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# Highly Anisotropic Polymer Composites Based on Carbon Nanotubes

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.71533>

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## Abstract

Properties of polymers can be optimized through processing methods or by the addition of nanofillers. Carbon nanotubes (CNTs) have gained attention due to their promising behavior. Carbon nanotubes are essentially a sheet of graphene wrapped into a cylindrical shape with either a single or multiple walls. Tube diameters are approximately nanometres, but they can be micrometres in length. Due to the unique properties of nanotubes, they offer promise in composite materials with current research dedicated to embedding them in a polymer matrix. If improvements are to be made, the nanotubes need to be in an aligned configuration. This presents challenges due to the strong intermolecular forces that cause nanotube agglomeration leading to poor quality dispersion and random CNT orientations. Thus, there are two particular challenges to the formation of polymer composites based on CNTs: dispersion and alignment, and these are the focus of this chapter. We consider recent developments in the synthesis of carbon nanotubes and their properties. Next, we detail the challenges of dispersion and alignment that are presented in the preparation of polymer/CNT composites. Finally, we review the literature to identify progress made in preparing high performance polymer/CNT composites and their properties and present one particular solution.

**Keywords:** composites, alignment, polymer, carbon nanotube

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## 1. Introduction

The properties of polymer-based materials can be substantially modified and enhanced through the inclusion of filler particles. Carbon nanotubes (CNTs) exhibit high flexibility, low mass density and high values of the aspect ratio in excess of 1000. Some types of carbon nanotubes can exhibit metallic or semi-conducting behaviour and coupled to the high

tensile strength and modulus; this combination is ideally suited to their use in composites. The first polymer nanocomposites using CNTs were reported in the 1990s [1] and since then there has been worldwide activity on the methodology to optimise the preparation of such nanocomposites to fully deliver on their promise. Major problems that have been encountered are aggregation of the carbon nanotubes, thereby limiting the full dispersion of the nanoparticles in the polymer matrix, which has a deleterious impact on the properties. Equally the image of a stiff rod embedded in a polymer matrix is far from the reality, and hence carbon nanotubes are often coiled within the polymer matrix and the lack of macroscopic alignment of the tubes severely limits their properties. A wide variety of approaches have been explored including in-situ polymerisation of the matrix, functionalisation of the carbon nanotubes and the use of electric fields to align the carbon nanotubes. This chapter reviews these challenges of dispersion and alignment in the light of recent work both by the authors and that reported in the literature. We identify an approach most likely to succeed.

## 2. Synthesis-property relationships for carbon nanotubes

The ideal carbon nanotube is a nanoscaled graphene (one leaf of graphite) that is rolled up into a cylindrical shape; structures containing only one wall of cylinder are called single walled carbon nanotubes (SWCNTs), whereas structures with two or more concentric graphene cylinders are termed multi-walled carbon nanotubes (MWCNTs) [2].

Since their discovery in 1991 by Iijima [3], carbon nanotubes have been the subject of a worldwide attention because of their unique properties and associated wide range of applications [4–15]. Over the past two decades, nanotubes have found applications in various areas, such as sources of field emissions, photodetectors, non-volatile memory, ultra-sensitive chemical and transparent conducting membranes, biosensing devices, double layer-type capacitors, transparent electrode films, radio wave absorbents and even in modern electronics.

The most common and widely used nanotube synthesis techniques are arc discharge, chemical vapour deposition and laser ablation [16–21]. CNTs were first produced by arc discharge process or by laser ablation methods; however, recently there has been a significant increase in the synthesis of CNTs by catalytic chemical vapour deposition (CCVD). The catalytic CVD method is an easy and cheap way to produce CNTs at low temperatures and pressures. Compared to the other methods, catalytic CVD provides a higher yield and higher purity of the grown nanotubes and allows control of the parameters of the growth and structure of CNTs.

Hydrocarbons obtained from fossil fuels and the hydrocarbons from plants are the two main sources of carbon for the synthesis of CNTs. There are natural precursors and products containing carboniferous materials. Common fossil fuel CNT precursors are methane, ethylene, acetylene, benzene, xylene and carbon monoxide. There are several reports on the use of natural precursors for synthesis of CNT, such as camphor, turpentine oil, palm oil, etc. Nanoparticles of transition metals (Fe, Ni and Co) are usually used for the catalytic growth of

CNT [22]. Recently, CNT has also been produced from precious novel metal [23–27], catalysts based on ceramic nanoparticles [28, 29] and semiconductor nanostructures [30–33]. This work has led to a new interpretation of the role of the catalyst in growth of nanotubes in which sites of adsorption of carbon are necessary for fixing the nanodimensional curvature. For the growth of CNTs, the formation of nanocrystals of metallic catalysts via CCVD as well as the formation of non-conducting substrates on the surface is necessary. Typical substrates include aluminium oxide, silicon and magnesium oxide. Nevertheless, in spite of the advantages of the CVD method, still there are many problems connected with the growth of high-density CNTs with high purity. Even though many years have passed since the initial discovery of CNTs, it remains challenging to synthesise good quality and high length CNTs because of the many factors that influence the growth process.

There are various ways to use other CVD methods, such as water-assisted CVD [34, 35], oxygen-assisted CVD [36], hot filament CVD [37, 38], microwave plasma CVD [39] or radiofrequency CVD [40]. It is known that the catalysed decomposition of hydrocarbons form carbon fibres as fibrous carbon has been received by a cyanogen transmission on the heated porcelain in 1890 [41]. In 1980, Endo [42] developed the floating catalytic reactor with the use of particles of the catalyst with a diameter of 10 nanometres. This method is a predecessor of the production of CNT widely used today involving an aerosol [43–49] where pyrolysis of hydrocarbons takes place in the presence of a catalyst (Fe, Ni, Co, etc.) generating both MWCNTs and SWCNTs. Key parameters of the growth of CNTs using CVD are the atmosphere, a carbon source, the catalyst and temperature of growth. Low temperatures (300–800°C) lead to the formation of MWCNTs, whereas reaction at high temperatures (600–1150°C) promotes the growth of SWCNTs [50, 51].

The choice of catalyst and catalyst support are very important aspects which affect CNT expansion. Therefore, the preparation stage represents a decisive step in synthesis of CNTs. The influence of the structure and the morphology of the nanoparticles of the catalyst on the growth of CNTs by means of CVD are summarised in the review of Szabo et al. [52]. Flahaut et al. have reported the influence of the conditions of preparation of the catalyst for synthesis of CNTs by means of CCVD using as fuel, urea or citric acid. They have found that the more moderate conditions of burning achieved in the case of citric acid limit the formation of carbon nanofibres or increase the selectivity of the synthesis of CCVD towards CNT with a lower number of walls depending on the catalytic composition.

In order to solve these problems and to improve the main characteristics of CNTs, many miscellaneous fabrication approaches for carbon nanotubes have been considered. For example, Xiang et al. prepared CNT through CCVD using acetylene with a series of catalysts prepared from two-layer double Co/Fe/Al (LDHs) hydroxides. They have noted that the Co content in precursors exerted a noticeable impact on the growth of CNTs. An increase in Co content led to the formation of CNTs with smaller diameters and lower structural frustration [53].

Lyu et al. produced high-quality and high-purity double-walled carbon nanotubes (DWCNTs) by catalytic decomposition of benzene and Fe-Mo/Al<sub>2</sub>O<sub>3</sub> as the catalyst at 900°C. They observed DWNT bunches without any amorphous carbon and a low level of defects [54].

Zhang et al. produced MWCNTs with a diameter of 40–60 nanometres by catalytic decomposition of methane at 680°C within 120 minutes together with the use of binary aerogels with nickel oxide as the catalyst [55, 56]. Sano and his colleagues have identified two systems of metal catalyst/source of carbon for growth of CNTs: Ethanol/Co and benzene/Fe. In addition, they investigated two different reactors (the reactor with a gas stream and a liquid reactor) on quality of CNT [57].

Jiang et al. investigated growth of CNT in situ on previously processed graphite electrode (GE) through CCVD with the use of  $\text{Ni}(\text{NO}_3)_2$  as the catalyst [58]. The CNTs prepared with this method had external and internal diameters of 80 and 20, respectively. The length of the CNTs was observed as 200–1000 nanometres; this was attributed to the shorter time of growth. These authors were interested in the concentration of carboxyl and hydroxyl groups on the surface of carbon nanotubes as they are essential features for applications in many fields of science, such as nanomedicine, biosensors or polymeric nanocomposites [58].

A promising one-step method of fabricating carbon nanotubes is flame synthesis. It involves the direct combustion of hydrocarbons in the presence of an oxidiser. The CNTs are normally grown directly on an alloy substrate. The use of metal-organics such as iron pentacarbonyl, ferrocene or metal nitrate dissolved in fuel has been reported. To date, CNTs have only been reported to grow on alloy substrates.

Synthesis using a flame is a very energy efficient process because the fuel is a source of both heat and carbon. The temperatures can reach 1600 K, which is difficult to achieve by means of CVD in a typical furnace. For the synthesis of CNTs over a large area, it is more economic to use a rastering system and a repeated flame for the control of both time and the area of a flame [59]. The higher production efficiency and a lower energy consumption compared to CVD make this method suitable for industrial production. Synthesis using a flame represents a simple single-step method without the need of a substrate. The mechanism of the growth of CNTs in the synthesis of a flame of hydrocarbons can be divided into three main stages. In the first stage of this, hydrocarbon fuel pyrolysis in a previously heated zone results in the formation of hydrocarbon particles which will be a carbon source for CNTs; in second, particles of metal are formed on the surface of the alloy and in final stage, hydrocarbons are absorbed by the catalyst resulting in the growth of CNTs.

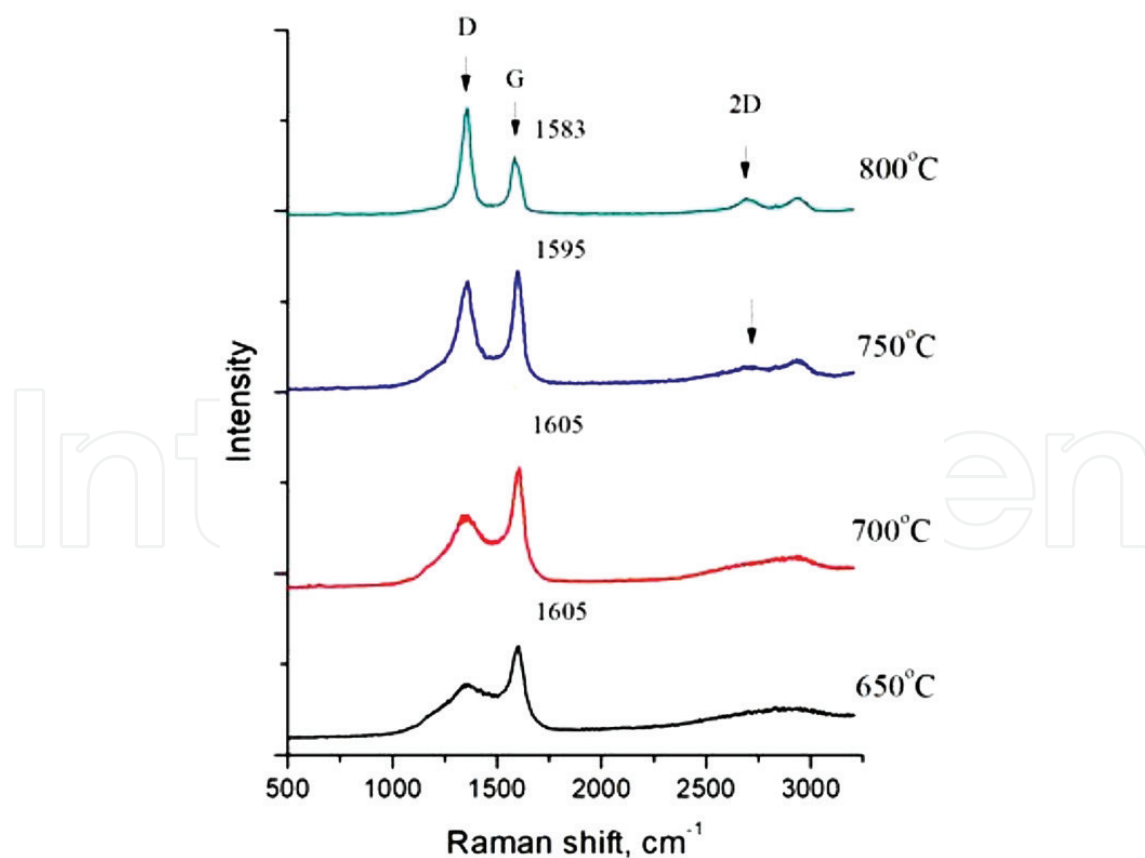
Institute of Combustion Problems (ICP), conducts research work on “Synthesis of carbon nanomaterials in flames.” We include here one example of report which has been performed in ICP. In this work, oil deposit soot, prepared when burning a propane-butane mixture with the use of electric field, has been chosen among various types of natural materials for preparing porous carbon material (PCM). The PCM is used as the catalyst carrier. We have prepared multiwalled nanotubes (MWNT). We are searching for new methods of creation of catalytic systems (catalyst/carrier), which allow for the control of the structure of carbon particles. This is an important problem, the solution to which can lead to the development of approaches to the synthesis of carbon nanotubes (CNT) with specific functional properties [60]. In addition, ICP has developed a new approach for CNTs synthesis from diatomite. In this work [61], multiwalled nanotubes were obtained using a chemical vapour deposition



method with diatomaceous earth as the substrate and nickel salt as a catalyst. In fact, the catalytic activity of Co and Ni is supported on diatomite and its role in the production of multiwalled carbon nanotubes has been investigated. In this specific example, the diatomite support was prepared by an impregnation method and the CNTs were synthesised on the surface of this as a substrate.

Diatomaceous earth, known as a diatomite, is a soft, powdery, porous and silica-rich mineral, which is found in fossilised deposits near dried up bodies of water. This mineral is the skeletal remains and the result of the accumulation of dead diatoms is found in marine sediments. Diatoms are microscopic single-celled algae that usually have shells that are divided into two halves. The shells of diatoms are hard due to the presence of silica in their cell walls. These silica-rich hard shells are usually found crushed up into tiny, sharp shards, which is the main characteristic of fossilised diatomite. Thanks to having properties, such as low density, high porosity, high surface area, abrasiveness, insulating properties, inertness, absorptive capacity, brightness and high silica content, diatomite has a wide variety of uses, and it is a component in many products. Many different methods of obtaining nanotubes from a variety of materials have been proposed up to this time, but to our knowledge, few have used diatomite.

**Figure 1** shows spectra for samples obtained on diatomite at temperatures of 650 and 700°C, peak G is located at 1605  $\text{cm}^{-1}$ .



**Figure 1.** Raman spectra of CNT samples on a diatomite.

The peaks D and G have a large width, which is characteristic of amorphous carbon. There is no clearly expressed second-order peak. These parameters, together with the analysis of SEM images, suggest that at these temperatures, the formation of CNTs on the diatomite does not occur or is weakly expressed [62].

When the synthesis temperature is raised to 750 and 800°C, the width of the peaks is significantly reduced, the position of the main peak G is shifted to the low-frequency region and in the case of 800°C is  $1583\text{ cm}^{-1}$ , which is a characteristic value for CNT, graphite and graphene.

There is a manifestation of the 2D peak, which indicates an increase in the degree of crystallinity of the structure and an increase in long-range order and, consequently, an improvement in the quality of CNTs [63].

The peak D arises as a result of defects in graphite structures, and the intensity ratio of the peaks D and G is usually considered an indicator of the quality of CNTs. In the case of CNT synthesised on diatomite, we observe an increase in the intensity of the defect peak with an increase in temperature. This is because an increase in the synthesis temperature makes it possible to reduce the volume of amorphous carbon, but increases the probability of oxidation and the formation of structural defects. In addition, at high synthesis temperatures, nanotubes with a large diameter predominate, which increase the probability of forming knots and strong bends and are manifested in an increase in the D peak intensity in the Raman spectrum.

### **3. The challenge with polymer nanocomposites: dispersion, alignment and compatibility**

To achieve the maximum advantage of carbon nanotubes, they need to be well dispersed, that is not form aggregates. Dispersion is a spatial property. Good dispersion requires the average number density of individual carbon nanotubes to be uniform through the object. Of course, one challenge in this respect is the experimental method requires high magnification and large spatial coverage as highlighted by Li et al. [64], both demanding requirements, moreover there are no standards or commonly accepted procedures to follow although transmission electron micrographs is generally accepted as the gold standard [64].

Achieving good dispersion is experimentally challenging and there is a considerable body of literature on the problem; the reviews of Xie et al. [65], Spitalsky et al. [66], Gkourmpis [67] and Huang and Terentjev [68] cover the key areas. There are many routes to solve basically the same problem. If we start with the situation of traditional thermoplastic polymer, then the basic requirements have been identified and further some simulation of the process achieved [69].

CNTs made by CVD techniques are usually entangled and the first stage of dispersion is to break up these aggregates. Sonication and high shear flow with a high molecular weight

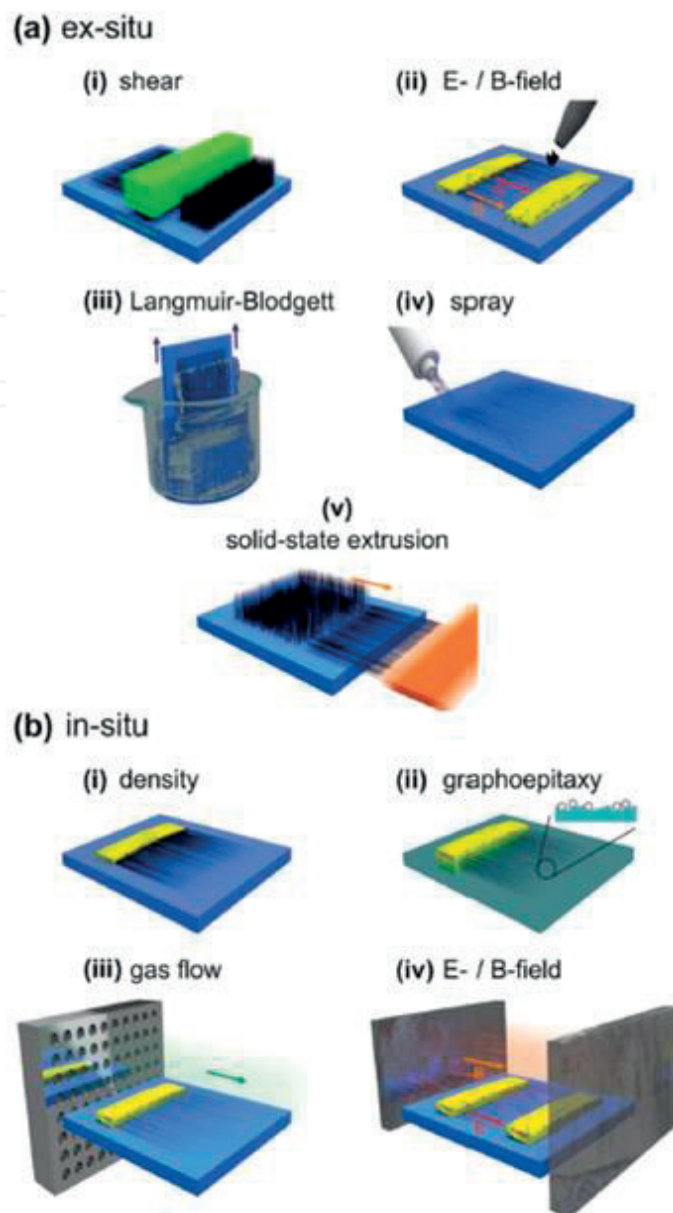
polymer melt are often chosen. However, such treatments may lead to damage or breaking the CNTs into smaller units. These may be advantageous for dispersion but it may at the same time increase the threshold concentration for percolation as the aspect ratio of the tube is lowered. It is common to add surfactants as used in electrospinning of polyethylene oxide with CNTs [70] or to functionalise the CNTs to increase compatibility with the polymer matrix without destroying the electronic properties of the CNTs [71]. Huang and Terentjev [72] studied in detail the use of sonication and melt mixing to disperse CNTs in polymers and they found a critical mixing time, although they indicate that they could not exclude the possibility of small tube clusters persisting after this time.

An alternative approach to that described above is to avoid the problems with the polymer by mixing with a monomer and after mixing carry out the polymerisation process. This is the only route for preparing thermosets containing CNTs, but has also been used to prepare systems with intrinsically conductive polymers such as polyaniline, for example the work of Cochet et al. [73]. Of course, a suitable solvent can be used to generate a uniform dispersion of the CNTs in the solvent and then introduce the polymer. This has been successfully used by a number of authors but of course the removal of the solvent becomes the challenge especially in the industrial production of objects.

A good dispersion of the CNTs is the first step to realise the full potential of CNT-based polymer composites. The second parallel requirement is to fully utilise the anisotropic properties of the CNTs by preparing a common alignment for the CNTs, the alignment depending on the application of the product. A variety of methods have been explored and these have been reviewed by Goh et al. [74], and it is fair to say that many are particularly suited to electronic and other thin film applications. **Figure 2** shows schematically the methodologies for producing a common alignment of CNTs. The introduction of preferred alignment into a polymeric system is usually achieved during processing, for example with fibre spinning [75]. In the case of injection, moulding or other processing, the flow of the polymer melt can be used to induce alignment, and of course in principle, CNTs are straightforward to align due to the high aspect ratio. Zhou et al. [76] have used dissipative particle dynamics to simulate these processes. They find that increasing the volume fraction and the length of CNTs leads to a significant increase in the alignment of the CNTs. The challenge is that the alignment follows the flow in the mould and it requires careful design to achieve the required alignment pattern.

Typically, the CNTs will align parallel to the flow direction, and hence an alignment in a sheet which is normal to the sheet plane is more or less impossible to achieve. The generation of alignment raises the question whether it is possible to prepare patterns of alignment. A number of reports have addressed this area. Goldberg-Oppenheimer et al. [78] used electrohydrodynamic patterning to produce defined patterns on a micrometre scale with the alignment of CNTs within those patterns. Dai has reviewed the use of pyrolytic procedures for large scale production of oriented and micropatterned carbon nanotube arrays normal to a substrate surface which can be transferred onto various substrates of particular interest in either a patterned or non-patterned fashion [79]. The perpendicularly aligned structure is particularly advantageous for surface functionalisation.





**Figure 2.** Methodologies for producing a common alignment of CNTs (a) ex situ and (b) in situ (reproduced from Matthew et al. [77], published by The Royal Society of Chemistry).

Alternative methodologies involved the application of electric or magnetic fields. Arguin et al. [80] have used electric fields of 40 kV/m, which can lead to the alignment of MWCNTs in an epoxy resin system. Gupta et al. [81] employed electric field and current-assisted alignment of CNTs in a polyvinylidene fluoride matrix. A promising methodology [82], which is discussed in more detail in Section 5, involves the use of an intermediate state specifically electrospinning. Electrospinning is an old technology which has seen resurgence in the last 10 years. Electrospinning enables the production of nanoscale and microscale fibres from a charged melt of solution [83]. The methodology is to encapsulate the CNTs in polymer nanofibres and deposit this in the sample with a common alignment [70, 82, 84, 85]. The electrospinning process naturally aligns the CNTs within the polymer fibre.

#### 4. Some selected recent examples of polymer/CNT composites

Interest in polymer/CNT composites has been particularly inspired by the success of carbon fibre reinforced composites, and as with these, more developed advanced materials with improved mechanical properties are an attractive benefit, but these are potentially combined with advantages of nanocomposites such as a large interfacial area per volume [86]. A review by Coleman et al. neatly sums up the mechanical advantages and point out there is an order of magnitude improvement over carbon nanofibres in terms of modulus [87]. These authors describe the crucial importance of even dispersion; aggregation (for example at high loading) results in a decrease in mechanical properties. Alignment in contrast improves mechanical strength but is less crucial and results in highly anisotropic properties which might be a disadvantage in bulk samples. That being said, in fibres, alignment is easy to achieve and anisotropic properties are unlikely to be a problem. Interestingly, recently Guzman de Villoria et al. have shown that CNTs [88] can be successfully used to bind together weak interfacial layer of reinforced laminate materials; they describe these reinforcing components as nanostitches. Micron diameter pinning techniques reduce some of the advantageous mechanical properties of the composite; in this case, a carbon fibre epoxy prepreg is arranged in layers. Thus, in addition to providing the advantages of highly anisotropic orientation, CNTs can be used to overcome the difficulties associated with this highly directional mechanical behaviour.

Thostenson and Chou [89] examined the benefits of aligned nanofillers on mechanical properties by preparing composites composed of randomly orientated and aligned CNTs in a polystyrene matrix. Samples were prepared at a loading of 5 wt% CNT in the polystyrene matrix. Films of the polystyrene/CNT composite were prepared from solution casting while sonicating. Once dry, the material was heated to 155° C in a microscale compounder with mixing performed at a screw speed of 100 rpm for 3 minutes. The molten material was extruded through a rectangular die and drawn down and passed over a chill roller to solidify, resulting in film thicknesses between 80 and 120 µm depending on the draw ratio. Samples of drawn and non-drawn polystyrene material were also prepared to differentiate between any potential impact on the properties arising from alignment of the polymer chains or the CNT nanofillers. The films produced showed good dispersion due to the mixing process in the compounder and the drawing of the material resulted in an overall alignment of the tubes about a common axis. The sample that had aligned CNTs within the matrix possessed a ~50% improvement to the storage modulus as compared to the bulk material, whereas the sample with randomly orientated CNT filler particles only exhibited a 10% increase. In addition to this, the sample containing the orientated filler showed improvements to the yield and ultimate strengths of the material along the common axis of alignment of the nanotubes, suggesting a load transfer between the polystyrene matrix and the MWCNTs.

Many studies of CNT composites focus on the mechanical advantages but their inclusion of these materials may also benefit the thermal, optical and electrical properties of the nanocomposite material. In a recent review [90], Liu and Kumar have collated the properties of a number of composites. It is clear that both thermal and electrical conductivity depend substantially on the alignment of the CNTs but it does seem that this can vary from one composite

to another. For example, a polypropylene/polyethylene/CNT composite has been found to exhibit a dramatic decrease in conductivity when drawn; in contrast, electrical conductivity of a PVA/SWNT composite showed a fourfold increase when stretched. This is a consequence of the relationship between the electrical conductivity and the percolation network; this network is likely to be distorted by drawing and the consequential change in properties will depend largely upon the loading and dispersion of the CNTs in the original sample.

Dai et al. [91] examined quasi-straight SWCNTs dispersed in a polymethyl methacrylate (PMMA) matrix material. Samples were prepared from solution by taking the SWCNT powder and dispersing it in dimethylformamide (DMF) followed by dissolution of PMMA. Sonication was used for 1 hour before dissolving the PMMA and for another hour after once the PMMA was fully dissolved in order to aid in the nanotube dispersion. The suspension was then air-dried in a fume cupboard until semi-dry, then subjected to a draw ratio of 50 along one direction, folded over and the process was repeated 100 times. The samples were then compressed under 10 MPa at 200°C for 5 minutes with a hydraulic press, transferred to a mould and allowed to dry and cool overnight in a fumehood at 20°C. The drawing method resulted in highly orientated nanotubes within the PMMA matrix. Samples of up to 10 wt% of nanotube loadings were prepared. Strips were cut and heated to 120, 5°C above the polymers glass transition, then a weight applied to act as the deforming force. Mechanical improvements were measured with increases to the draw ratio of the material with increase in loading of the filler particle; however, this was limited to the direction of the tubes long axis alignment. Perpendicular to the common alignment of the tubes long axis, the material exhibited worse draw ratios (weaker mechanical properties), similar to that observed with the SWCNT-epoxy resin composites looked at by Wang et al. [92]. The induced aligned arrays of SWCNTs in the PMMA matrix with the electrical conductivity significantly improved along the draw direction as compared to the perpendicular direction. Electrical conduction of the polymer/CNT nanocomposite is possible through the development of an interconnecting CNT network structure within the polymer matrix. Tube contact is a necessary for the transport of electrons across the material, with adequate dispersion of the tubes and a sufficient quantity of CNT within the matrix material being required to make the material conducting throughout. The electrical conductivity of carbon nanotubes displays anisotropic properties, with electron transport more favourable along the tubes axis [93]. Due to this anisotropy in the electrical properties of the CNTs, any composite materials prepared would benefit from alignment of the tubes along a common axis as was demonstrated in this particular study. Dai et al. also measured improved thermal stability of the material with higher loading percentage of the nanofiller, increasing the maximum mass loss temperature of the material compared to pure PMMA alone [91].

Similar electrical and mechanical improvements to a matrix material along the tube orientation direction have been observed by Wang et al. who prepared composite samples of epoxy resin/SWCNTs [92]. The orientation of the SWCNTs was induced through manual stretching of semi-dried composite films with a draw ratio of 50, followed by folding of the sample and repeating the process 100 times. This drawing process resulted in a high degree of orientation of the CNT filler particles. Samples containing different weight percentage

loadings of the filler were prepared and observations on the conductivity and mechanical properties were made. It was observed that the conductivity was significantly better along the direction of common alignment of the tube axis. In this study, composite films that did not undergo stretching were also prepared for comparison purposes. The results showed that the alignment resulted in higher conductivity levels along the stretching direction, for example the 3 wt% loading of SWCNT that had undergone the stretching process had a conductivity of  $\sim 1 \times 10^{-6}$  S/cm along the stretching direction ( $2.8 \times 10^{-9}$  S/cm perpendicular), whereas the unstretched sample had a conductivity of  $5 \times 10^{-8}$  S/cm. The addition of 3 wt% of the SWCNTs to the epoxy resin improved the Young's modulus by  $\sim 2\%$  and the tensile strength by  $\sim 2.6\%$  with respect to the CNTs common axis of alignment; however, at loadings greater than 6 wt%, it was observed that the mechanical properties perpendicular to the tube orientation were lower than the epoxy resin on its own, possibly related to flocculation of the SWCNTs. When compared to the composite samples that had not undergone the stretching procedure, the samples with the aligned filler showed superior mechanical properties along the stretching direction when comparing the values of the Young's modulus and tensile strength to the unstretched samples, however perpendicular to the stretching direction the mechanical properties are not as good as the unstretched samples.

Exposure to an electric field has shown to provide an effective method for the alignment of the carbon nanotubes. Martin et al. have examined the use of both AC and DC fields to aid in the alignment of carbon nanotubes [94]. Low concentrations of CVD-grown MWCNTs were dispersed in an epoxy resin based on bisphenol-A. In the field, it was observed that a fraction of the nanotubes move towards the anode during the epoxy drying stage. These align with the tubes long axis perpendicular to the anode. The tubes themselves then act as a very high field strength at its tip attracting more tubes which form a connecting network between the anode and cathode. The AC field provided a more uniform connecting pathway between the anode and the cathode. Both fields exhibited a concentration of tubes highest at the anode.

Measurements made by Gupta et al. [81] on the electrical conductivity of polyvinylidene fluoride (PVDF), MWCNT composite materials exhibited improved electrical conductivity with improved alignment of the MWCNT filler particles. Five films of the composite materials were prepared with a solution cast method. During casting, two samples were exposed to an alternating voltage at 220 V and 500 V, whereas two others were exposed to alternating pulsed currents from a 220 V and 500 V source. The fifth sample was not exposed to any field resulting in a film that possessed a randomly orientated filler. It was observed that both the alternating voltage and alternating pulsed currents resulted in alignment of the nanotubes within the matrix (with the exception of the sample prepared with an alternating voltage at 220 V). However, differences between the two alignment techniques were observed; the sample exposed to an alternating pulsed current developed conducting channels across the matrix material, where the CNTs joined up in an end-to-end fashion. Meanwhile the films exposed to the alternating voltage resulted in alignment of the CNTs along a common axis, while maintaining their uniform dispersion throughout the matrix. The alternating pulsed current method provided the necessary channels of CNTs for conduction across the matrix, where measurements of the conductivity show a 360% improvement to the electrical conductivity as compared to the sample possessing randomly orientated



CNTs. It was observed that for the sample prepared at 500 V with an alternating pulsed current, the film only exhibited 60% increase in conductivity compared to a randomly orientated sample. Observations of this film during its preparation showed electrical sparking and therefore higher temperatures in areas causing a partial melting and distortion of the film, explaining the drop in conductivity of the film prepared at 500 V compared to the one at 220 V. The conductivity of the nanocomposites was observed to be significantly higher in the direction of the tube alignment compared to perpendicular to the alignment, as would be expected given the anisotropic electrical properties of the CNT filler particles and the channels formed in the material. In addition to the electrical properties, the mechanical properties of the films were measured and showed significant improvements to the Young's modulus and the ultimate tensile strength (180% and 150% respectively) compared to the pure PVDF. However, only slight improvements were measured (26% to the Young's modulus and 30% to the ultimate tensile strength) for the samples possessing the aligned CNT filler when measured along the CNT alignment direction as compared to the samples containing the randomly orientated CNT filler.

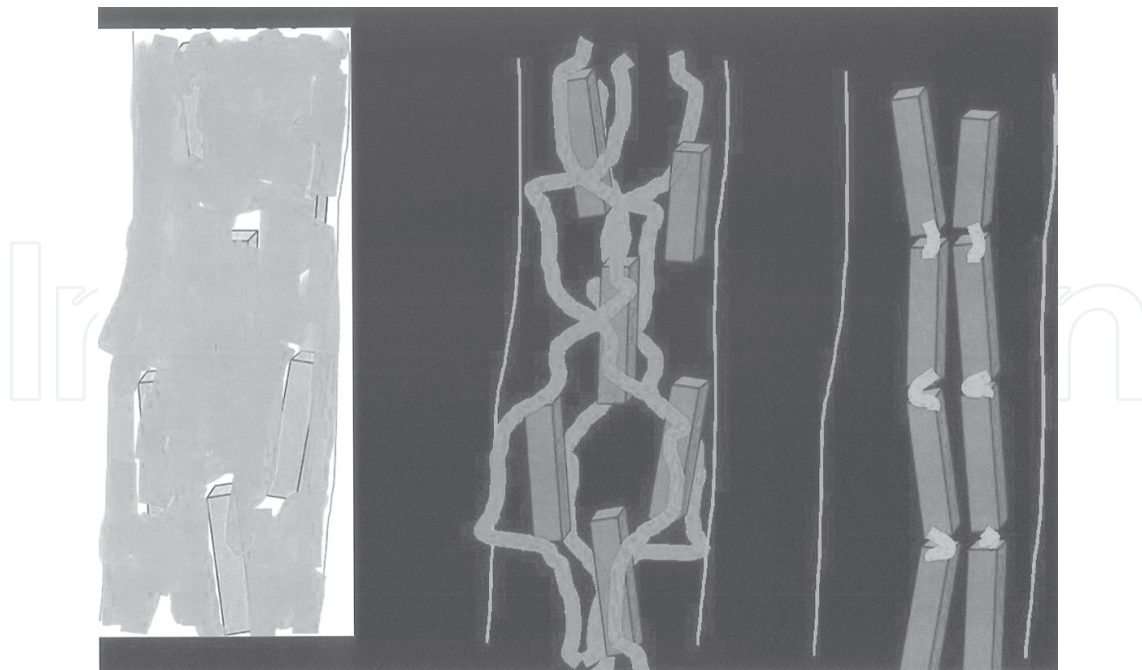
More recent developments in alignment of carbon nanotubes involve encapsulation into a narrow fibre using techniques such as electrospinning. Nazhipkyzy et al. have examined [70, 82] electrospun fibres as a potential medium for the encapsulation and alignment of carbon nanotubes. Polyethylene oxide fibres were electrospun from aqueous solution containing different concentrations of nanotubes. To aid in the spinning process, a surfactant, Triton X-100, was added to the solution that greatly aided in the spinning process. Fibres were spun onto a rotating collector that resulted in aligned arrays of parallel fibres. The fibre diameters varied from 100 to 400 nm and TEM images revealed encapsulation of the tubes with the alignment of the CNTs along the electrospun fibres long axis [82].

## 5. The way forward

The earlier parts of this chapter have identified the critical need for good dispersion and control of alignment of the CNTs. In Section 3, we identified a number of possible routes to achieving a high level of common alignment. However, many of the approaches reviewed were most suited for application with thin films. The authors have recently reported a methodology for preparing CNT-based composites using additive manufacturing technology, and we review this approach here as it underlines the challenges in preparing highly anisotropic CNT-based composites for bulk samples (**Figure 3**).

There has been a huge surge of research in the area of additive manufacturing (AM) over the last few years. The methods used in AM range from thermal extrusion, where a polymer is melted, extruded and deposited in a layer by layer process; granular processing, through melting powder layers using, for example, a laser, and photopolymerisation, where selective areas of a liquid, photocurable polymer are exposed to electromagnetic radiation to induce polymerisation and solidification [71]. Through the use of computer-aided design (CAD), the additive manufacturing technique allows for the manufacturing of complex shaped parts. The methodology which we believe [70, 82] is the best way forward involves





**Figure 3.** Methodologies for creating fibres from nanoparticles (dark grey). (a) Particles aligned with fibre axis and stabilised in this arrangement by a solid polymer matrix (light grey); (b) particles aligned with fibre axis and stabilised in this arrangement by cross-linking chains which link the particles together; (c) particles aligned with fibre axis and joined end-to-end by short cross-linking chains, which link particles together (reproduced with permission from Mohan et al. [82]).

the encapsulation of the CNTs within a fibrillar structure, where the process of drawing out and enclosing into a narrow diameter fibre can result in the nanoparticles alignment. We use the electrospinning technique to achieve this. During the spinning process, the jet undergoes a shearing force and a narrowing in which the nanoparticulates can be aligned and encapsulated within the fibre as it forms. These fibres themselves have the potential to be used in composite materials to provide mechanical reinforcement; for example, Shinde et al. were able to incorporate electrospun fibres into a resin to improve interlaminar shear stresses of glass fibre composites [95].

The use of layer by layer technology selected by Mohan et al. [82] makes it straightforward to organise the deposition of electrospun fibres, followed by an embedding layer of photocurable resin. The process is completed by photocuring using both UV-visible and IR light [71]. The cycle is then repeated multiple times until the thickness of the object is achieved. Since each layer is deposited sequentially, it is possible to prepare composites with 0 and 90 degree alignment of fibres to prevent defibrillation as might take place in the single orientation case. The use of a low molar mass resin which is then cross-linked means that the resin can flow and wet all fibre surfaces. In the work reported by Mohan et al. [70], the electrospun mean fibre diameter was 360 nm. As the cross-linkable resin is deposited at room temperature, it means that the polymer encapsulation of the CNTs is unaffected by the resin and the spatial distribution remains intact. Thus, this multistep process overcomes both challenges of dispersion and alignment.

## 6. Summary

In this chapter, we show that CNTs offer some exceptional properties for the design of multi-scale composite materials. In terms of production in bulk, the technology is not quite routine, but clearly promise exists. We have laid out an approach, which we have shown, overcomes the challenges of both dispersion and alignment and deserves wider application.

There are great opportunities for the inclusion of CNTs in the emerging technology of additive or direct digital manufacturing. The future is especially promising in this area.

## Acknowledgements

The research work was funded by the Fundação para a Ciência e a Tecnologia (Portugal), through the Project reference UID/Multi/04,044/2013 and by the National Agency of Innovation (ANI) (Portugal) through project i.FILM – Multifunctional Films for Intelligent and Active Applications Project Number: 17921.

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