliminated by for instance washing then vacuum drying the fibers at high temperatures (50-90°C) for several hours [74].
The liquid can exhibit different instabilities the most frequent one being bending. Firstly some small buckling happens due to the stochastic nature of electrospinning, atmospheric disorder, or other noises of the system. This small buckling begins to grow because of the repulsive forces induced by charge. Finally the whole jet coils up to a spiral which has a continuously growing size. This is called first-order or whipping [69] instability. A spiral is formed because it requires less kinetic energy to hold the head of the jet before the following parts [75]. Electric energy is mostly expended to stretch the thinning jet. As it becomes even thinner the inertia of the jet reduces dramatically which leads to other instabilities superimposed on the former ones. The forming structure is a bit fractal-like because the first-order instability is akin to second-order, the second-order is akin to third-order instability and so on. All instabilities are escalated in a monotonous way. The scheme of the instability region can be seen in Figure 7 as drawn by Reneker and Yarin [75, 76]. Figure 8 shows the first and multiple order instabilities through a real example. The picture was taken with stroboscopic method [77].

![Figure 7 Instabilities of the electrospinning jet [76]](image-url)
After the linear section, in the instability region the radial increment of the moving path of the jet is constant, thus the fiber formation space is conical. The vertical speed of the emerging jet was estimated to be approximately 3 m/s [77] and the rotation direction of the jet can even be both clockwise and counterclockwise depending on the first-order instability formation. Deitzel et al. [78] placed electrically charged rings in front of the spinneret electrode which could reduce the space of fiber formation and could focus the jet.

Depending on material and process parameters there can be other types of instabilities, although with lower probability. These instabilities can be: bead formation on fibers (instability parallel with the axis of the jet), branching of the jet (in case of high charge densities), or buckling of the jet which occurs when the jet hits the collector screen. In this latter case conical or zigzag fibers are formed.

A special case is when the viscosity is low for homogeneous fiber spinning but higher than required for jet breakup. In this case beads are formed on fibers as droplets as at some places the liquid jet springs back and becomes twitched in specific locations because of the viscoelastic-behavior of the solution. An SEM micrograph of typical beaded fibers can be seen in Figure 9 [79]. Usually in this case the charge density is relatively low.
Figure 9 SEM images of beaded polystyrene (PS) fibers obtained from 10 wt% DMF solution [79]

On the other hand, when charge density on the jet surface is high branching of the polymer jet can occur. Bead formation and branching generally does not occur simultaneously [75]. Stroboscopic picture of a branching jet can be seen in Figure 10 [80].

Figure 10 Stroboscopic image of branching electrospinning jet [80]

Buckling instability occurs when the jet dynamically impacts the collector’s surface. Therefore this instability is independent of other ones and can happen even in the straight zone of the jet or in the bending instability region depending on the position of the collector [77]. Due to the sudden impact of the jet a wide variety of fiber shapes also known as patterns can be obtained.
Fibers can gain sinusoidal, zigzag, eights, spiral and other periodic shapes [77]. The bending and buckling instabilities have different frequencies therefore they can be differentiated easily. The most important parameters which play important roles in this instability are speed of the jet, fiber diameter, viscosity and density [77].

**14.2.2 Process optimization for gaining ultrafine nanofibers**

The aim is generally to produce fibers with well-determined fiber diameter which has a small standard deviation and fibers should be without defects [43]. These can be obtained by adjusting solution, process and environmental parameters which affect electrospinning. Solution parameters are: solvent, conductivity, concentration, viscosity, molecular weight, temperature of the solution, etc. Electrospinning set-up parameters which affect electrospinning are: voltage, electric field strength and shape, polarity, capillary geometry, the arrangement of the device (vertical, horizontal, etc.), application of special spinnerets and collectors. Ambient conditions such as relative humidity, temperature, pressure can play also an important role as they modify the evaporation of the solvents, or the maximum field strength without electric breakdown, for instance. Although there are no specific rules or comprehensive predictive models [25] for creating homogeneous electrospun structures, some simple amendments can be given.

In overall it can be said that there are things that make the jet fragmented and there are parameters which increase its stability. Surface tension has a stabilizing effect, but it can sometimes clog the jet formation. The effect of surface tension on fiber diameters can be seen in Figure 11 [81]. Surfactants, such as glycerine can be used in these cases. Viscosity has jet-stabilizing effect, but on the other hand higher repulsion forces are required to stretch a more viscous liquid. Below the proposed viscosity, bead formation on fibers can be seen, and further decrease of the viscosity leads to electrospraying. To avoid bead-forming instability the viscosity and surface tension should be increased [25]. Even increasing conductivity can help [82].
Figure 11 Effect of the surface tension on the diameter of the electrospun nanofibers [81]

Molecular weight is also an important factor. The linear molecules which orient along the spinning direction are continuously overlapping with one another which can clog the breakup of the jet [83]. Therefore the higher the molecular weight the better the stability. In most cases electrospinning usually works above a molecular weight of approximately 30 kDa. Other parameters are not detailed here, but there are several books and reviews which deal with this topic [25,84].

14.3 Industrialization attempts for producing electrospun materials in a high volume

Although electrospinning is a very simple, single-step and cost-effective process, it is important to emphasize that the low productivity is the key problem or disadvantage of the method. It is also important to consider that nanofibers usually make less than 1 percent by the weight of hybrid PPCs, so it is still important to implement more efficient production technologies. Nanofibrous materials can be produced in industrial scales [85] and there are companies which produce nanofibers for over 40 years [86].
There are several patents and methods describing modified electrospinning setups that make possible to electrospin other materials or other formats for specific applications or in order to gain better productivity. Some kind of rule of thumb is that modified spinneret electrodes should be used for higher output and modified collector systems are developed to change the shape of the output material. A few of these inventions have begun to work in industrial scale.

14.3.1 Modified spinnerets for higher outputs

Spinnerets are modified to get higher output, but the final product remains a fiber mat. In the electrospinning literature capillaries made of metal or even glass are commonly used. One capillary can produce 0.01 to 2 grams of nanofibers per hour, which is not an industrial scale. Arranging capillaries in rows and/or columns multiplies the output volume. This increase of the number of capillaries also results in higher voltage and current during the process. Varabhas et al. [87] used a piece of poly-tetra-fluoroethylene (PTFE) tube and drilled capillary holes axially in one line at every 10 mm and placed a customized grid-like metal electrode inside. The collector was a moving belt therefore nanofibers could be continuously collected on a substrate material. The solution flow rate can be easily adjusted by increasing the pressure within the tube electrode and the spinneret can be cleaned or exchanged easily therefore the maintenance seems to be easy. Tubular spinneret was also applied by Heikkila and Harlin [88] who simply placed a linear wire electrode along the tube. Andrady et al. [89] patented a spinneret configuration which also operates with a plenty of capillary holes. The scheme can be seen in Figure 12. Holes are located on a superficies of a cylinder and the collector is also cylindrical and concentric with the spinneret. The solution can be fed into the spinneret through a conduit or even manually. The flow rate can be regulated by adjusting the rotation speed and/or the pressure within the spinneret tube. High output rates can be achieved, but the collector’s surface is limited or can be extended only in a complicated way.
Another group of modified electrospinning spinnerets operates with open liquid surface. The first one was reported by Yarin and Zussman [90]. In their experiments a magnetic fluid composed of magnetite powder and silicone oil was poured in a plate vessel. A thin polymer film of polyethylene-oxide (PEO) was carefully set on the top of it. The magnetic fluid was placed under magnetic field which can be induced by permanent magnet or coil which could interact with the fluid. Vertical toes are formed due to the magnetic field and the magnetic fluid actuated the polymer film as well, as if it would be a ship on rippling water. When applying an additional electrostatic field Taylor cones are formed from the PEO solution at the tips of the ripples. In this case electrospinning occurred from the open liquid surface thus the authors called their method needleless electrospinning. The productivity is quite high it was estimated that approximately 26 Taylor cones are formed on every cm$^2$ of the surface. On the other hand the process seems to be a bit complicated, because the magnetic fluid and the polymer solution must not be mixed during the production and additional magnetic field is needed. The large open surface leads to the evaporation of the solvent and therefore the concentration of the solution is changing continuously which can modify the properties of the nanofibers, such as diameter distribution, bead-forming, etc.
NanoSpider® [85] (Figure 13) is a modified needle-free and free liquid surface process where the role of the solution droplet which is formed at the tip of a capillary is replaced by a thin liquid surface of the solution destined for electrospinning. This thin layer is formed on the surface of a rotating spinneret. This rotating part is dipped to a reservoir filled with solution therefore the spinneret wets its own surface with the electrospinning polymer solution. The rotating spinneret can be smooth or rugged cylindrical or spiny for instance but it highly affects the quality of spinning. Collection of fibers happens on a moving substrate material which is usually a nonwoven textile. The substrate is reeled from one drum to another and electrospinning is performed between them.

The spinneret can be easily changed. By placing more spinnerets mixed-fiber mats can be produced. The whole production line can be scaled by applying shorter or longer electrodes and the width of the substrate material can be changed to fit the spinneret. The thickness of the product can be varied by changing the speed of the substrate material.

Chang and Lee [91] patented an electrospinning apparatus (Figure 14) which also operates with open liquid surface, but in their setup the rotating drum takes up the solution onto a wire electrode.
Figure 14 Electrospinning apparatus which operates with wire electrode [91], 1: Electrospinning solution, 2: take-up drum, 3: wire electrode, 4: electrospinning space, 5: collector, 6: rotating mandrel.

Bubble electrospinning is also an interesting method. It was invented and reported by Liu and He [92-94] in China, Smit and Sanderson in South Africa [95] and in USA by Reneker et al. [96] at almost the same time in 2008. There are only few differences in the PCT submission dates. The invention scheme drawn by Reneker can be seen in Figure 15 and Figure 16. Bubble electrospinning can operate with even a static reservoir or with a rotating spinneret and moreover the gas inlet can be diverse.
Figure 15 Bubble electrospinning setup with multiple gas inlets for mass production of nanofibers [96]

Figure 16 Bubble electrospinning apparatus with a rotating spinneret [96]

Bubbles are produced on the surface of the spinning solution with the aid of air/nitrogen gas. These bubbles are able to play the role of Taylor-cones. The fiber formation can principally be affected by the size of bubbles, thus even 50 nm diameter fibers can be obtained. When the bubbles crack it would not splash on the collector screen, but the altering surface during bubble pop is also eligible for spinning fibers.

The charge injection method which was originally developed for electrospraying but it can also be applied for electrospinning as patented by Kelly [97] and can be seen in Figure 17. It can be applied for materials with poor conductivity, for example polymer melts. The liquid destined for spinning is touched by two electrodes: a blunt one from outside and a tapered one which is dipping in. The high voltage is connected with one of the electrodes while the other one is grounded. Spinning is carried out with the aid of high pressure, for instance air flow, which forces out the polymer material through the spinneret hole. No Taylor cone comes into existence, but as the liquid is charged electrically, therefore the jet undergoes the same instabilities as in case of the capillary electrospinning. The productivity of this spinning technique is 2 or 3 orders
of magnitude higher than that of the classical capillary electrospinning. The method is a kind of hybrid of electrospinning and melt spinning techniques.

![Diagram](image)

Figure 17 Scheme of charge injection electrospinning [97]

### 14.3.2 Modified collector systems for producing special electrospun structures

Composite materials have the advantage that the layup and fiber orientations can be well-designed according to the appropriate loads.

In case of electrospinning the product is a fiber mat without any specific fiber orientation. It is quite similar to microfibrous mats, but there are strong cross-linking points between fibers. It also means that this material is quasi-isotropic. It also means that one of the main advantages of composites is lost because the material can not be designed to fit the loads. There are several methods which allow preparing uniform fiber structures contrary to quasi-isotropic mat structure via electrospinning.

One dimensional electrospun structures can be created by stretching the nanofibrous fibers during their generation. By stretching technique the diameter of the nanofibers can be reduced and excellent orientation can be obtained [98]. A rotating disk or drum [99] (Figure 18) can be applied as collector where fibers are deposited on the superfcies. Although this technique is simple it is very limited because yarns can be created only with a finite length. The most important factors which affect fiber orientation are the circumferential rotational speed and the width of the disk and the geometry of the edges are also important due to the coronal discharge
phenomenon or Franklin’s lightning rod principle. It is necessary to avoid intense ventilation of the disk, because nanofibers can be blown away instead of sticking to the small collector surface.

![Schematic representation of electrospinning setup equipped with a rotating drum collector](image)

Figure 18 Schematic representation of electrospinning setup equipped with a rotating drum collector [99].

Another good laboratory solution for producing parallel fibers is placing two grounded metal rods, plates or even wires [100-101] parallel with each other as collectors (Figure 19) [102]. The spinneret is placed equidistantly between them. With this method parallel fibers can be generated between the two collector electrodes although the fiber length is strongly limited. On the other hand there are usually no mechanical interactions between fibers and the orientation is even better then in case of rotating disk collector. Because of the lack of contacts between fibers, monofibers can be picked up from the sample for various investigations, such as mechanical tests.
Two ring electrodes can also be applied instead of rods. It is a very easy way to produce nanofibrous yarns by rotating one of the rings by the desired number of twists after electrospinning. The scheme and the realization of the system can be seen in Figure 20 and Figure 21 [103].
As it can be seen through a few examples, there are several tricks which allow to produce linear structures, but these practically can not be implemented to industrial scales. Different continuous yarn-preparation methods are developed which can be classified into two different groups. The first one consists of processes operating with special electrode geometries or spinning conditions, while the members of the other group apply liquid collector systems.

Two, perpendicular rotating disks can be used as collector system \([104]\) instead of one. In case of two disks the fibers cannot stick to the first one and the other disk can continuously wind up the yarn. The orientation and twisting of fibers occurs between the drums. Potentially infinite twisted yarn can be produced, with relatively high (approx. 10 m/s) haul-off.

A tip of a needle can focus fibers by the “lightning rod” principle. The focused jet of fibers would not stick to the tip of the needle it is rather blown away. Fibers are twisted around one another due to the whipping instability in a small space forming a yarn. This phenomenon is called self-bundling in electrospinning literature \([105]\). Fibers can be reeled with the aid of an auxiliary rotating drum to get continuous yarns or even with only one drum \([92]\). If the electrospinning parameters are adequate the already twisted part of the forming structure can act as a needle-tip and an automatic process is being started with further twisting and yarn formation. Continuous yarns can be produced by conjugate electrospinning technique also. The fibers are produced from two capillaries which are located in front of each other having the same axis but in different
directions. The parallel forming fibers from the two spinnerets twist each other as they contact, resulting a yarn which can be reeled continuously.

Smit et al. [30] developed a method which uses open liquid (water for instance) surface to collect nanofibers. The wet nanofibers are then pulled out of the liquid bath with a rotating drum. Fiber orientation is formed when the nanofibrous mat leaves the bath resulting in a continuous yarn. The scheme of the process can be seen in Figure 22 and the yarn formation mechanism from top-view can be seen in Figure 23.
Teo et al. [29] developed a liquid support system which allows creating continuous yarns which can be seen in Figure 24. Here the fibers are twisted due to the formation of a continuous vortex of water in the upper tank. The liquid is continuously restored from the lower reservoir with the aid of a pump. Twisted fibers are collected with a rotating mandrel therefore yarns can be produced with potentially infinite length.
14.4 Composite nanofibers

Nanofibers can be composites themselves if they are reinforced with smaller nanoparticles. On the other hand they can be the reinforcement of mono- and hybrid composites. Some processing techniques and applications of electrospun fibers are summarized in this subsection.

14.4.1 Testing and modeling the mechanical behavior of nanofibers for composite applications

Determination of the tensile properties of nanofibers and structures built of

The mechanical performance of electrospun nanofibers concerning nanocomposites can be discussed at different levels such as mechanical properties of single nanofibers, mechanical properties of nanofibrous self-products, and nanofiber reinforced composites as well. When designing composites it is crucial to know the mechanical parameters, behavior and damage process of the nanofibrous materials.

Determination of the mechanical properties of nanofibrous mats and yarns is quite simple. In case of mats, dumbbell specimens or even stripes can be cut and attached to paper frames by adhesive tapes and tested by traditional tensile testers after removing the edge of the frames (see Figure 25).

Figure 25 Tensile tests carried out on nanofibrous mat samples. A: gripping the specimen, B: cutting the edge of the frame, c: beginning of the test.
For determining the tensile properties, it is necessary to know the cross section of the specimens. In case of electrospun materials which are deposited on a flat metal collector [106] the area density is not uniform. To avoid this problem, it is suggested to use a rotating drum with low velocity. This slow motion does not affect the orientation of fibers, but the structure has a quasi-constant thickness in the direction of the rotation [107]. And in this case the linear density in the direction of rotation can also be considered constant. The cross section can easily be determined by knowing the density of the bulk material, the weight and length of the sample [25,107]. When testing nanofibers embedded in a matrix material, this method can also be used and paper frames can even be discarded.

In case of single fibers the determination of tensile parameters are far more complicated. These methods require special and also expensive apparatus, for example atomic force microscopy (AFM), micromanipulators, etc. That is the reason why testing of nanofibers is usually limited to the determination of geometrical or drug release properties [107]. For the determination of single nanofibers it is suggested to produce oriented nanofibrous samples for instance with the ‘two parallel rods’ collector configuration (Chapter 14.3.2). The sample can be attached to a paper frame, and under a microscope, all fibers can be removed, but one. This single fiber then can be manipulated for further experiments. Figure 26 shows a single fiber test setup designed for determining the modulus of a single nanofiber within a chamber of SEM. The modulus of single carbon nanofibers can be determined using the natural resonance vibration method where the modulus-frequency relation is given from the classical linear elasticity [108].

As these methods are quite complicated, modeling can also be applied to determine the tensile properties of nanofibers. The modeling method and software developed by Vas and Tamás [109] were applied to determine the tensile properties of single nanofibers via experiments carried out on nanofibrous Polyamide-6 (PA-6) mats. The modeling method was found to be appropriate because the results were agreed well with the experimental results of Hwang et al. [110] who measured the tensile strength of single PA-6 nanofibers by using nanomanipulator and AFM cantilever in a SEM.
Figure 26 SEM image of a carbonized nanofiber clamped between an AFM tip and a tungsten wire. A smaller AFM cantilever on the same AFM chip is present in the background [108].

As the damage of nanofibers happens due to the flaws of the material which are strongly related to the volume and extent of nanofibers, e.g. Weibull-analysis can be used to describe the failure characteristics [108].

Properties of nanofibers in respect of composite applications

Nanofibers have excellent flexural properties and high specific volume because of their small diameters. In principle, disregarding the differences in tensile strength they may be used for reinforcing at much smaller fiber content as compared to microfibers. For example, supposing regular quadratic arrangement of fibers (Figure 27) and microfiber content of 50% the same interfibrillar distance (here 12.5 μm) that is the matrix layer thickness between micro- and nanofibers of 10 and 0.1 μm diameters, respectively, can be realized at a nanofiber content of 0.005 % which means a difference of 4 magnitudes.

Therefore it is a big challenge for scientists to develop nanofibers with appropriate tensile properties as a primary reinforcement of PPCs. The idea to utilize nanofibers as reinforcement in composites is based on very strong arguments. Their high surface compared to their volume makes them able to make a strong adhesion with the matrix. If the critical fiber length is 1000 times more than the fiber diameter it still only means that a few hundred microns can be adequate in length in case of continuous electrospun nanofibers, it can be seen that theoretically nanofibers
could still reinforce the composite and properly bear the stress even in case of a meager compatibility between the fiber and the matrix.

Nanofibers generally have a moderately higher tensile strength and modulus than the bulk or film material due to the inner orientation of polymer molecules. Figure 28 [111] shows the E-moduli of submicron fibers as a hyperbolic function of the fiber radius as usual concerning this relationship. As fiber diameters are decreased somewhere below 300 nm, the tensile properties also increase notably [110] and the nano-effect takes place.
Figure 28 The \( E \) modulus of nanofibers. Redrawn and reanalyzed by He et al. [111] according to Gu and co-workers’ experimental data [112] shown by the dots.

It is believed that during the elongation of the liquid jet a very high molecular orientation is formed, but the chains are relaxed during and after the evaporation of the solvent (solidification of fibers) which leads to moderate inner orientation [113] and that is the reason why only very thin fibers can have highly increased strength. WAXD (wide-angle X-ray diffraction) experiments revealed that molecular chains are just moderately oriented within nanofibers and the crystal structure did not change significantly compared to the film of the same material [114]. Gu et al. examined nanofibrous polyacrylonitrile (PAN) material by FTIR (Fourier transform infrared spectroscopy). They found that the dichroic ratio significantly decreased from 1 for cast film to 0.881 for aligned electrospun fibers and the orientation factor was also increased. Zussman et al. [108] found that Herman’s orientation factor of carbonized nanofibers was 0.34. It is a low value compared to the orientation factor of highly-oriented melt-spun fibers (0.6) and wet-spun fibers (0.66).

All in all the tensile strength and moduli of nanofibers are usually far lower than those of the microfibers of the same material. The origin of the morphological difference can be attributed to the different fiber drawing mechanisms. In case of microfibers the high inner orientation is formed during the drawing and the solidification also befalls under mechanical tension thus the high orientation remains along the fiber length unlike in case of nanofibers. Nanofibrous structures cannot be drawn efficiently during solidification and relaxation of molecular chains can be expected. The material can be subjected to mechanical post-drawing, but only in a complicated way otherwise its structure, which is generally not composed of ideally parallel fibers would be damaged.
Compensation of the decrease in tensile strength caused by smaller orientation of nanofibers by decrease in diameter

Yet, in principle, the increase in strength of nanofibers due to the smaller diameter can be of such degree that it might overcompensate the difference being due to the higher strength of microfibers (Figure 29).

14.4.2 Composite nanofibers incorporated with smaller nanoparticles

The incorporation of nanofibers with smaller nanoparticles can be classified in two different categories, which also mean two different approaches. The first one is to embed nanoparticles into nanofibers. In this case the aim is to reinforce or functionalize nanofibers. The other one is the group of exo-composites or decorated nanofibers where nanoparticles are located or grafted onto the surface of electrospun nanofibers. The adequate dispersion of nanomaterial is crucial in all cases in order to get uniform nanofibers which really contain them.

Composite nanofibers reinforced with CNTs

As CNTs bear particular properties, such as excellent tensile properties, low density, and they are good electric and thermal conductors [115] therefore they are widely used as reinforcement in hybrid composites. Their tensile strength can be two times higher than that of certain reinforcement fibers therefore a high increase in tensile properties of composite materials can be expected, at least theoretically. As CNTs have diameter one-two orders of magnitude less than electrospun nanofibers they can be embedded into nanofibers in order to use them as reinforcement. Both single (SWCNT)-, double (DWCNT)- and multi-wall (MWCNT) CNTs can be applied [116].
Generally the most profitable dispersion method is to mix the nanoparticles to the solvent then add and mix to the polymer destined for electrospinning. For example Hou et al. [117] mixed SWCNTs in DMF with bath sonication. The process took 12h to reach adequate dispersion. After ultrasonication they added the polymer and stirred further for 12h by using magnetic mixer. Hou et al. [117] pointed out that if the CNT concentration is too high the fibers surface is rough. It is because CNTs are not completely embedded in the fiber in this case. TEM micrographs of CNT embedded polyamide fibers can be seen in Figure 30[118].

![Figure 30 TEM micrographs of (a) CNT reinforced nylon 6,6 fibers showing the agglomeration of CNTs. The CNTs were dispersed in the nylon 6,6 polymer solution; and (b) CNTs are embedded in the core region of the fiber and are aligned along the fiber axis][118].

Well-dispersed nanotubes are oriented along the nanofibers axis and in specific cases they increase the molecular orientation. The conductivity of CNT-loaded nanofibers is significantly increased [119-120].

The mechanical properties of nanofibrous materials can significantly be improved by embedding CNTs. The electrospun fibers which contained 0.75 wt% SWCNTs had nearly 60% higher tensile strength and more than 60% higher modulus than that of the reference material [117]. It is possible to produce composite nanofibers by an industrialized and cost-effective way as Kostakova et al. [121] did via needleless electrospinning from PVA (Poly-vinyl alcohol), crosslinking agents and applied either MWCNTs or SWCNTs as a nano-reinforcement of the nanofibers. It is not obvious whether CNTs are embedded in the fibers in case of needleless electrospinning, because there is no such continuous flow through a capillary which assures the
CNTs flow with the liquid jets of electrospinning. They carried out Raman spectroscopy and pointed out that CNTs are located within the fibers spun from the open liquid surface. There are several other types of carbons which can be embedded in fibers, such as carbon black [25], exfoliated graphite [122] and there are other types of nanoparticles, such as montmorillonite [122-124], metal nanoparticles [125], nano-silica [126], etc. but these latter ones are not strongly-related to PPCs.

**Exocomposite polymer nanofibers**

Another group of composite nanofibers are decorated or exocomposite nanofibers which are particularly developed for biomedical and sensor applications. The nanoparticles are located at the surface of nanofibers which can lead to ultra-fast drug release, but do not play reinforcing role. Exocomposite nanofibers can be processed by different methods. E.g. nanoparticles are electrosprayed on the forming fibers. The other possibility is to carry out electrospinning in a dusty environment. Nanoparticles can be stuck to the surface of the forming nanofibers the same way. The amount of nanoparticles can be adjusted by the flow rate or density of the nanoparticles in the spinning space, respectively. A wide variety of nanoparticles can be processed, and there are other methods also, for example physical or chemical vapor deposition can be used for metal particles. Exocomposite fibers can also be produced via wet methods where nanoparticle coating is obtained by immersing nanofibrous mats into a liquid containing nanoparticles. It is also especially used for metal nanoparticles. These other solutions which are not strongly related to polymer-polymer composites are reviewed by Andrady [25]. Hou and Reneker [127] produced CNTs via CVD method *in situ* on the surface of nanofibers. With this, the dispersion of CNTs is solved because they cannot form aggregates. SEM and TEM micrographs of the structure can be seen in Figure 31. In their study PAN nanofibers were electrospun and then carbonized to obtain carbon nanofibers. The formed structure can be a possible reinforcement of hybrid composites.
Figure 31 TEM (A) and SEM (B) micrographs of CNTS on carbon nanofibers [127].

14.4.3 Core-shell nanofibers prepared by coaxial electrospinning

Core-shell nanofibers, where the material of the outer shell is different from that of the inner core(s) can be produced by an advanced electrospinning technique, so-called coaxial electrospinning. These fibers can be called composites, as there can be good adhesion between the shell (matrix) and core (fiber) structure. The setup (see Figure 32) is quite simple, but requires much experience to produce defect-free core-shell fibers [64]. It operates with composite capillary with inner and outer solution feed which can independently be regulated. The inner solution is constrained to be flown within the shell solution. Core-shell electrospinning enables to prepare nanofibers from polymers without electrospinnability owing to lack of suitable solvents through coagulating in a surrounding solvent environment [128].
The shell and core has different functions, although in general the aim is not reinforcement. For example drug release [129] or better biocompatibility, shape memory and antibacterial aspects [130] should be taken into account. Core-shell nanofibers have smooth surface morphology and high structural uniformity [128]. The thickness of the core and fiber diameters can well be adjusted through varying the ratio of the flow rates [131] which is represented in Figure 33.

Figure 33 Effect of varying the feed rate of the core stream on the average fiber diameter of the core/shell nanofiber with a fitc–BSA/polycaprolactone core and a PEG shell [131]
In several cases the aim is to eliminate the core from the fibers and gain nanofibers with hollow conduits inside or with simple holes. SEM images of core-shell fibers prepared by coaxial electrospinning can be seen in Figure 34. The other option is to create beaded fibers where the beads are porous [81]. Presently these are not strongly-related to composite applications.

![Figure 34 Cross sections of hollow fibers prepared by coaxial spinning having two, three, four and five channels, respectively. The scale bars are 100 nm [64]](image)

Composite nanofibers with for example CNT loading can also be prepared via coaxial electrospinning, where high concentration of CNTs can be embedded [132]. Kim et al. [133] produced PAN nanofibers by coaxial electrospinning and combined the technology with decoration of fibers with palladium and forming small holes within fibers with water vapor. The fibers were then heat-treated to obtain carbon nanofibers. These materials can be used as fuel cells and had a specific surface area of more than 800 m$^2$/g. Nagamine et al. [134] produced carbon-core/TiO2-sheath nanofibers with diameters of a few hundred nanometers and sheath thicknesses of tens of nanometers by coaxial electrospinning. This material has an excellent conductivity and could be used in functional of composite applications as well.

14.5 Synthetic polymer-polymer composites containing or based on electrospun nanofibers
Classical SPPCs can further be incorporated with nanofibers, in order to get hybrid composites. The nanofibrous structure can modify their interlaminar properties or even other properties to get functionalized hybrids for specific applications. On the other hand nanofibers can be the primary reinforcement of composite materials. This subsection summarizes the potential of nanofibers in nanocomposites.

14.5.1 Nanofibers as interlaminar reinforcement of composites

The interlaminar properties of laminated thermosetting composites can often become their dominating weakness. E.g. laminated composite parts must have adequate interlaminar shear strength to avoid damage such as delamination, buckling, and peeling. There are several ways developed to increase the interlaminar shear strength, such as physical blending, placing special thin films [135-137] or CNTs [138-140] between laminate layers, etc. but these solutions usually modify the geometry and increase the weight of laminates. Stitching, Z-pinning or other methods can be applied to clench the layers but these can cause fiber breaks of the primary reinforcement of the material and also generate additional costs.

The idea of incorporating and placing small diameter fibers within microfibrous reinforcement layers was patented by Dzenis and Reneker [141] in 2001. Their invention is not limited to any particular matrix type, therefore nanofibers can be used both in thermosetting and thermoplastic matrices, theoretically. The small diameter fibers (typically electrospun nanofibers) can be applied at one or more ply interfaces or at a portion thereof and provide improved interlaminar toughness, strength, and delamination resistance without substantial reduction of in-plane properties and without substantial increase in weight. They intercalated graphite/epoxy unidirectional prepregs with polybenzimidazole (PBI) electrospun fibers and reported 15% increase in the Mode I and 130% improvement in the Mode II critical energy release rates. Nanofibers can be generated by using a plate collector or by spinning them directly onto the surface of the reinforcement fabric or prepreg. In the first case the electrospun fibers must be removed from the collector surface carefully, for example by washing. Figure 35 shows a unidirectional carbon fabric partly coated by electrospun nanofibers.
Figure 35 Unidirectional carbon reinforcement coated with nanofibers (left) and without coating (right) [142]

The latter method is favorable because the nanofibrous mat (which sometimes has an area density of only 1 g/m² or less) in this case will not be damaged during transport or processing which is especially important in industrialization. According to other considerations there is no need to use release agent between the collector and the nanofibrous mat because the collector is the reinforcement material. If metal mould is used for laminating the composite part or product and the fibers have enough conductivity (which is true for example for carbon nanofibers) then electrospun interlaminar layers can be produced in situ during the layup. The spinneret should be moved along the mould to have an even nanofibrous coating on the whole interfacial surface. Robots can even be used for automation.

The coating can be done before the product preparation, and before the pattern making, where the reinforcement is available in roll or in tow formats. In this case the reinforcement material is rewound between two rollers and electrospinning happens in-between by using stationery spinneret electrode(s). Therefore there is some technological flexibility: production of nanofibrous interlayers can be taken upon by both the fiber manufacturer and the composite product manufacturer.

Beyond the good automation possibilities the most important difference between the two approaches which emphasize the efficiency is that nanofibers can twist and encompass
microfibers (see Figure 36). Nanofibers can act as anchors of microfibers after impregnation, resulting in better shear performance [142].

Figure 36 Scanning electron micrograph of carbon micro- and PAN nanofibers [142]

According to the experiences in this field, it is crucial to impregnate well the nanofibers. Although nanofibrous mats have a high porosity and the wetting of the resin is often adequate, heed must be given to the small size of the micro- and nanopores which can require high pressure to be filled with resin [142]. It is recommended to use vacuum or pressure for impregnation to eliminate bubbles and cavities. There are different, simple methods for better impregnation, such as vacuum pressing [142], vacuum bag technology [143], using autoclave for curing [144], VARTM, H-VARTM [145], etc.

Zhang [146] et al. investigated the effect of the thickness of the nanofibrous interleaves and the effect of nanofiber diameters on the Mode I fracture toughness, flexural and DMTA properties. They investigated carbon fiber fabric reinforced epoxy composites with approx. 0.2-0.7 wt% polyetherketone cardo (PEK-C) toughening.

Finer nanofibers resulted in better improvement in the interlaminar properties without compromising the in-plane performance of the toughened composites [146], thus decreasing the fiber diameters is favorable. It must be noted that the increase in $G_{ic-INI}$ (critical energy release rate for crack initialization) was increased primarily due to the presence of nanofibers and the effect of fiber diameters had only secondary, minor effects. The smallest fiber diameter they
investigated was 450 nm but nanofibers strength typically increases significantly under 300 – 200, nm of which we do not have experience, only predictions.

The thickness of nanofibrous toughening layer had a significant effect on crack initiation and propagation properties. Figure 37 shows the critical energy release rates as a function of the thickness of nanofibrous interleaves. The critical energy needed for crack initiation and for crack propagation are increased considerably, by approx. 60% and 80%, respectively in the case of 70 and 105 µm thicknesses.

![Figure 37](image)

**Figure 37** Effect of the thickness of nanofibrous interleaves on the crack initiation and propagation behavior [146]

Increasing the thickness even more can have negative outcome. For instance Liu et al. [143] found that approximately, when the sum of the thickness of nanofibrous toughening layers reaches one tenth of that of the composite the flexural modulus and the interlaminar shear properties began to drop. When increasing the amount of nanofibers this effect becomes even heavier.

Different nanofibrous interlaminar layers in the same composite material can lead to different toughening effects. Liu et al. [143] investigated this problem by applying a rigid, general thermoplastic and elastomer nanofibers. The rigid one increased the tensile modulus considerably, while the elastomer helped more in toughening and lead to lower modulus. It gives the opportunity to adjust the mechanical performance of composites by choosing the adequate
toughening material. On the other hand the exact amount which gives the best toughening is unknown in these days.

Kelkar et al. [145] investigated the Mode I fracture toughness of glass fiber reinforced composites incorporated with tetra-ethyl-orthosilicate (TEOS) nanofibrous interlayers and alumina nanoparticles. They found no significant improvement, however only one interlaminar layer was placed between 10 layers of glass fabric. On the other hand they experienced significant increase in $G_{IC}$ in case of alumina nanoparticles. Nanoparticles can also be constructed from nanofibers, through phase-separation.

Polysulfone (PSF) is used as an interlaminar toughener in film form [147], acting through the mechanism of reaction-induced phase separation. The film between the layers forms small (several micron sized) spheres and sea-island morphology can be obtained. Li and his co-workers [148-149] had the idea to utilize this phenomenon in case of nanofibers and created polysulfone nanofibrous mats on the surface of carbon fiber reinforced epoxy prepregs because they presumed that the phase separation occurs in the same way as in the case of nanofibers. They prepared composite laminates by hot pressing the prepregs at 130°C for 2h, 180°C for 2h and 200°C for another 1h. The composite coupons had a PSF nanofiber content of 1 wt%, 3 wt% and 5wt%. They investigated the morphology via SEM, and the Mode I fracture, DMTA and 3-point bending properties of the samples taken from the coupons. The found that the due to the high porosity of nanofibrous mats they could be well-impregnated and on the fracture surface it can be seen that complete phase-separation occurred during the curing at high temperatures. They found PSF spheres with diameters of 2-6 µm, with uneven distribution. It can be attributed to the high scattering of nanofiber diameters. They concluded that the Mode I interlaminar fracture toughness ($G_{IC}$) which means the magnitude of adsorbed energy for crack propagation and which is related to the morphology of the laminate was higher in case of nanofiber-reinforces composites than in case of PSF films and also higher than in the reference sample without any interlaminar layer (reference material). They found 158%, 261% and 281% increase in case of the 1 wt%, 3 wt%, 5 wt% sample compared to the reference material and 132%, 150%, 140% compared to the PSF film toughened composite samples. The flexural properties were slightly increased but not in case of the 5 wt% sample.

Dynamic mechanical thermal analysis (DMTA) showed that the $T_g$s (glass transition temperatures) of the PSF nanofiber mat toughened composites were slightly higher which can be
attributed to the better cross-linkage of a part of the epoxy/amine molecules resulting in better compatibility between the matrix and PSF nanofibers than in case of applying PSF films instead. It can be concluded that the thickness of nanofibrous layer somehow again affects the properties considerably. In this case the 3 wt% sample gave the best results.

14.5.2 Electrospun nanofibers and their modifications as potential reinforcement of polymer-polymer composites

Reinforcing nanofibers of different materials

It turned out that thermoplastic nanofibers such as PA, PAN, PS, etc. do not have a tensile strength high enough to reinforce thermosetting composites. In the thermosetting composites the most prevalent reinforcement materials are: glass fibers, carbon fibers and aromatic polyamides (such as Kevlar®). It must be noted that basalt fibers as reinforcement are also gained a high importance during the last years [150], and also in thermoplastic ones [151] and there are numerous other high performance reinforcements for polymeric matrix thermosets such as polybenzobisoxazole (PBO), etc.

Glass fibers are industrially produced from melt, above 700°C that is why it is not used for melt-electrospinning. Bioactive glass fibers have already produced via electrospinning from sol-gel [152], but they are not strongly related to PPCs.

Aramid fibers which are also widely used in PPCs can also be electrospun the only difficulty is to find the best solvent system. For instance meta-aramid fibers were electrospun by Yao et al. [153] and Bai et al [154] who measured moderate mechanical properties of these fibers. Srinivasan and Reneker [155] reported electrospun para-aramid fibers. PBO fibers can also be electrospun [156]. There are not many studies dealing with these electrospun fibers, scientists are rather interested in producing carbon nanofibers form nanofibrous electrospun precursors.

Carbon nanofibers derived from electrospun precursors

The world’s carbon micro fiber production is based on polyacrylonitrile (PAN), which takes more than 90% of the total quantity. Generally high strength and/or high modulus carbon fibers
are PAN or pitch-based, while in case of nanofibers the former one is far more popular although there are attempts to create carbon nanofibers from metaphase pitch, but they usually have a diameter of several microns [157-158].

For carbon fiber manufacturing the PAN base material is copolymerized, in most cases with methyl methacrylate. In the electrospinning literature both PAN homopolymer and copolymer are used. The applied solvent of PAN is commonly $N, N$-dimethylformamide (DMF) [108] but other solvents can also be used, such as dimethylsulphoxide [159].

The precursor material is produced by electrospinning method and can have different formats: such as yarn, mat, etc. Nanofibrous PAN precursor yarn can be seen in Figure 38.

![SEM micrograph of PAN precursor yarn](image)

The optimal precursor material consists of fibers which are defect-free and should be continuous for industrial purposes. The solution and electrospinning process should be optimized considering the parameters affecting fiber quality, such as concentration, applied voltage, etc. [160-161].

Carbon fibers are prepared from the precursor fibers through thermo-chemical reactions. The first phase is stabilization under oxygen atmosphere, then follows carbonization under inert gas atmosphere at higher temperature and finally graphitization follows at even higher temperatures. In case of nanofibrous precursors this method is practically the same but pyrolysis parameters are different.
The pyrolysis of nanofibers is not a fully-developed field. The temperature of stabilization is usually between 200 and 350°C and then carbonization and graphitization (optional) takes place somewhere between 700 and 1500°C, but sometimes this interval can be even higher, between 500 and 3000°C [159].

There are different approaches, for instance Dhakate et al. [162] stabilized PAN in air atmosphere and under stretching, at 275 and 320°C. The stabilized fibers were carbonized so that the temperature was raised slowly from 550 up to 1000°C in nitrogen atmosphere. Zussman et al. [108] stabilized PAN precursors for 30 min at 250 °C, carbonized in nitrogen fog 1h at 750°C and graphitized at 1100°C for another 1h. The ramp rate between the 250, 750 and 1100°C plateaus was 5°C/min. Zhou et al. [163] stabilized PAN nanofibrous yarns with a heating rate of 2°C/min up to 280°C and holding it for 3 h. Carbonization followed at 1000°C with the same heating rate. The final carbonization (graphitization) followed in vacuum at 1400, 1800 and 2200°C, respectively with a heating rate of 5°C/min. It can be concluded that there is no standard approach.

Similarly to carbon microfibers it is profitable to increase the final graphitization temperature because the carbon nanofibers become more graphitic and structurally ordered [164] which is reflected by increased tensile properties. The graphitic structure of PAN-derived carbon nanofibers can be seen in Figure 39 [165].

Figure 39 TEM images showing the graphitic structures in GCNFs made from electrospun PAN nanofiber bundles with phosphoric acid [165]
The nitrile groups in electrospun PAN nanofibers have a higher reactivity compared to microfibers and the structural conversion occurs faster in the stabilization phase [113] therefore stabilization time is shorter than in case of microfibers.

The thermal behavior of the nanofibrous precursor made from PAN copolymer was investigated by Dhakate et al. [162]. It was found that during differential scanning calorimetric (DSC) experiments the nanofibers behave differently as compared to microfibers of the same material. Microfibers and films have one exothermic peak which indicates the cyclization of nitrile groups, formation of the ladder-like polymeric structure. On the contrary, nanofibers have two separate peaks. The first one is similar to the peak that observed in case of microfibers and films (at 275°C), but there is a second one, which is at a higher temperature (317°C) have a higher intensity which can be seen in Figure 40.

![DSC curve](image)

Figure 40 DSC curve of (1) micron size PAN-CP fiber, (2) thin film of PAN-CP solution, and (3) electrospun PAN-CP nanofibers [162].

It can be attributed to the difference in their surface to mass ratio. In case of nanofibers the chemical reactions are somehow not completed at the first peak. Liu et al. [113] have also compared the DSC curves of PAN microfibrous precursor of a carbon fiber manufacturer with nanofibrous mat of the same base material. They also found one peak in case of microfibers and two separated ones for electrospun material. It means that in case of nanofibers there are two
different types of thermo-chemical reactions. They concluded that it can be ascribed to the discrepancies in macromolecular conformations and packing structures. In case of highly-stretched microfibers the molecules are highly extended which makes the intra-molecular cyclization among neighboring nitrile groups dominant during the early stages of the stabilization process. Due to the low activation energy of this type of thermo-chemical reaction it happens at lower temperature. On the other hand electrospun fibers contain a significant percentage of molecules having helical conformations with nitrile groups being located on the outside of the helices. It is because relaxation of chains happens before the solvent totally evaporates during electrospinning and thermodynamically these helices are favorable, so the relaxed structure would be like that. In case of this conformation the intra-molecular cyclization is hampered. The intra-molecular cyclization has higher activation energy and occurs at higher temperature. That is the reason why a second dominant peak appear on the DSC curves. Gu et al. [114,166] also measured the DSC behavior of PAN nanofibers spun form homopolymer. They have found only one peak, but it was shifted to a slightly lower temperature. They concluded that in case of nanofibers the cyclization can be initiated easier.

The adequate copolymerization is a key problem in order to avoid degradation during the oxidative stabilization of nanofibers. The specific exothermic heat energy which can lead to a sudden degradation or burn of nanofibers instead of stabilization was found to be one order of magnitude higher in case of PAN nanofibers than in case of films and microfibers of the same material [162]. Moreover, it was found in TGA experiments, that PAN nanofibers are especially sensitive for temperature-induced degradation (see Figure 41).
Figure 41 TGA curve of (1) PAN-CP micron size fiber, (2) film made from PAN-CP solution, (3) PAN-CP nanofibers from 5 wt.% solution, (4) PAN-CP nanofibers from 7.5 wt.% solution, and (5) PAN-CP nanofibers from 10 wt.% solution [162].

To increase the tensile properties, hot-stretching can be applied to PAN fibers [117]. Hou et al. used PAN copolymer where the co-monomers were methyl acrylate (5.3 w%) and itaconic acid (1.7 w%) and SWCNTs were mixed to the solutions in different concentrations between 0 and 1%. At first they electrospun a nanofibrous mat precursor then it was hot-stretched at 135°C for 5 minutes. For this both ends of the stripe-shaped nanofibrous mat were clamped. One end was fixed to the ceiling of the oven while on the other ending there was a weight to induce the desired tension. Hot-stretching increased crystallinity from 11% up to 38% and also the crystallite size grew from 4 nm to 11 nm. The tensile strength was improved by 55% and the modulus had an even higher improvement of 156%. On the other hand hot-stretching slightly increased the exothermic heat during the stabilization which is, emphasized again, crucial to be minimized not to degrade nanofibers instead of stabilizing them.

The higher weight losses can possibly be attributed to entrapped and residual solvents between polymeric chains. Although it means that higher weight loss is not necessarily a problem, but at the same time it can lead to a higher shrinkage of fibers during stabilization and carbonization. The higher shrinkage can possibly lead to the realignment of the nanofibrous structure as well as to other morphological changes.

It was found that although fibers shrank, their morphology did not alter [162]. The final diameters of carbon nanofibers were in the range of 75-100 nm, which is approximately the half of the diameter of the precursor. Moon and Farris [164] reported 55-59% decrease of fiber diameters after carbonization. Zussman et al. [108] also experienced similar, 50% decrease in diameter after carbonization. Gu et al. [166] found that the shrinkage after the carbonization was 25% in diameter, and as the pyrolization process had different parameters in all cases, thus these parameters can somehow be closely related to the morphological changes, shrinkage and weight loss. Kurban et al. [159] revealed that adequate stabilization is very important to avoid high weight losses and on the other hand the final graphitization temperature can significantly affect the final fiber diameter through shrinkage and weight loss. They also found that the final graphitization temperature can affect the surface morphology of carbon nanofibers. The surface
was found to be smooth in case of 1500°C and graphitizing at higher temperature (3000°C) resulted in rougher, and more ridged surface which can also be seen in Figure 42 [159].

![Figure 42 SEM images of heat treated non-oxidized fibres: (a) HTT = 1500 °C, (b) HTT = 2800 °C, and oxidized fibres (c) HTT = 1500 °C and (d) HTT = 2800 °C [159].](image)

The resulting carbon nanofibers can have a rough and pitted surface which can be assigned to the vapor pressure of the solvent [166]. The size of pits was about 5 nm in width and 10 nm in length on the surface of the investigated carbon nanofibers. Dhakate et al. [162] measured the surface roughness of electrospun carbon nanofibers by using scanning probe microscopy (SPM) which was found to be 27.0 nm, which is about 10 to 20 percent of the fiber diameter. This kind of roughness can be an advantage, because the specific surface is further increased which is favorable for good adhesion and functionalization. The surface roughness is also typical for carbon microfibers which are derived from wet-spun precursors [113] (Figure 43 [167]). Zussman et al. [108] found that crystalline sheets were oriented radially in the skin which has a thickness of approximately 10 nm, but in the core of the fibers it formed a random-granular structure. Aggregations of elongated crystals could be found parallel to the fiber axis which is a preferable structure. Carbon microfibers can also have this typical core-shell structure.
The mechanical properties of these carbon nanofibers neither exceed nor even approximate the properties of microfibers. Although the strength of the classical microsized PAN precursors is one order of magnitude larger than that of PAN nanofibers oxidizing and carbonizing them makes this difference significantly smaller.

Moon and Farris [164] produced PAN co-polymer yarns in a finite length with different degrees of alignment. They applied tension during stabilization and carbonization. The yarn samples were drawn at different temperatures. They concluded that the drawing temperature should be above $T_g$ and the best results were got at 155-160°C (approximately 60°C above $T_g$).

It should be mentioned that the diffusion rate transfer in nanofibers would be hundred times faster than in case of industrial microfibers, because diffusion is related to the inverse square of the dimensions (fiber diameter).

Zussman et al. [108] measured the mechanical properties of single carbon nanofibers by the way introduced in subsection 14.4.1. The average bending modulus of nanofibers were $63 \pm 7$ GPa and the failure stress was between 0.32 and 0.9 GPa, where failure occurred at the gauge region. The carbon fibers were prepared from PAN homopolymers, which is not easy to compare with carbon microfibers based on PAN copolymers. They also carried out Weibull-analysis which gave a failure stress of 640 MPa where 63% of nanofibers would break with a confidence interval of 95%.

Zhou et al. [163] also measured the tensile properties of carbonized PAN yarns. The 1000°C carbonized bundle had a tensile strength of $325 \pm 15$ MPa and a modulus of $40 \pm 4$ GPa. These
values are increased to 542 ± 45 and 58 ± 6 GPa, respectively with the increase of the final graphitization temperature to 2200°C. These values are measured for the bundle which can differ from the properties of single fibers to a great extent.

Moon and Farris [164] investigated different carbonization parameters in case of yarn samples and the best one resulted an ultimate strength of approximately 1 GPa, but this value was increased to 1.7 GPa when they impregnated the yarn with an adhesive. The problem with the nanofibrous structure is that no single fibers can easily be tested. The tensile properties of single fibers can be estimated from the tensile properties of the product for example by modeling (see subsection 14.4.1). Single fibers can even have approximately 3 times higher tensile strength than nanofibrous mats which are built up of the same single fibers [107]. In case of the experiments of Moon and Farris [164] the adhesive blocked the slippage of nanofibers and this is the reason why higher tensile values were got. The twisting of nanofibrous yarns which would also clog the slippage surprisingly led to a decrease in the tensile properties. Finally, SEM micrographs showed there were more broken fibers within the yarn samples which could cause a drop in strength.

Zhou et al. [163,165] concluded that the electrical conductivity of carbon nanofibers were approximately 180 S/cm parallel and 8 S/cm perpendicular to the fiber axis. This difference is because the carbon fibers are continuous but in the perpendicular direction there are only small contacts between them. The conductivity of the bundle strongly depends on the contacts/entanglements among nanofibers. Increasing final graphitization temperature can strongly affect conductivity through improved graphite structure. By increasing the temperature from 1000°C up to 2200°C resulted 3.6 times higher in parallel and 7 times higher conductivity in perpendicular directions.

Beside composite applications of electrospun carbon nanofibers, these materials can be used as filter media also and can be applied to remove disinfection byproducts from water [168], for gas separation, solvent recovery and catalyst support [169]. These activated carbon nanofibers have low pressure-drop compared to granular activated carbon.

14.6 Conclusions and outlook
Electrospinning gained a high interest in the last years because it is a cost-effective and feasible technology to produce nanofibers. Although these nanofibers have various applications, the propagation of them in the fields of composites is being established. There are several problems which have to be solved before industrialization. These are, just to mention a few, the moderate productivity rate of the process, the immaturity of the technology. The technology has a limitation that only mats with random fiber orientations can be produced easily, and it is originated from the stochastic nature of the method, such as instabilities arising during spinning. Composites industry, on the other hand often requires other structures. Therefore, it can be expected in the near future that other modified setups will be developed in order to create structures similar to the ones already used in composites such as different textiles. Electrospinning is a technique which principally differs from classical spinning methods and it should be taken into account. This difference also reveals in the inner orientation of fibers which is far less than that of microfibers and it also appears in lower tensile properties. Temporarily, that is why nanofibers are basically not applied as composite reinforcements. On the other hand nanofibers have the potential to become widely-used reinforcements of composites if their properties could be set to an appropriate level. Nanofibers are easy to be incorporated with other nanomaterials and can also be functionalized easily therefore these nanofibers can become the basis of smart materials which have an increasing demand from the industrial side. Application of electrospun nanofibers in higher volumes can have a potential future in the composites industry.

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