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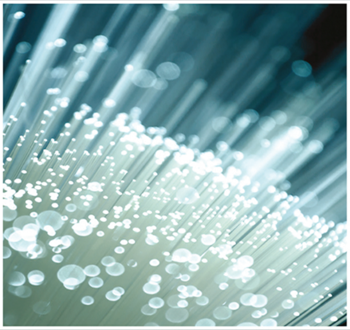

Fiber Technology for Fiber-Reinforced Composites

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Nanofibers for fiber-reinforced composites

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12.1 Introduction and historical perspective

The presence of nanomaterials in nature provides an inspiring way of bridging nanoscience into the classroom. Discovering that common natural materials such as paper and clay or materials such as feathers and spider silk have properties that depend not only on their chemistry but also their nanostructure is especially stimulating. Controlling of the surface chemistry of functional fibers has become an active research field in the last two decades, because of the increasing interest in fabricating fiber-reinforced composites (FRCs) with superior properties crucial in many applications.

12.1.1 Micro- and nanofibers

From past to present, the research on the fabrication of synthetic fibers has been increasing. The need for the improvement of both chemical and physical properties of fibers and being their use in many different application areas have led to the rapid development of fiber technology. The fibers that has the linear density lower than 1 dtex are generally accepted as microfibers. The traditional engineering microsized fibers such as glass, carbon, and Kevlar fibers are being used as reinforcing materials in composites [1]. FRCs can provide better structural properties having high modulus of elasticity and strength to weight ratios. On the other hand, fibers having diameters below 0.5 μm are considered as nanofibers, which will ultimately find significant applications in the fabrication of nanocomposites. Compared with microfibers as reinforcement materials, the nanofiber-reinforced composites have more superior mechanical performance and structural properties.

12.1.2 Methods used to form micro- and nanofibers

Traditional methods used to obtain micro- or nanofiber webs include melt spinning, solution spinning, and melt blowing [2]. The melt spinning process is based on the drawing down extruded strands of polymer melt [3]. However, this technology can only be applied to viscoelastic materials that can undergo strong deformations to

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withstand the developing stresses during drawing [1]. Typically, fibers having diameters greater than 2 μm can be produced by melt spinning [4]. Islands-in-the-sea (fibers within fibers) process, which is a variation of melt spinning, involves production of several individual strands of a polymer component (island) within a larger single strand of a second polymer component (sea). The bicomponent strands are extruded through dies, cooling, or attenuating of fibers by high-velocity air streams. This process allows to produce fibers with a diameter ranging from 0.1 to 5 μm [5]. The main restriction for this technique is that the removal of sea component from the fibers, which often creates an environmental issue due to the need for solvents, and consequently, a limited number of polymers can be processed [6].

Solution spinning includes dry-spinning, wet-spinning, and gel-spinning processes [7,132]. In both dry and wet spinning, a viscous solution of polymer passes through fine holes of a spinneret to form fibers. In dry-spinning case, the solvent is evaporated using a heated column where the polymer solidifies. In wet spinning, the polymer solution is pushed through a spinneret into a chemical bath in which the polymer is precipitated by dilution or chemical reaction to form fibers. It is possible to draw fibers with diameters ranging 100 μm to over a millimeter [132]. Gel spinning can also be described as dry-wet spinning, since the filaments pass through the air and then are cooled in a liquid bath. High-strength polyethylene and aramid fibers are produced by gel spinning [8].

Since the 1990s, there has been a growing interest in electrospinning due to its applicability to a variety of polymers and easy fabrication of ultrafine fibers. Electrospun fibers are produced from polymer melt or solution by electrostatic forces. This process is able to produce fibers with diameters in the range from 40 nm to 2 μm [9].

Melt blowing is another method for the fabrication of nonwoven network of fibers, based on the extrusion of molten polymer through an orifice, attenuated by heated high-velocity air stream. This method has been used to produce microfibers ranging in diameters from 1 to 50 μm [4,10].

A novel solution blow spinning (SBS) method is the combination of both electrospinning and melt blowing technologies. Micro- and nanofibers with diameters ranging from a few tenths of nanometers to several microns can be produced [3,133].

12.2 Electrospinning

12.2.1 The fundamental aspects

The uses of nanofiber materials have attracted quite extensive attention over the last 25 years with the increasing popularity of the simple electrospinning technique [9], which has now become a scalable fabricating technique. Although electrospinning is mostly a technique that is biased to laboratory-scale work, the ever increasing number of commercial electrospinning companies instills confidence that the future will see industrial-scale usage of nanofiber materials. Nanofiber materials have found uses in many areas including composite reinforcements, filters, tissue engineering, battery cells and capacitors, drug delivery, smart textiles, protective clothing, catalysts, wound dressings, sensors, and cosmetics [11].

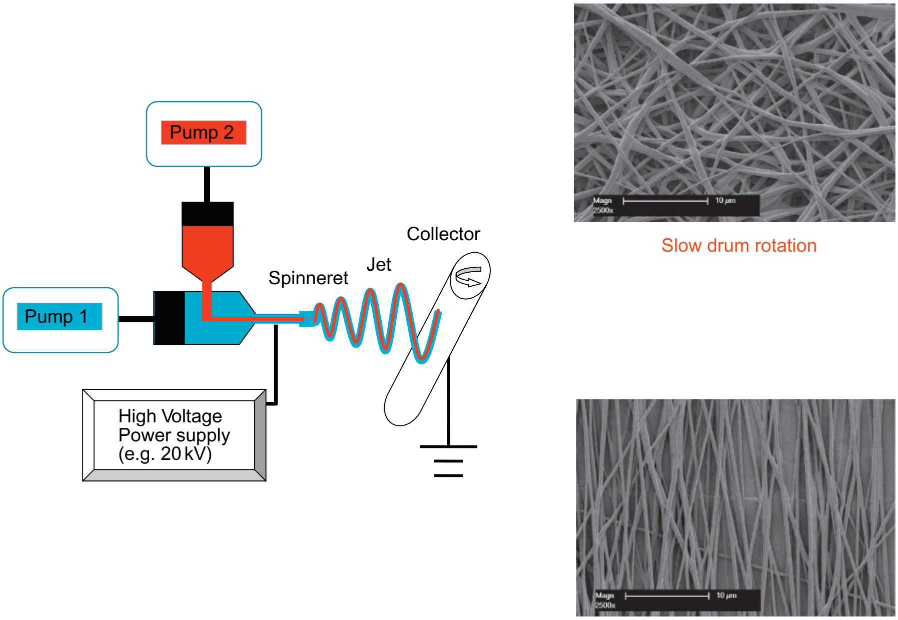
A thorough history of electrospinning can be found in a review paper by researchers in New Zealand [12]. Although there are discrepancies on the exact origin of electrospinning, most of the patents were filed between 1931 and 1944 by Anton Formhals. The "Taylor" cone commonly used to describe the theory of electrospinning by many novices and experts originated from Sir Geoffrey Ingram Taylor, who between 1964 and 1969 developed the theoretical underpinnings of electrospinning by mathematical modeling of the shape of a cone formed by a fluid droplet under the effect of an electric field.

Electrospinning is a technique for producing fibers from submicron down to nanometer in diameter with high surface area. The technique can be further divided into two main categories: solution electrospinning and melt electrospinning. In solution electrospinning, the polymer(s) and other additive materials are firstly dissolved in a suitable solvent at an optimized concentration before electrospinning, whereas in melt electrospinning, the polymer is heated to an optimized temperature to form a melt. In either case, a high electric field is applied to the droplet of fluid coming out of the tip of a die or spinneret, which acts as one of the electrodes. When the electric field supply is strong enough, it will lead to the droplet formation and finally to the ejection of a charged jet from the tip of the cone accelerating toward the counter electrode leading to the formation of fibers. While solution electrospinning relies on evaporation of the solvent to produce fiber, melt electrospinning requires cooling of the polymeric jet [13].

In its simplest form, electrospinning can be carried out using a single spinneret system (monoaxial using pump 1 only) with one polymer dissolved in a solvent at the right concentration, for example 20% polyurethane in *N*,*N*-dimethyl formamide solution and processing parameter of 0.2 mL/h pump rate, 23 gauge needle spinneret size, at gap distance and applied potential of 20 kV [14]. The collector geometry used in this study was a rotating drum and by changing the drum speed from 1 to 9 m/s, while keeping all other material and process variables constant, membranes in which the fibers were randomly distributed or aligned were fabricated (Fig. 12.1).

Functional additives and mixtures of two or more polymers dissolved in a solvent or mixture of solvents can also be electrospun monoaxially using a single spinneret. However, there are different variations on the simple monoaxial electrospinning described above. The most commonly described variation is coaxial electrospinning where two different solutions can be coelectrospun without direct mixing, using two concentrically aligned spinnerets. The same voltage is applied to both spinnerets, and it deforms the compound droplet. A jet is generated on the tip of the deformed droplet and, in an ideal case, a core-shell nanofiber is formed. This type of electrospinning is mainly used in developing structures with higher strength using stronger core, drug delivery products using sheath and core materials degrading at different rates, and better tissue engineering products obtained by coating a less biocompatible but desirable material with a more biocompatible one [15].

The incorporation of active agents, such as drugs to nanofibers has been heavily pursued by either simply mixing or blending the active compound with the polymer



Slow drum rotation

Fast drum rotation

Fig. 12.1 A schematic view of electrospinning setup (monoaxial without pump 2 and inner red spinneret) or coaxial with both pumps.

solution prior to electrospinning or by adding the additives that are prefixed to a holder type material to attain controlled release [16]. Other methods of incorporating active compounds or to add functionality to the nanofibers are to perform post treatment of the electrospun nanofibers by different coating treatments or by performing surface functionalization to change the existing functional groups [17].

Industrial-scale eletrospun production is becoming a reality [18] with several companies including Inovenso and Elmarco offering industrial-scale electrospinning machines. An exhaustive list of companies currently supplying electrospinning products can also be found in Persano et al. review paper [18], and some of the more prominent companies include Donaldson, DuPont, and Finetex Technology. With such knowledge at hand, it can be said that nanofibers fabricated by electrospinning have a promising future in materials manufacturing for numerous and varied applications.

12.2.2 Factors affecting fiber formation

Variables that can affect electrospinning can be classified into two categories; the material variables relating to the polymer and choice of solvents and the process variables pertaining to equipment and processing parameters. The material and process variables listed in Table 12.1 can affect both the ability of producing nanofibers and the quality of the nanofibers.

Table 12.1 **Material and process variables in electrospinning**

Material variables	Process variables
A: Polymer solution or melt • Concentration • Solvent choice • Additives B: Environment • Temperature • Humidity C: Collector • Geometry • Dielectric properties	D: Applied potential E: Pump rate F: Spinneret properties G: Gap distance

During electrospinning, the concentration of polymer solution is one of the most important parameters in the fiber formation. It should be noted that surface tension and viscosity have a significant role in the determination of the concentration range, which continuous fibers can be fabricated by electrospinning. As the concentration is too low, electrospraying occurs in the form of macro/nanoparticles instead of electrospinning, due to the low viscosity and high surface tension of the solution. If the polymer concentration is not adequate for electrospinning, beaded fibers are obtained. For solution of low viscosity ($\eta < 1$ poise), surface tension has a dominant effect on fiber morphology. At very high viscosities ($\eta > 20$ poise), the ejection of jet from the solution becomes difficult [19]. If the solution has a suitable viscosity, continuous fibers can be obtained. Polymer concentration does affect not only the electrospinnability but also the fiber diameter. In general, increasing the concentration of electrospinning solution results in larger fiber diameter.

Another parameter is the selection of solvent in terms of its viscosity, surface tension, dielectric constant, and vapor pressure. Supaphol and coworkers reported that smooth polystyrene (PS) fibers were fabricated from the as-prepared PS solutions that have high polarity, conductivity, boiling point, low viscosity, and surface tension [20]. The effect of solvent system on the morphology of fibers was also studied for electrospinning of polyvinylpyrrolidone (PVP) solutions. Continuous fibers were produced from PVP solutions in ethanol because of higher dielectric constant and lower surface tension of the solvent [21].

The existing literature on the effect of additives such as inorganic salt and surfactant is extensive and focuses particularly on the fiber morphology and diameter. By changing the conductivity and surface tension of the solutions, the elimination of beads is possible.

By increasing the conductivity, density of net charge increases; then, accordingly, the jet is stretched under viscoelastic force, which in turn leads to formation of bead-free fibers. Fallahi et al. investigated the fabrication of uniform PS fibers by incorporating salt (LiCl) and nonionic surfactant (polyether modified polysiloxane).

They claimed that increasing the amount of surfactant resulted in larger bead and thinner fiber formation, whereas increment in fiber diameter was observed with addition of salt into the solution [22]. Addition of increasing amount of NaCl and LiCl into the polyamide-6 solution in formic acid, resulted in increase in fiber diameter due to the increase in both viscoelastic force and mass flow [23]. Similar results were reported with the addition of triethylbenzylammonium chloride to a polyurethane/DMF solution [24].

Ambient temperature and relative humidity strongly affect electrospinning. As for the temperature, high temperature promotes solvent evaporation rate but reduces viscosity of the solution, thus thinner fibers are obtained. De Vrieze et al. reported these two opposing effects on the average fiber diameter of PVP nanofibers as a function of temperature [25]. At higher temperatures, the fiber formation process can be completed by rapid solidification of the jet because of higher solvent evaporation rate. The polymer chains move more freely, leading to lower solution viscosity and thus producing higher stretching rate and thinner fibers. The inverse relationship between the solvent evaporation rate and solution viscosity has been also proved for polyamide-6 fibers that had thinner fiber diameter with the increase in temperature [23]. The humidity of the electrospinning environment affects the fiber diameter depending on the chemistry of the polymer. De Vrieze et al. have observed that as the humidity increased, the average fiber diameter of cellulose acetate nanofibers increased, whereas average diameter of PVP fibers decreased. The different trends in diameter was explained not only by the variations in chemical and molecular interaction but also by its effect on the solvent evaporation rate [25]. In general, at high humidity, water condenses on the fiber surface preventing the fiber drying during the nanofiber jet flight, and this may have an influence on the morphology of the fiber particularly when the polymer is dissolved in volatile solvents. On the contrary, at low humidity, the rate of evaporation increases and fiber formation occurs. Recently, Liang et al. have demonstrated that increasing the relative humidity to a critical point (73% RH) resulted in self-alignment of nanofibers into a 3-D honeycomb-like structure. Above the critical point, no structure was observed, only few nanofibers was obtained because of the slow evaporation rate [26].

The structuration of the nanofiber mat is also possible for particular applications depending on the geometry and dielectric properties of the collectors. There are two basic approaches currently being adopted in research into the collectors. One is the use of mobile collectors that can provide fiber alignment onto a rotating drum or disk. The other induces a modification of electric forces on the charged fibers reaching to the collector. Furthermore, tuning the local differences of the dielectric properties by using different dielectric materials for the collector is another way for nanofiber mat structuration. Lavielle et al. [27] produced “microwoven” PCL scaffolds with good mechanical properties using various collectors with microscopic patterns prepared by photolithography.

In regard to the process variables, a critical voltage value exists, which if exceeded, a stable polymer jet can be obtained. However, further increasing applied voltage results in higher instability and stretching of the jet, leading generally to thinner fibers. A decrease in tip-to-collector distance increases the electric field, thus semisolidified and bead-defected fibers can be formed. At constant electric potential and tip-to-collector distance, fiber diameter gradually increases with increasing feed rate of the polymer solution. If the feed rate is too low, nonuniform fibers with broad diameter distribution are obtained. It is worth mentioning that the diameter or length of needle may affect the fiber diameter. Macossay et al. fabricated poly(methyl methacrylate) (PMMA) fibers using needles with different internal diameters. No correlation between the needle diameter and the average fiber diameter has been observed, but the fibers obtained using thinner needle diameter have a broader diameter range [28].

12.2.3 Nanofibers containing nanoparticles

The combination of electrospun nanofibers and inorganic nanoparticles in one object yields hybrid materials that are intrinsically porous and possess higher chemical and thermal stability. Although nanoparticles have a larger surface area than nanofibers of the same diameter, nanoparticles are usually difficult to separate from the reaction media due to the lack of mechanical integrity. In this respect, polymer fibers can be used as supports to place inorganic particles in a structural template, in an isolated and nonaggregated fashion [29]. The different strategies to produce hybrid electrospun fibers were categorized as (i) electrospinning of precursors followed by heat treatment, (ii) electrospinning of ex situ synthesized inorganic materials, (iii) surface crystallization on electrospun fibers, and (iv) combination of these methods.

Table 12.2 summarizes the recent studies related to nanofibers containing nanoparticles. Although the most common method is the heat treatment of polymer/inorganic precursor fibers, the resulting fibrous materials after this process are often brittle and lose their mechanical strength [41]. On the other hand, simultaneous electrospinning of ex situ synthesized nanoparticles and polymer leads to the reduction of the performance of available active sites due to the polymer shielding [42,43]. Hence, the fabrication of nanofiber/nanoparticle composites by the in situ formation of the nanoparticles on the surface of electrospun fibers allows the possibility of synthesis at lower temperature without any additional heat treatment and a controlled nanoparticle formation on the surface of the fibrous template. Surface treatment of electrospun fibers is also advantageous in terms of prevention of nanoparticle aggregation and providing uniform distribution of the nanoparticles on the fibers.

12.2.4 Fiber-reinforced composites

FRCs consist of fibers and matrix [44]. High-strength, high-stiffness structural fibers and low cost, lightweight, environmentally resistant polymers are combined to make a composite [45]. Fibers or other reinforcing materials strengthen the polymeric matrix [44]. The mechanical properties and durability of the composites become better than plain polymer [45]. The matrix holds the fibers, provides load transfer, whereas the fibers contribute to the strength and stiffness [44]. In the 1960s and 1970s, fibrous materials such as boron, carbon, and aramid were commercialized due to their higher strength and stiffness and lower density to meet the higher-performance challenges of space exploration and air travel. Initially, fabrication of composites made up of fibers

Table 12.2 **The recent literature on nanofiber-nanoparticle composites**

Nanofiber	Nanoparticle	Composite	Strategy	Application	Reference
Polycaprolactone (PCL)	Fluorescent polystyrene (PS)	Nanoparticle/nanofiber composite	Electrospinning of polymer blend with ex situ synthesized inorganic materials	Cell adhesion	[30]
Polyacrylonitrile (PAN)	Magnesium oxide (MgO)	PAN-MgO nanofiber	Electrospinning of polymer blend with ex situ synthesized inorganic materials	Air filtration	[31]
Amphiphilic block copolymer [poly[methoxy poly(ethylene glycol)methacrylate]-block-poly(butyl acrylate) (PMPEGMA-b-PBA)], phenolic resin, and polyethylene oxide (PEO)	Nickel (Ni)	Ni/NiO/MnO_x/Carbon nanofiber	Electrospinning of precursors followed by carbonization	Lithium-ion battery anode	[32]
Polyvinyl pyrrolidone (PVP)	TiO_2	TiO_2 nanofiber	Electrospinning of precursors followed by calcination	Photoanode	[33]
Polyacrylonitrile (PAN)	SiO_2	SiO_2/PAN hybrid nanofiber	Electrospinning of solution containing a sol–gel precursor and a polymer	Membrane separator for lithium-ion battery	[34]
Polyacrylonitrile (PAN)	SnO_x and ZnO	SnO_x-ZnO/carbon nanofiber	Electrospinning of precursors followed by carbonization	Lithium-ion battery anode	[35]

Polyvinylpyrrolidone (PVDF)	SiO_2	PVDF-SiO_2 nanofiber	Electrospinning of polymer blend with ex situ synthesized inorganic materials	Forward osmosis desalination	[36]
Polyvinyl pyrrolidone (PVP)	Fe_2O_3	Fe_2O_3 nanofiber	Electrospinning of precursors followed by calcination	Chromate adsorption from waste waters	[37]
Polyvinyl alcohol (PVA)	CuO	CuO nanoparticle	Electrospinning of precursors followed by calcination	Hydrazine hydrate electrooxidation	[38]
Polyvinyl alcohol (PVA)	CuO	CuO nanoparticle	Electrospinning of precursors followed by calcination	Hydrazine hydrate electrooxidation	[38]
Polyvinyl pyrrolidone (PVP)/ polyacrylonitrile (PAN)	$NiCO_2O_4$	$NiCo_2O_4$ NPs-decorated N-doped carbon nanofiber	Electrospinning of precursors followed by multi-step heat treatment	Lithium-ion battery cathode	[39]
Polyvinyl alcohol (PVA)/chitosan oligosaccharide (COS)	Ag	PVA/ COS-AgNPs nanofiber	Electrospinning of precursors	Wound healing	[40]

that have superior properties were too costly. Therefore, researchers have studied on this problem until now, and they achieved to produce cheaper fibers that are used in current studies [45].

The key aspects of effective reinforcement can be listed as high aspect ratio, uniform dispersion, alignment, and interfacial stress transfer [46]. The aspect ratio of the fibers is an important factor that contributes to the properties of new types of composites. Homogeneous dispersion of fibers prevents agglomeration and provides efficient load transfer minimizing the presence of stress concentration centers. The difficulty in controlling fiber alignment decreases the efficiency of reinforcement, structural, or functional performance [47]. The orientation and length of fibers should be considered for a particular application [48]. In engineering applications, various types of fibers with different orientations and lengths have been used for decades. The fiber-reinforced plastics for commercial use have attracted great attention in the aviation industry in the 1930s [49]. The other significant requirement for FRCs is the applied external stress to the composite that is transferred to the fibers. Thus, it allows them to take a disproportionate share of the load affecting the performance of composites.

Nowadays, FRCs are commonly used in aerospace, marine, armored vehicles, automobile, railways, civil engineering applications, sporting goods, etc. due to their high specific strength and hardness [50]. Glass fiber is widely used as a reinforcement due to its low cost, high tensile and impact strength, light weight, and having a corrosion resistance. Furthermore, polyester resin reinforced with glass fiber is the material of many application areas such as marine, constructions, automobile, and railway industry. Another example is vapor-grown carbon nanofiber-reinforced polymer composites having improved mechanical properties through better interfacial adhesion and fiber alignment. Hossain et al. [50] investigated the use of carbon nanofibers (CNFs) as nanofillers in woven glass fiber-reinforced polyester composites. They observed 0.2 wt% CNFs-loaded polyester resin had better dispersion of CNFs. The results of this investigation show that the incorporation of even low amount of CNFs improved mechanical properties of the composite system. Besides enhanced mechanical strength, it is possible to fabricate conductive polymer composite by the addition of carbon fibers. The increment in volume fraction of carbon fibers results in higher effective electric conductivity of the composite [51].

12.3 Carbon nanotubes/nanofibers

Conductive nanofiller/polymer fibers are functional nanomaterials since they have remarkable electrical, thermal, and mechanical properties. The successful combination of high aspect ratio and one-dimensional conductive nanofillers, including carbon nanotubes (CNTs) and CNFs with the various electrospun nanofibers, leads to significant enhancement in the aforementioned properties. The tensile strength and modulus of elasticity depend on the polymer matrix, and types, synthesis method, dispersion and concentration of carbon nanofillers in the polymer matrix [52].

The preparation of CNT/polymer solution for electrospinning involves mixing polymer solution and nanotube dispersion to obtain homogeneously oriented CNTs in the resultant fibers. To date, CNTs have been embedded into various polymer matrices including chitosan [53,54], epoxy [55], nylon 6,6 [56], polyacrylonitrile [52,57–61], polyaniline [62], polycaprolactone [63], polycarbonate [64], poly(ethylene oxide) [65–67], polylactic acid [68], polymethyl methacrylate [69,70], polystyrene [71], polyurethane [72], poly(vinyl alcohol) [73–75], and regenerated silk [76,77].

Apart from considering different polymer matrices, extensive research has been conducted to demonstrate the application potential of various types of carbon nanomaterials, mainly single-walled (SW) and multiwalled (MW) carbon nanotubes and vapor-grown carbon nanofibers (VGCNFs), as reinforcements in polymer matrices. CNTs can be produced by arc discharge, laser evaporation/ablation, thermal and plasma-enhanced chemical vapor deposition (CVD) [78]. Depending on the manufacturing methods, the diameter of SWCNTs can be close to 1 nm, and MWCNT can have a diameter larger than a few nanometers. Besides this, VGCNFs, which are also termed MWCNTs, typically have diameters in the range of 50–200 nm [79]. VGCNFs can be synthesized by catalytic CVD of a hydrocarbon gas, such as acetylene and propane, or carbon monoxide using metals, usually Fe, Ni, Co, Au, or metal alloy catalysts at temperatures around 500–1500°C [78]. Although carbon nanomaterials differ from one another not only in their size but in their also electric and mechanical properties, very few related works have been reported. Ashrafi et al. studied on the influence of CNT types in improving the mechanical properties of epoxy resins [80]. A comparative study between SWCNT- and MWCNT-modified laminated composites showed that SWCNTs are more effective in enhancing the mechanical performance of the composites. The flammability behavior of SWCNT and MWCNT membranes (buckypaper) and carbon nanofiber (CNF) paper on the epoxy/carbon fiber composite surface was investigated by Wu et al. [81]. The flame-retardant efficiency of MWCNT-based buckypaper was correlated with its high-temperature thermo-oxidation and dense network. CNF paper composite showed low flame-retardant efficiency due to its large pore size and thus high gas permeability.

Uniform dispersion and orientation of carbon nanomaterials within the polymer matrix are two other significant parameters in preparation of composites. Because of strong van der Waals interaction and small size, CNTs or CNFs tend to aggregate to form bundles preventing uniform dispersion within the polymeric resins, which results in lower physical and mechanical properties of the composite material [82]. In order to improve the carbon nanomaterial dispersion, several approaches have been followed, including solution-evaporation methods with high-energy sonication [83] and surfactant-assisted processing [84,85]. Furthermore, deposition of carbon nanotubes suspension under an electric [86] or a magnetic field [87], onto a chemically modified substrate [88], solution casting [89], melt processing [90], and in situ polymerization [91,92] are the most commonly used techniques.

It is worth mentioning that the length and concentration of carbon nanomaterials also affect dispersion behavior and, therefore, electrical, thermal, and mechanical properties of nanocomposites. Abu Al-Rub et al. reported that low concentration long CNTs (10–30 μm) are more effective than high volume of short CNTs (1.5 μm) in filling nanosized voids leading to enhancement in the packing density of the cementitious composite. It was also shown that the Young's modulus increases as the concentration of long CNTs decreases, whereas the increment in the concentration of short CNTs results in higher modulus of elasticity. Both the flexural strength and ductility increased while using short 0.2 wt% MWCNTs or long 0.1 wt% MWCNTs as reinforcements for the nanocomposites [93]. Recently, MWCNTs/PVP composite nanofibers were fabricated by electrospinning. Effects of MWCNTs concentration on the electric conductivity, complex permittivity, and electromagnetic interference shielding effectiveness (EMI SE) of the nanocomposite were investigated. Total EMI SE was found to be ~42 dB at 10 wt% MWCNTs/PVP nanofibers [94]. In another study, electrospun nanofibers of the MWCNTs/P(St-co-GMA) were embedded into an epoxy matrix for exploring the reinforcing abilities. The flexural modulus of the nanofiber-reinforced composite increased even positioning a single layer of MWCNTs/P(St-co-GMA) nanofibrous mats of 1%, 1.5%, and 2% CNT weight fraction. This increase was attributed to the well-dispersed MWCNTs in addition to the modified chemistry of the nanofibers with epoxide moieties enabling cross-linking between the polymer matrix and the fibers [95].

12.4 Cellulose nanofibers

Cellulose is one of the most important biopolymers. Having many features such as biocompability, biological degradability, availability, and sustainability, it is commonly preferred to use [96]. This polysaccharide is found in everywhere and plenty in nature, given its industrial use in sails, timber, ropes, and paper. For example, wood is the most commercially utilized natural resource containing cellulose [97]. Like wood, plants, marine animals (tunicates), algae, and bacteria can be counted as cellulose source materials. Cellulose has a nonbranched chain of variable length of 1–4-linked β-D-anhydroglucopyranose units. Fig. 12.2 shows the structure of cellulose repeating unit. The hydrogen bonding between hydroxyl groups and oxygens of adjacent molecules stabilizes the glycosidic linkage resulting in the linear configuration of the cellulose chain. Intermolecular hydrogen bonds and van der Waals forces promote parallel stacking of cellulose chains aggregating into the repeated crystalline structure to form microfibrils (5–50 nm in diameter and several microns in length) in the plant cell wall [98].

Cellulose nanofibers are usually insulated from lignocellulosic plants [99]. They can also be produced from annual plants and agricultural by-products, and they have widely renewable resources [100]. Because cellulose nanofibers have semicrystalline structure, their thermal expansion coefficient is close to that of quartz [101]. The

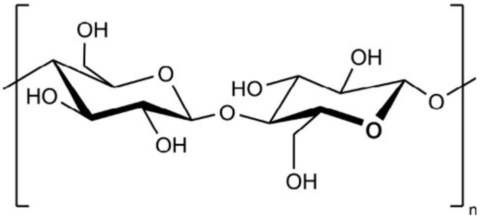


Fig. 12.2 The repeating unit of cellulose in chair conformation.

fibrillated cellulose with a nanoscale structure is generally composed by some combination of chemical, enzymatic, and/or mechanical improvements of lignocellulosic materials [102,103]. Cellulose nanofibers are characterized by a large surface area ($\sim$800 m^2 g^{-1}), high strength (2–3 GPa), high elastic modulus ($\sim$140 GPa) [104], low weight, biodegradability, and biocompatibility [105,106].

The natural nanostructured cellulose has been the main field of many research areas and has been used by different industries, particularly in biomedical and pharmaceutical applications [102]. Moreover, cellulose nanofiber-reinforced composites have potential applications in food packaging, paper, thin components in the electric and electronic devices, etc. [107].

12.4.1 Nanocellulose for fiber-reinforced composites

Cellulose nanofiber-based materials establish a comparatively new class of naturally sourced reinforcements. Due to their high mechanical properties, incorporation of cellulose nanofibers into the composites has gained significant interest. Furthermore, good transparency, barrier properties, and dimensional stability are advantages of cellulose nanofiber-based composites [103]. Cellulose nanofibers have been widely used with various polymers to produce nanocomposites.

Recent studies have been performed on the production of cellulose nanofiber-reinforced epoxy composites. The mechanical performance and thermal stability of the cellulose nanofiber-reinforced composites increase with the reinforcement loading [107]. Masoodi et al. performed assessment of swelling and tension/fracture behavior of bio-derived epoxy composites [108]. The preparation of high-nanocellulose-content biocomposites from well-dispersed nanofibrillated cellulose in epoxy matrix was also described by Ansari et al. [109]. The successful combination of nanocellulose and epoxy provided high strength, modulus of elasticity, and ductility, and moisture stability for a cellulose-based biocomposite. In another study, epoxy has been used for surface modification of cellulose nanofibers used as a reinforcement in a polyvinyl alcohol (PVA) matrix. The chemically functionalized cellulose nanofiber-reinforced PVA showed higher elastic modulus, strength, and strain compared with the composite prepared by unmodified cellulose nanofibers [110].

Nanocomposites are usually reinforced with low percentage of cellulose nanofibers (usually $<$10%) in contrast with the high level of fibers (40%–60%) used in common composites [107]. Petersson et al. produced the nanocomposites by incorporating 5 wt% of the different cellulose nanowhiskers into a poly(lactic acid) matrix [111]. The effect of various cellulose nanofiber percentages by mass in the epoxy matrix was evaluated [107]. The authors showed that the addition of 0.25% and 0.5% cellulose nanofibers was homogeneously dispersed in the polymeric matrix, whereas agglomeration of the nanofibers was detected in the matrix with 0.75% content. Although there are still many obstacles remaining for usage of cellulose nanofibers, they have great potential for use as reinforcement in polymer matrices [111]. The main problem is the dispersion of highly hydrophilic nanocellulose into the hydrophobic polymer matrices. The homogeneous distribution of cellulose nanofibers in a polymer is too difficult on account of their high surface energy and the existence of hydroxyl groups on the surface; thereby, it has strong hydrogen bonding. Different chemical modifications have been applied to overcome this problem. The dispersibility of nanofibers in a polymer matrix and dimensional stability of the final composite can be enhanced by acetylation. In acetylation process, hydroxyl groups on the cellulose react with the chemical; accordingly, hydrophilic surface of the cellulose is modified and becomes hydrophobic [99,106]. The other process is topochemical trimethylsilylation. Grunert and Winter reported the preparation of nanocomposites with a cellulose acetate butyrate matrix using trimethylsilylated cellulose whiskers [112]. However, these modifications not only are complicated to perform but also have negative effect on the properties of the composite, from using modified cellulose nanofibers. It has been found that the unmodified nanofibers showed better mechanical and reinforcing performance than the modified ones [112,113]. Besides the difficulty in dispersion of cellulose nanostructures, they are not commercially available, and their production is time-consuming, resulting in a low yield [111].

12.5 Applications

The advanced nanofiber-reinforced polymer composites (NFRCs) contribute to enhancing the development of new resin composite materials for a wide range of applications. Fig. 12.3 shows a survey of publications related to the applications of NFRCs.

The data clearly demonstrate that the improvement of durability and longevity of the materials constitutes the major application area, and hence, the NFRCs can be applied to design constructions such as aircraft, automotive industry, buildings, bridges, and railways. However, most of the studies conducted are focused mainly on the characterization and mechanical properties of the composite materials. The applications of NFRCs can also be extended to the electric and electronic field starting from flexible electrodes to conductive support materials. Through the use of NFRCs in fuel cells [114,115], dye-sensitized solar cells [116], lithium-ion batteries [117,118], and supercapacitors [119,120]; it seems to be possible to promote energy storage and efficiency. Furthermore, NFRCs are one of the extensively used membranes for

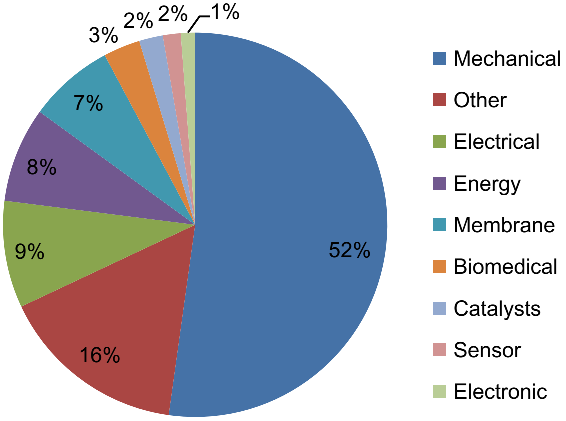


Fig. 12.3 Publication distribution showing application fields of nanofiber-reinforced composites (data analysis of publications was done using the Web of Science at 07 Nov. 2016).

separation and filtration applications such as water treatment and food processing [121–123]. In addition, NFRCs are finding potential applications in biomedical engineering, particularly in the areas of drug delivery systems [124] and scaffolds for tissue/bone [125,126]. Recently, the interest on nanofibers as reinforcing agent in dentistry has been rapidly growing [127,128]. Currently, available resin composites are made of fibers at a larger scale. Although nanoscale fibers that can be used to make resin composite stringer and tougher are desirable for their benefits, there are no commercially available nanofiber materials in dental applications. Moreover, the use of natural nanofibers such as cellulose, chitin, and chitosan is highly promising to develop new bio-based composites for regeneration/remineralization in endodontics or drug delivery systems for periodontal diseases [129]. NFRCs can also be used as supports for catalysts and sensors [130,131]. In the near future, NFRCs will be applied to a wide variety of applications as novel materials/tailored structures, since the properties of the composites can be adjusted by changing the parameters of the fiber such as fiber type, volume fraction, and diameter.

12.5.1 Future trends

The field of nanofiber-reinforced composites has been growing considerably in recent years. Both the use of electrospun fibers within the polymer matrix and incorporation of nanomaterials including fibers, particles, and tubes into the polymer fibers lead to improvements in mechanical strength, modulus of elasticity, and conductivity of the composite. Considerable work is still required including the successful incorporation of nanomaterials into polymer matrix with a high loading content, understanding of the structure-property relationship, and fabrication of low-cost nanofiber-reinforced composite at a large scale. A significant issue to be considered is nanosafety for the safe and sustainable development of advanced composites. Although it is not known which side effects nanomaterials can have on living cells so far, necessary precautions should be taken while using nanomaterials in laboratory and industrial scale. To this respect, development of natural fiber-reinforced biocomposites based on green polymer forms one of the emergent areas in material science raising awareness for use in a variety of applications.

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