Novel nanocomposites and nanoceramics based on polymer nanofibers using electrospinning process—A review

Ioannis S. Chronakis

IFP Research, Swedish Institute for Fiber and Polymer Research, Box 104, SE-431 22 Mölndal, Sweden

Abstract

Electrospinning is a very simple and versatile process by which polymer nanofibers with diameters ranging from a few nanometers to several micrometers (usually between 50 and 500 nm) can be produced using an electrostatically driven jet of polymer solution (or polymer melt). Significant progress has been made in this process throughout the past few years and the resultant nanostructures have been exploited to a wide range of applications. This review covers the active research area of producing ceramic and composite nanofibers with various compositions and properties by means of the electrospinning process. Current critical issues are discussed, such as carbon nanofibers made from electrospun precursor polymer nanofibers, encapsulation and alignment of carbon nanotubes within nanofibers to construct unique functional composite nanostructures, and organic–inorganic nanofibers (hybrids).

Keywords: Electrospinning process; Polymer nanofibers; Nanocomposites; Nanoceramics; Carbon nanotubes; Carbon nanofibers

1. Introduction—electrospinning process

Electrospinning is a simple and versatile method for generating ultrathin fibers from a rich variety of materials that include polymers, composites and ceramics [1–9]. This non-mechanical, electrostatic technique involves the use of a high voltage electrostatic field to charge the surface of a polymer solution droplet and thus to induce the ejection of a liquid jet through a spinneret (Fig. 1). In a typical process, an electrical potential is applied between a droplet of a polymer solution, or melt, held at the end of a capillary tube and a grounded target. When the applied electric field overcomes the surface tension of the droplet, a charged jet of polymer solution is ejected. The route of the charged jet is controlled by the electric field. The jet exhibits bending instabilities caused by repulsive forces between the charges carried with the jet. The jet extends through spiralling loops; as the loops increase in diameter the jet grows longer and thinner until it solidifies or collects on the target [10–15]. In the case of a melt the discharged jet solidifies when it travels through the air and is collected on the grounded metal screen.

The following parameters and processing variables affect the electrospinning process [5,6,16]: (i) system parameters such as molecular weight, molecular weight distribution and architecture (branched, linear, etc.) of the polymer, and polymer solution properties (viscosity, conductivity, dielectric constant, and surface tension, charge carried by the spinning jet) and (ii) process parameters such as electric potential, flow rate and concentration, distance between the capillary and collection screen, ambient parameters (temperature, humidity and air velocity in the chamber) and finally motion of the target screen. For instance, the polymer solution must have a concentration high enough to cause polymer entanglements yet not so high that the viscosity prevents polymer motion induced by the electric filed. The solution must also have a surface tension low enough, a charge density high enough, and a viscosity high enough to prevent the jet from collapsing into droplets before the solvent has evaporated. Morphological changes can occur upon decreasing the distance between the syringe needle and the substrate. Increasing the distance or decreasing the electrical field decreases the bead density, regardless of the concentration of the polymer in the solution. Applied fields can moreover influence the morphology.
in periodic ways, creating a variety of new shapes on the surface. In addition to creating round nanofibers, electrospinning a polymer solution can produce thin fibers with a variety of cross-sectional shapes. Branched fibers, flat ribbons, ribbons with other shapes, and fibers that are split longitudinally to form larger fibers have been observed [17,18].

2. Characteristics of electrospun nanofibers

Polymer nanofibers (Fig. 2) have a diameter in the order of a few nanometers to over 1 μm (more typically 50–500 nm) and possess unique characteristics, such as: extraordinary high surface area per unit mass (for instance, nanofibers with ~100 nm diameter have a specific surface of ~1000 m²/g), coupled with remarkable high porosity, excellent structural mechanical properties, high axial strength combined with extreme flexibility, low basis weight, and cost effectiveness, among others.

Choice of the polymer solutions, co-processing of polymer mixtures, chemical cross-linking of the formed nanofibers, etc., can provide a variety of pathways for controlling the chemical composition of electrospun nanofibers with a wide range of properties (such as strength, weight, elasticity, porosity, charged surface area, etc.). The electrospinning technique also provides the capacity to lace together a variety of types of nanoparticles or nanofillers to be encapsulated into an electrospun nanofiber matrix. Carbon nanotubes, ceramic nanoparticles, etc. may be dispersed in polymer solutions, which are then electrospun to form composites in the form of continuous nanofibers and nanofibrous assemblies. Various preparation techniques that allow the simultaneous introduction of specific functions into nanofibers have recently been developed [5–9]. Electrospun nanofibers can furthermore be aligned to construct unique functional nanostructures, such as nanotubes and nanowires.

Another interesting aspect of using nanofibers is that it is feasible to modify not only their morphology and their (internal bulk) content but also their surface structure to carry various functionalities [19,20]. Nanofibers can be easily post-synthetically functionalized (for example by chemical or physical vapour deposition). Furthermore, it is even feasible to control secondary structures of nanofibers in order to prepare nanofibers with core/sheath structures, nanofibers with hollow interiors and nanofibers with porous structures [6].

Overall, the main advantage of this top-down nanomanufacturing process is its relatively low cost compared to that of most bottom-up methods. The resulting nanofiber samples are often uniform and continuous and do not require expensive purification (unlike submicrometer-diameter whiskers, inorganic nanorods and carbon nanotubes) [1]. Hence, polymer nanofibers mats are being considered for use in composite materials reinforcement, sensors, filtration, catalysis, protective clothing, biomedicai applications (including wound dressing and scaffolds for tissue engineering, implants and membranes), space applications such as solar sails, and micro- and nanoelectronics (nanowires, LEDs, photocells, etc.). Carbon nanofibers made from polymeric precursors further expand the list of possible uses for electrospun nanofibers [6,8].

This review covers the active research area of the production of composite and ceramic nanofibers with various compositions and properties using electrospinning. Current critical issues are discussed, such as encapsulation and alignment of carbon nanotubes within nanofibers to construct unique functional composite nanostructures, carbon nanofibers made from electrospun precursor polymer nanofibers, and a new class of nanocomposites materials based on organic and inorganic species (hybrids) combined using electrospinning.
3. Carbon nanotubes within nanofibers

Nanotubes of carbon (CNT) and other materials are arguably the most fascinating materials that are important in nanotechnology today. Their unique mechanical, electronic and other properties are expected to result in revolutionary new materials and devices [1].

The idea of dispersing or aligning carbon nanotubes in a nanofiber matrix to form composite materials seems to be very promising from a mechanical and electrical perspective. The combination of high aspect ratio, small size, high strength and stiffness, low density, high conductivity, high flexibility and extensibility, ability to withstand cross-sectional and twisting distortions, and ability to withstand compression without fracture makes carbon nanotubes perfect candidates for the production of nanocomposite materials [21].

The electrospinning process was successfully used to embed single-walled carbon nanotubes (SWCNTs) in a poly(ethylene oxide) (PEO) matrix, forming composite nanofibers [22]. Initial dispersion of SWCNTs in water was achieved by the use of an amphiphilic alternating copolymer of styrene and sodium maleate. Nanotube alignment within the nanofibers was shown to depend strongly on the quality of the initial dispersions. Well-dispersed and separated nanotubes were embedded in a straight and aligned form, while entangled non-separated nanotubes were incorporated as dense aggregates. A high degree of orientation of the PEO crystals in the electrospun nanofibers with embedded SWCNTs was also observed.

The reinforcement and the rupture behaviour of carbon nanotubes–polymer nanofibers was studied in detail by Ko’s group [23-25]. Both single-wall carbon nanotubes and multi-wall carbon nanotubes (loadings as high as 10 wt.%) were used to reinforce polyacrylonitrile composite fibers synthesized by electrospinning (Fig. 3). A two-stage rupture behaviour of the composite fibers under tension, including crazing of polymer matrix and pullout of carbon nanotubes, was observed. They suggest that carbon nanotubes reinforce the polymer fibers by hindering crazing extension, reducing stress concentration, and dissipating energy by pullout (Fig. 4). Distribution of nanotubes in the polymer matrix and interfacial adhesion between nanotubes and polymers are two major factors that determine the reinforcement effect.
of carbon nanotubes in polymer fibers. Ko et al. treated car-
bon nanotubes in their presentation at the ASC 16th Annual
Technical Conference [26]. In that work, they co-electrospun a
mixture of carbon nanotubes and PEO solution. This pro-
cess aligns the carbon nanotubes (if well dispersed in the
polymer solution) in the resulting nanocomposites fibrils.
According to models, the mechanical properties of carbon
nanotube composites are higher than ordinary composites.

The electrospinning process was used by Ko et al. [27]
to process carbon nanotube reinforced spider silk. With
strengths approaching 4 GPa and a strain-to-failure exceed-
ing 35%, spider silk has been recognized as a model of a
strong, tough fiber. SWCNTs were successfully dispersed in
transgenic spider silk with various combinations of silk pro-
teins to form spinning dope for electrospinning. Nanofibers as
small as 10 nm were co-electrospun to form aligned and ran-
don nanofiber assemblies. Initial tensile testing of the aligned
silk composites showed a 10-fold increase in modulus, 5-fold
increase in strength, and 3-fold increase in toughness with
only 1 wt.% of SWCNT in a silk matrix. These initial find-
ings may have implications in a broad range of applications
including tissue engineering, scaffolds and ballistic armor
[21].

Mack et al. [28] also utilized electrospinning to study the
elastic properties of nanoplatelet/PAN nanocomposite fibril-
s. The goal of this work was to develop linear, planar and
3D assemblies of the nanocomposite fibrils for macroscopic
composites. Graphite was intercalated with potassium to form
the first stage intercalation compound, KC₈, and then exfol-
iated in aqueous solvents to produce graphite nanoplatelets.
The nanoplatelets were then dispersed in a 7 wt.% polyacryl-
oneitrile (PAN) solution in N,N-dimethylformamide to form
nanoscale fibrils by electrospinning. The elastic moduli of
the nanocomposite fibrils were measured by atomic force
microscopy. The average moduli were \(\sim 77, 113, 121,\) and
133 GPa, respectively, for nanoplatelet contents of 1, 2, 3,
and 4 wt.%.

Reneker and co-workers [29] observed for the first time
that the orientation of the carbon nanotubes within the
nanofibers was much higher than that of the PAN polymer
matrix crystal. This suggests that not only surface tension
and jet elongation but also slow relaxation of the carbon
nanotubes in the nanofibers is a determining factor in the
orientation of carbon nanotubes. The extensive fine absorp-
tion structure detected in UV–vis spectroscopy indicated that
charge-transfer complexes formed between the surface oxi-
dized nanotubes and negatively charged (\(-\text{CN})\) functional
groups in PAN during electrospinning, leading to a strong
interfacial bonding between the nanotubes and the surround-
ing polymer chains. As a result of the highly anisotropic
orientation and the formation of complexes, the composite
nanofiber sheets possessed enhanced electrical conductiv-
ity, mechanical properties, thermal deformation temperature,
thermal stability, and dimensional stability.

Haddon and co-workers [30] also studied single-walled
carbon nanotube reinforced polymer composite membranes
using the electrospinning technique. Nanofibers with diam-
eters in the range of 50–100 nm were obtained by elec-
trospinning SWCNT filled polystyrene composites. TEM
observations revealed the incorporation of small SWCNT
bundles oriented parallel to the nanofiber axis. As-prepared
and ester functionalized SWCNTs have also been electrospun
with polyurethane to demonstrate the effect of the chemical
functionalization of SWCNTs on the mechanical properties
of SWCNT reinforced composites. The tensile strength of
ester functionalized SWCNT-PU membranes was enhanced
by 104% as compared to electrospun pure polyurethane mem-
branes, while an increase of only 46% was achieved when
as-prepared SWCNT was incorporated in the polyurethane
matrix. The tensile modulus of as-prepared and ester func-
tionalized SWCNT-PU membranes were found to be 215% and
250% higher, respectively, than the control polyurethane
membranes.

The above studies furthermore highlight the fact that
the intrinsic crystalline quality and the straightness of the
embedded nanotubes are significant factors influencing the
reinforcement capability. It should be mentioned that, owing
to the chaotic oscillation of the electrospinning jet (a char-
acteristic feature of the electrospinning process), randomly
oriented and isotropic structures in the form of nonwoven
nanofibers mats or webs are often generated due to a lack of
control over the forces driving fiber orientation and crystal-
lization.

4. Carbon nanofibers using electrospinning

The electrospinning technique is a novel way to prepare
carbon precursor fiber fabrics and yarns with fiber diameters
in the sub-micron to micron range. Production of nondirec-
tional, isotropic, nonwoven fabrics, unidirectionally oriented
nonwoven fabrics and yarns, and shaped pre-forms using
isotropic, continuous precursor fibers via electrospinning
is feasible [31]. Successful control of the fabrication and
manipulation of carbon nanofibers is possible by control-
ling some of the properties for the fabrication of nanofibers.
For instance, the thickness of the fibers can be controlled by
varying the voltage and viscosity. In addition, changing the
heating temperature can control the carbon contents. Other
factors, such as distance, shape of the collection plate, angle
of the syringe, etc. and the ability to orient the precursor fibers
during fabrication, can also alter some of the properties.

Various carbon nanofibers have been produced from elec-
trospun precursor fibers and characterized physically and
structurally (Fig. 5). Chun et al. from Reneker's group [32]
used electrospinning to produce carbon nanofibers with very
high aspect ratios. Electros spun carbon precursor fibers, based
on polyacrylonitrile and mesophase pitch, having diame-
ters in the range of 100 nm to a few microns, were sta-
bilized and carbonized. Nanopores were then produced in
carbon nanofibers by a high temperature reaction with water
vapour carried in nitrogen gas, a process known to increase
the surface area per unit mass of carbon black. The same group [33] also prepared composite nanofiber sheets of well-aligned polyacrylonitrile nanofibers (PAN) containing multi-wall carbon nanotubes (MWCNTs) by electrospinning. It was noted that carbonization processes showed that a higher concentration of MWCNTs effectively resisted the heat shrinkage of the composite nanofiber sheet.

The concept of assembling nanofibers into aligned nanorays and highly ordered structures for functional embedment in composites has significant technological implications. The electrospinning process was examined by Fennessey and Farris with the aim of preparing carbon nanofibers for the reinforcement of thin films and nanocomposites [31]. Various system (polymer solution) and process parameters were examined and the results were used to scale up fiber collection. Tows of unidirectionally and molecularly oriented PAN nanofibers were prepared using a high speed, rotating take-up wheel. The aligned tows were twisted into yarns, and the mechanical properties of the yarns were determined as a function of twist angle. Unidirectional and non-directional nonwoven fabrics and yarns of continuous carbon precursor filaments were also prepared. They suggested that the ability to orient the precursor fibers during the fabrication of the fabrics allows for the production of carbon nanofibers with mechanical properties comparable to those of carbon fibers prepared by conventional methods.

The fabrication and properties of carbon nanofibers are furthermore interesting because of the fiber’s expected conductivity properties. If the fabrication and manipulation of carbon nanofibers can be controlled successfully it should be possible to build nanoscale electronics. In an attempt at this, Santiago-Avilés and co-workers [34–36] successfully controlled some of the properties in the fabrication of nanofibers and produced aligned, structurally oriented, and mechanically useful carbon precursor fibers with diameters in the nanoscale range. Carbon nanofibers were obtained by electrospinning polyaniline and heat treating the material on a vacuum furnace to obtain carbon nanofibers.

Kim et al. [37–39] electrospun polybenzimidazol (PBI) solutions of dimethyl acetamide and poly(acrylonitrile) solutions in dimethylformamide to form webs consisting of 250–300 nm ultrafine fibers. The webs were carbonized and activated by steam, which gave activated carbon nanofibers. The characteristics of supercapacitor electrodes of PBI-based carbon nanofiber web were studied. The same group also fabricated high-purity carbon sheets consisting of 250 nm nanofibers through the fiber formation of PBI by electrospinning and subsequent heat treatment up to 3000 °C without using the stabilization process (the most time-consuming step). As stated, the non-graphitic character of these nanofibers was the result of: (i) the low graphitization ability of the polymer itself, (ii) the limited graphitization of the size effect (small diameter) and (iii) the existence of internal pores formed during the electrospinning process.

In another study, the petroleum based isotropic pitch precursor (IPP) with a broad molecular weight distribution was electrospun [40]. After the dimethylformamide (DMF) soluble fraction was cut off from the IPP, the DMF insoluble pitch (DIP) solution in tetrahydrofuran was electrospun into web and then carbonized. Cutting out the DMF
soluble fraction from the IPP improved the spinnability in comparison with the IPP solution itself at the same spinning conditions. The prepared fibers showed a dumbbell-like cross-sectional shape, indicating an incompleteness of the splitting in the spinning process with the fiber size of 4–6 \(\mu m\) in the long axis and 2–3 \(\mu m\) in the short axis. The electrical conductivity of the web was high and increased from 63 to 83 S/cm with an increase in carbonization temperature from 1000 to 1200 \(^\circ C\). It was suggested that such carbonized fibers can have applications in various kinds of electrodes.

Electrospun polyacrylonitrile nanofibers with Fe(acetylacetonate) as the catalyst precursor were carbonized and used as substrates to form multi-walled carbon nanotubes [41]. The multi-walled carbon nanotubes were formed by an iron catalyzed growth mechanism (Fig. 6). Electrospun polymer nanofibers were made with diameters ranging from a few nanometers to several micrometers and were collected in a highly porous thin sheet. Multi-walled carbon nanotubes grown on such carbonized nanofibers substrates form a characteristic hierarchical structure. Hexane vapor was used as a source of carbon for the formation of carbon nanotubes. The length of the carbon nanotubes depended on the length of time the hexane vapor was supplied (longer times yielded longer carbon nanotubes and shorter times yielded shorter carbon nanotubes). These structures can be used for example to design and construct high-performance filters, reinforced composites and highly porous carbon nanoelectrodes.

5. Organic–inorganic nanofibers (hybrids)

A new class of nanocomposites materials based on organic and inorganic species combined at a nanoscale has recently obtained more attention [6,20,42,43]. These so-called organic–inorganic hybrids have both the advantages of organic materials, such as light weight, flexibility and good moldability, and inorganic materials, such as high strength, heat stability and chemical resistance. These composites are expected to find applications in catalytic membranes, ultrafiltration, scratch- and abrasive-resistant hard coating, non-linear optical materials, contact lenses, and reinforcement of elastomers and plastics [42,43].

Larsen et al. were the first to combine electrospinning with sol–gel methods to design vesicles and nanofibers made from inorganic oxides and hybrid (organic/inorganic) materials with diameters in the micrometer and submicrometer range [43]. One of the advantages of the proposed technique is that the core-to-shell mass ratio can be precisely set by adjusting the two liquid flows, effectively providing a means (in conjunction with voltage) to control shell and core size. As they concluded, the proposed approach is also quite general. Various ceramic metal oxide fibers (with diameters between 200 and 400 nm) were obtained by high temperature calcinations of the precursor organic–inorganic composite nanofibers assembled by electrospinning (Figs. 7 and 8 and Table 1). It was generally observed that the calcination temperature has a great influence on both the crystalline phase and the surface morphology of the fibers.

Fig. 6. Transmission (a) and scanning (b) electron micrographs of carbon nanotubes on nanofibers produced by electrospinning polyacrylonitrile fibers, carbonization of the polyacrylonitrile, and catalytic growth of carbon nanotubes [41].

Fig. 7. Morphology of palladium acetate/poly carbonate (PdAc/PC) composite fibers. SEM photographs of (a) PdAc/PC calcined fibers at 550 \(^\circ C\) and (b) PdAc/PC calcined fibers at 800 \(^\circ C\) (PdAc/PC fibers with 70 wt.% of palladium acetate are used for the calcinations under air) [54].
Xia and co-workers [44–46] extensively studied the formation of polymeric and ceramic nanofibers as uniaxially aligned arrays as well as the fabrication of composite and ceramic hollow nanofibers by electrospinning (Fig. 9). Thus, for instance, when an ethanol solution containing both poly(vinyl pyrrolidone) (PVP) and titanium tetraisopropoxide was injected through a needle under a strong electrical field, composite nanofibers made of PVP and amorphous

\[ \text{TiO}_2 \]

were formed as a result of electrostatic jetting. These nanofibers could subsequently be converted into anatase

\[ \text{TiO}_2 \rightarrow \text{anatase} \]

without changing their morphology via calcination in air at 500 °C. The average diameter of these ceramic nanofibers could be controlled in the range of 20–200 nm by varying a number of parameters, such as the ratio between PVP and titanium tetraisopropoxide, their concentrations in the alcohol solution, the strength of the electric field, and the feeding rate of the precursor solution [44]. Moreover, hollow nanofibers with walls made of inorganic/polymer composites or ceramics were prepared by electrospinning two immiscible liquids through a coaxial, two-capillary spinneret, followed by selective removal of the cores. The capability and feasibility of this technique were demonstrated by the fabrication of titania/polymer or anatase nanotubes whose size and wall thickness could be independently varied by controlling a set of experimental parameters. The presence of a sol–gel precursor in the sheath liquid was necessary for the formation of stable, coaxial jets and hollow fibers with robust walls. The authors pointed out that the circular cross-section, uniform size, and well-controlled orientation of these long hollow nanofibers are particularly attractive for use in fabricating microfluidic devices and optical waveguides.

6. Nanofiber-featured composites matrices

The mechanical properties and reinforcing behaviour of continuous nanofibers differ significantly from the finite length of their conventional counterparts (engineering fibers such as carbon, glass and Kevlar fibers) that are used as reinforcements in composite developments. The high aspect ratio (l/d), large available surface area, surface morphology, and potential homogeneous dispersion of nanofibers throughout the matrix make electrospun fibers of great interest as fillers in composite matrices [31]. Continuous, electrospun fibers are expected to have better interfacial adhesion than conventional fibers due to electrospun fibers’ large surface-to-volume ratio. This gives an increase in the surface area that is available

![Fig. 8. Morphology of niobium oxide fibers. SEM images of 50 wt.% niobium oxide/poly(vinyl acetate) fibers: (a) calcined at 700 °C and (b) calcined at 1000 °C [47].](image)

<table>
<thead>
<tr>
<th>Ceramic metal oxide fibers prepared by high temperature calcinations of electrospun organic–inorganic composite nanofibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor electrospun nanofiber</td>
</tr>
<tr>
<td>----------------------------------</td>
</tr>
<tr>
<td>Aluminum di-sec-butoxide ethylacetate/acidic H₂O/EtOH</td>
</tr>
<tr>
<td>Cobalt acetate/nickel acetate/poly(vinyl acetate)</td>
</tr>
<tr>
<td>Cobalt acetate/poly(vinyl acetate)</td>
</tr>
<tr>
<td>Copper acetate/poly(vinyl acetate)</td>
</tr>
<tr>
<td>Magnesium titanate/poly(vinyl acetate)</td>
</tr>
<tr>
<td>Nickel acetate/poly(vinyl acetate)</td>
</tr>
<tr>
<td>Nickel acetate/zinc acetate/poly(vinyl acetate)</td>
</tr>
<tr>
<td>Nickel titanate/poly(vinyl acetate)</td>
</tr>
<tr>
<td>Niobium oxide/poly(vinyl acetate)</td>
</tr>
<tr>
<td>Palladium acetate/poly(vinyl pyrrolidone)</td>
</tr>
<tr>
<td>Ruthenium-doped titanium dioxide/poly(vinyl acetate)</td>
</tr>
<tr>
<td>Titanium tetraisopropoxide/poly(vinyl pyrrolidone)</td>
</tr>
<tr>
<td>Zirconium oxychloride/poly(vinyl acetate)</td>
</tr>
<tr>
<td>Zinc acetate/poly(vinyl acetate)</td>
</tr>
<tr>
<td>Vanadium sol/poly(vinyl acetate)</td>
</tr>
</tbody>
</table>
Fig. 9. SEM images of uniaxially aligned nanofibers made of different materials: (a) TiO$_2$/poly(vinyl pyrrolidone) composite, (b) polycrystalline TiO$_2$, (c) polycrystalline Sb-doped SnO$_2$ and (d) polycrystalline NiFe$_2$O$_4$. The insets show enlarged SEM images of the corresponding ceramic nanofibers [45].

to adhere to a matrix material, leading to better reinforce-
ment than conventional fibers. Because of the electrospun
fibers’ irregular void structure between fibers of the fabric
and the hairiness of the yarns, electrospun fabrics and yarns
are also expected to take advantage of the mechanical inter-
locking mechanism of load transfer between the matrix and
nanofibers, and may significantly enhance the performance
of a composite.

Kim and Reneker [59] investigated the use of aro-
matic heterocyclic polybenzimidazole (PBI) nanofibers fab-
ric as reinforcement in an epoxy and a rubber matrix
(styrene-butadiene). The average diameter of the electro-
spun fibers was about 300 nm and the mass per unit area
of this fabric was a few tens of g/m$^2$. They observed that
the epoxy was toughened by the nanofibers (15 wt.%), and
this reinforcing effect was higher than that of PBI fibroids
(whisker-like particles). Moreover, the PBI nanofibers can
provide dramatic reinforcement of a rubber matrix (i.e. the
Young’s modulus was 10 times higher and the tear strength
was twice as large as in the unfilled rubber). The electrospun
nanofibers were found to be birefringent, which indicates
that the molecules were aligned. In another work, the rein-
forcement effect of the ultrathin fibers of Nylon-4,6 with
a semi-infinite length prepared by electrospinning solutions
of the polymer in formic acid was clearly demonstrated by
Bergshef and Vancso [60]. These nanofibers can be applied
to prepare transparent composites with an epoxy matrix. They
observed that, at certain given process parameters, the jet of
Nylon-4,6 solution that is pulled from the capillary tip during
the electrospinning process can splay into several finer jets.

The potential of using polymer nanocomposites as a founda-
tion for fabricating nanofibers structures was illustrated by the
work of Fong et al., who demonstrated the dissolution and
reprocessing of exfoliated montmorillonite-Nylon 6 (NLS)
nanocomposite [61]. They also exerted hierarchical control
of morphology and form through the combination of a nanos-
structured material and a nanoscale fabrication technique. The
electrospinning process resulted in highly aligned montmo-
rillonite layers (layer normal perpendicular to the fiber axis)
and Nylon 6 crystallites (layer normal parallel to fiber axis).
Moreover, because the cross-sections of electrospun fibers are
small, composites fabricated using this method can maintain
their optical transparency, which can make them suitable for
various kinds of novel composite applications.

Because of the difficulty in handling micro- and nanoscale
fibers and measuring the small load required for deformation,
the mechanical properties of these fibers have not been widely
characterized. It should be noted that reports of measure-
ments of the elastic properties of electrospun fibers are very
limited in the literature. Investigation the failure behaviour
of electrospun polymer nanofibers reveals that the nanofibers
fail by a multiple necking mechanism, sometimes followed
by the development of a fibrillar structure [62]. Ko et al.
[23] used the AFM technique to measure the elastic modulus
of a single fiber of the electrospun PAN polymer solution.
Details on the use of AFM to measure the elastic prop-
erties of a nanocomposite made from electrospun graphite
nanoplatelets and SWCNT dispersed in PAN polymer solu-
tion were also discussed. They found a five-fold effect for
both nano-reinforcements in the nanocomposites more than
the rule of mixture and called that the nano-effect value.

More recently, a tensile test of a single-strand polycaprolac-
tone electrospun ultrafine fiber was done using a nano tensile
tester [63]. The tested fiber exhibited the characteristic low
strength and low modulus but high extensibility at room tem-
perature. The mechanical properties were also found to be
dependent on fiber diameter. Fibers with a smaller diameter
had a higher strength but lower ductility due to the higher
There is currently strong interest in materials with the flexibility and non-corrosiveness of polymers and the electrical conductivity of metals. Thus a great deal of interest in the development of nanofiber reinforced polymer composites exists, not only because of their potential for high strength but also for their electrical and thermal properties. El-Aufy in Ko’s group [64] successfully co-electrospun single-walled carbon nanotubes (SWCNTs) and conductive poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonate) (PEDT/PSS) with poly(acrylonitrile) to form conducting nanofibers. The inclusion of SWCNTs showed a further increase in the electrical conductivity of nanofibrous yarn, and the tensile strength increased by 50%. In this study a rotary dry electrospinning disc was designed to align the electrospun fibers and the rotating speed of the disc was studied to find the optimum condition for aligned uniform nanofibers. Note that intrinsically conductive polymers such as poly(3,4-ethylene dioxythiophene) (PEDT) are an important class of electroactive polymer that are used in the form of films for electronic devices such as LED. In another work, however, poly(methyl methacrylate) (PMMA) nanocomposites containing well-dispersed, multi-walled carbon nanotubes (MWCNTs) were prepared via an in situ bulk polymerization of methyl methacrylate (MMA) in the presence of carbon nanotubes (CNTs) and then electrospun [65]. It was reported that the conductivities were reduced to \( \sim 10^{-10} \text{S/cm} \), even though the dispersion of the MWCNTs in the electrospun nanofibers was superior to the conventional polymer composites with carbon nanotubes. The diameter of the electrospun fibers ranged between 120 \( \pm \) 30 and 730 \( \pm \) 20 nm and MWCNTs in the electrospun nanofibers were found to be embedded in the polymer matrix and to align along the fiber axis.

In addition, natural materials such as bone, tooth and nacre are very effective examples of nanocomposites consisting of proteins and minerals. The concept of exploiting the unusual properties of nanoscale reinforcement using electrospun nanofibers may find widespread interest in restorative bioocomposites. Some work has been done, although it is not within the scope of this review to address these efforts. Recently, for instance, electrospun Nylon PA 6 nanofibers were used to improve the mechanical properties of Bis-GMA/TEGDMA (50/50, mass ratio) dental restorative composite resins (Fig. 10) [66]. Three-point bending test results indicated that the flexural strength, elastic modulus and work of fracture of the nanofiber reinforced composite resins were all significantly increased with relatively small amounts of Nylon 6 nanofibers. The addition of 5 wt.% PA 6 nanofibers in the composite resin improved the flexural strength by 36%, the elastic modulus by 26% and the work of fracture by 42% over that of the neat resin. However, a further increase of the mass fraction of nanofibers did not improve the mechanical properties of the composite resin. SEM observations showed that the fracture surface of the composite resin was rough, while the fracture surface of the neat resin was smooth and had large fracture steps. It is suggested that the presence of nanofibers deflected the crack. When the crack finally broke away from the nanofibers, numerous fracture lines and steps were created on the fracture surface, resulting in a consumption of energy during the fracture.

7. Conclusions and remarks on future challenges

Electrospinning is a very simple and versatile method of creating polymer-based high functional and high performance nanofibers that can revolutionize the world of structural materials. The process is versatile in that there is a wide range of materials that can be spun. At the same time electrospun nanofibers possess unique and interesting features. This assembly approach can also be expanded into a hierarchical assembly of produced nanofibers in other well-defined functional nanostructures. The various approaches that have recently been developed for the scientific understanding, engineering control and potential implementation of electrospun nanofibers to form functional composites and ceramic nanofibers are summarized in this review. Nevertheless, certain essential studies are still required and many challenges remain to be faced.

Integration of nanofibers into nanomatrices requires nanofibers with well-controlled orientation, size, and other target characteristics, as well as reproducibility in locating...
them in specific positions and orientations. The ability to do so, however, remains a major challenge in the field.

The use of carbon nanotubes to reinforce and enhance the performance of composite can produce a new generation of nanocomposite materials. Obviously, several difficulties arise when nanotubes are embedded in composite matrices. Particular problems have to do with dispersion and an understanding of nanotube behaviour in solutions. Alignment in the matrices is another major difficulty (since CNTs are anisotropic, they must be aligned in the composite matrix to achieve the optimal mechanical properties), while bonding to the matrices can also be difficult (carbon nanotubes have inert graphite surfaces). Thus, further studies are needed to overcome critical issues with CNT embedment in nanocomposites during processing and large scale manufacturing. Moreover, further attention must be given to organic–inorganic nanofibers by electrospinning, as such materials combine the advantage of nanocomposites and ultrathin nanofibers. Furthermore, as is evident, there is less information available on the mechanical properties of nanofibers and nanofiber composites with or without the use of carbon nanotubes. Research on the mechanical properties of nanofibers and their composites from a variety of polymers is essential for a greater understanding of their contribution and performance.

Combining the new well-established field of electronic polymers with the emerging field of nanofibers can potentially develop a new technology. Introducing the electrospinning process for the purpose of forming nanofibers of pure electronic polymers (in their semiconducting and metallic regimes) and/or their blends in conventional organic polymers opens the way for enormous applications. The use of nanofibers in conducting media is of significant interest because of the potentially high range of conductions that can be obtained with significant processing versatility and because of their flexibility and light weight. Conductive nanofibrous assemblies can provide the fundamental building blocks for the construction of nanostructures. Producing smart nanostructures that possess electrical, electronic, magnetic, optical properties, mechanical and sensing properties (mass, strain and pressure sensing) and demonstrate processability as a result of embedded nanofibers remains a major challenge. It is worth mentioning that other functional molecules, biomolecules or nanoparticles could also easily be incorporated into the electrospinning solutions to generate a combination of nanofiber functionalities.

Finally, the design and construction of process equipment for controllable, reproducible and continuous mass electrospinning production would represent the most efficient translation of the properties of nanofibers and could act as a stimulus to the manufacture of new products.

References


