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Carbon Nanotubes Reinforced Electrospun Polymer Nanofibres

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1. Introduction

With the rapid development in nanoscience and nanotechnology, there is an ever increasing demand for polymer fibres of diameters down to a nanometre scale having multiple functionalities. Electrospinning, as a simple and efficient nanofibre-making technology, has been used to produce polymer nanofibres for diverse applications. Electrospun nanofibres based on polymer/carbon nanotube (CNT) composites are very attractive multifunctional nanomaterials because they combine the remarkable mechanical and electronic properties of CNTs and the confinement-enhanced CNTs alignment within the nanofibre structure, which could greatly improve the fibre mechanical, electrical and thermal properties. In this chapter, we summarise recent research progress on electrospun CNTs/polymer nanofibres, with an emphasis on fibre mechanical properties and structure-property attributes. Outlook towards the challenge and future directions in this field is also presented.

2. Carbon nanotubes

Carbon nanotubes (CNTs) which were first reported by Oberlin *et al.* [1] and later by Iijima [2] have remained the focus of intense academic investigation since early 90's. They are still at the forefront of research in many areas of nanoscience and technology due to their spectacular combination of mechanical, electrical and thermal characteristics.

a. Structure of carbon nanotubes

Carbon nanotube is a new form of carbon which has a seamless hollow cylindrical structure, consisting of carbon hexagons with both ends capped with fullerene molecule. There are two general types of carbon nanotubes, namely single walled nanotubes (SWNTs) and multi walled nanotubes (MWNTs). SWNTs consist of one single layer of hexagonal carbon atom rolled into tubular form the diameter of which ranges from 0.4 to over 3 nm, while MWNTs have several concentric cylinders with diameter from 1.4 to over 100 nm [3]. SWNTs are varied in chiral angle i.e. the angle at which the atoms of CNTs are twisted about the main axis of the CNTs. According to their chiral angle and diameters, SWNTs are classified to three forms of structures including armchair, zigzag and intermediate [4] as shown in Figure 1. The chiral angle governs the electrical conductivity. While the armchair structure exhibits very high conductivity, the zigzag and the intermediate forms show semi-conductivity.
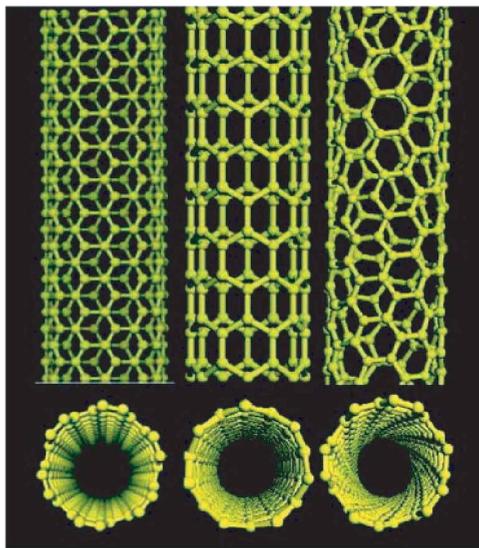
Fig. 1. Schematic illustration of various carbon nanotube structural forms, from left to right: armchair structure, zigzag structure and intermediate or chiral structure [3] [Copyright AAAS].

Several techniques have been developed to synthesise SWNTs and MWNTs. The most used methods are carbon arc discharge [2], laser ablation of carbon [5] and chemical vapour deposition (on catalytic particles) [6]. Either vacuum or process gas is used in the production. The defining issue in selecting an appropriate method is the ability to produce nanotubes on a large scale. Advances in catalysis and continuous growth processes are making CNTs more commercially feasible.

b. Mechanical properties

CNTs combine outstanding mechanical, electronic, thermal properties, and low density. However, their extraordinary mechanical properties due to carbon-carbon sp2 bonds and cylinder structure set them apart from many other different materials and other forms of carbons. Soon after Ijima's discovery and before the large scale production of CNTs, computer simulation was used to calculate the rigidity of SWNTs [7]. The calculated Young's modulus was 1500 GPa. However, later studies predicted that Young's modulus of CNTs is approximately 1 TPa [8]. It was not until 1997 that the first direct mechanical measurement was carried out on arc-MWNTs using atomic force microscopy and an average Young's modulus value of 1.28 TPa was obtained [9]. The highest Young's modulus and tensile strength measured for MWNTs produced by chemical vapour deposition method is 0.45 TPa and 4 GPa, respectively. The highest measured tensile strength for arc-MWNTs is 63 GPa [10]. Mechanical measurements on SWNTs did not commence until the late 1990's due to difficulties in handling them [11]. The highest measured values for Young's modulus and tensile strength of SWNTs are 1.47 TPa and 52 GPa, respectively [12]. The tensile strength of SWNTs could be more than 5 times higher than that of a steel fibre with the same diameter, yet only one-sixth of its density [13][14].

c. Electronic properties

The remarkable electronic properties of CNTs make them particularly attractive for the creation of miniaturized electronic component. While the resistivity values for high quality graphite, the measured resistivity copper is approximately 0.40 and 0.017 μΩm, respectively, and the measured resistivity of CNTs falls into the range of 0.05 μΩm ~ 10 mΩm [15]. Due to structural defects catalytically produced CNTs are expected to have a higher resistivity, similar to those of disordered carbon (i.e of the order of 10~100 μΩm). Earlier studies suggested that electronic properties of CNTs could vary widely from tube to tube and they could be metallic or semiconducting depending on their structure (*e.g.* tube chirality) and diameter [16][17][18][19]. However, recent studies showed that the electronic properties of a given nanotube were not only specified by the diameter and chirality of nanotubes but also depended on their chemical environment particularly gas exposure history [20][21]. Exposure to air or oxygen significantly influences CNTs electrical resistance. Semiconducting CNTs can be converted into metals through room temperature exposure to oxygen [20].

d. Carbon nanotubes/ polymer composites

Because of the exceptional properties and large aspect ratio, incorporation of nanotubes into polymer matrix has been proven to be a promising approach leading to structural materials and composites with excellent mechanical and physical properties. Various researches have been conducted and comprehensive reviews on mechanical properties of carbon nanotubes/polymer composites have been given by Coleman *et al.* [22][23]

The significant challenges in processing of CNTs/polymer composites lie in the uniform dispersion and orientation of nanotubes within the polymer matrix. CNTs tend to aggregate to form tight bundles due to strong van der Waals interactions and small size [24][25]. Dense and entangled CNTs network in the bundles prevent the CNTs from dispersing uniformly within the polymeric resins. As a result of uneven dispersion, the physical and mechanical properties of the composite material are considerably lower than the expected.

The difficulties in obtaining uniform dispersion were highlighted in the literature [26][27][28][29][30][31][32][33] and several techniques have been developed to improve the CNT dispersion. Ultrasonication has been used to de-aggregate CNT bundles and force the nanotubes to disperse uniformly throughout the material [27]. Other investigators have utilised solution-evaporation methods with high-energy sonication [26], surfactant-assisted processing through the formation of a colloidal intermediate [34][35] and melt spinning [36], as well as mechanical stretching of nanotube/polymer composites [37][38]. Others considered deposition of carbon nanotubes suspension under a magnetic field [39] and onto chemically modified substrate [40]. The most commonly used techniques to fabricate CNT/polymer composites are solution casting [41][42], melt processing [43][44], electrospinning [45] and *in-situ* polymerisation [46][47]. Electrospinning is an efficient processing method to produce CNT/polymer nanofibres with the CNTs orienting to the axes of the as-spun nanofibres [48][49]. There is a fast growing interest in applying this technique to produce nanofibres using various polymers [48]. This chapter summarises the research and development of electrospun carbon nanotube/polymer nanofibres with an emphasis on processing conditions, fibre morphology, mechanical properties and applications.

One of the interesting features for CNTs is the nucleation crystallisation of surrounding polymer molecules when the CNTs are dispersed into some polymer matrices. It has been observed that the introduction of CNTs to some polymer matrices alters the crystallisation

dynamics of polymers [42][50]. In other words, the presence of CNTs induces crystallisation of host polymer. As a result of the crystalline polymer layer formed around the embedded nanotubes, the interaction between the CNT and polymer matrix is enhanced leading to improved mechanical properties.

Since 1998, several publications have reported the nucleation crystallinity of polymer in CNT/polymer composites [51][52][53][54][55][56][57]. The transmission electron microscopy (TEM) studies by McCarthy *et al.* [51] identified that carbon nanotubes were coated with a thin layer polymer when they were dispersed in a semi-conjugated polymer, poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene). The nucleation crystallisation of proteins such as streptavidin around carbon nanotubes was also reported [52][54][56]. Also, polycarbonate has been found to form a thin layer around MWNTs. A clearly observable polymer sheath was identified at the fracture surface of a composite by scanning electron microscope (SEM) [54]. The nucleation crystallinity of other polymers, such as polypropylene (PP), was also studied [50][58][59][60][61][62][63]. However, no direct evidence for the formation of PP coating on the nanotubes was presented, except that the differential scanning calorimetry (DSC) measurements revealed an increase in the crystallinity due to the presence of CNTs.

It was also reported that the presence of CNTs in polyvinyl alcohol (PVA) improved the composite mechanical properties more than in other polymer systems [42][64][65][66][67][68][69]. The nucleation crystallisation of PVA was confirmed by microscopic investigations of fractured PVA composite film, which showed that a thick PVA coating covered the nanotubes [69]. It has been established that the presence of ordered polymer coating is the main reason leading to the enhanced mechanical strength [66].

3. Electrospinning and electrospun nanofibres

Electrospinning is a relatively low cost, fast and versatile method to produce continuous nanofibres mainly from polymer solutions. This technique has not been well studied until last decade even though it was invented in 1934 [70].

a. Basic electrospinning principle

A basic electrospinning setup, as shown in Figure 2a, consists of a container for polymer solution, a high-voltage power supply, spinneret (needle) and an electrode collector. During electrospinning, a high electric voltage is applied to the polymer solution and the electrode collector leading to the formation of a cone-shaped solution droplet at the tip of the spinneret, so called "Taylor cone" [71]. A solution jet is created when the voltage reaches a critical value, typically 5-20 kV, at which the electrical forces overcome the surface tension of the polymer solution. Under the action of the high electric field, the polymer jet starts bending or whipping around stretching it thinner. Solvent evaporation from the jet results in dry/semidry fibres which randomly deposit onto the collector forming a nonwoven nanofibre web in the most cases (Figure 2b).

Extensive research has been carried out on various aspects of electrospinning including operating parameters (e.g. applied voltage, feeding rate, distance between the nozzle and collector), material properties (e.g. viscosity, surface tension, conductivity), spinningability of many different polymers [72][73][74][75][76][77][78][79][80][81][82][83][84][85][86][87][88], process modelling [88] [89] [90] [91] [92] [93] [94] [95], nanofibre characterisations and morphology [87].
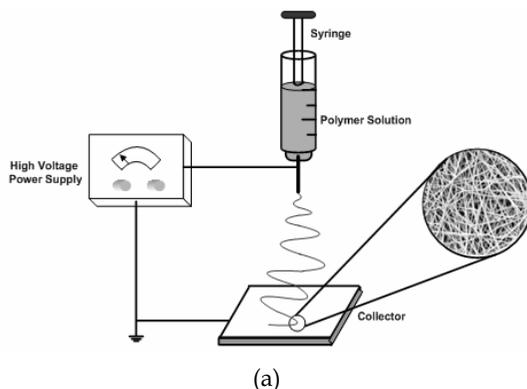
(a)

(b)

Fig. 2. (a) Basic apparatus for electrospinning, (b) A photo of typical electrospun nanofibre mat.

b. Electrospun nanofibres

Fibres obtained from electrospinning vary from uniform fibres to fibres with an irregular beads-on-string structure. The morphology of the electrospun fibres are dependent upon a number of factors including the polymer solution parameters such as molecular weight, molecular weight distribution, electrical conductivity, surface tension, viscosity and solvent, and the operating parameters such as electrical field, the distance from the nozzle tip and the collector and the flow rate of the polymer, as well as ambient conditions [84][96][97]. The diameter of electrospun fibres can be in the range between several microns to tens of nanometres. The small fibre diameter and large aspect ratio lead to extremely high surface-to-volume (weight) ratio, which makes the electrospun nanofibre desirable for many

applications [98]. Recently, several review articles have been published on electrospinning [99][100][101], which demonstrate the great potential of electrospun nanofibres in diverse application fields.

c. Mechanical properties of electrospun polymer nanofibres

Although several experimental investigations have been carried out on the mechanical properties of nanofibre mats, only a few studies have been reported on the stress-strain behaviour of single electrospun nanofibres [102][103][104]. These studies have demonstrated that single electrospun nanofibres have promising mechanical properties. Gu *et al.* [102] calculated the Young's modulus of a single electrospun polyacrylonitrile (PAN) fibre from the force displacement curves obtained by bending a single fibre attached to an atomic force microscopy (AFM) cantilever. High Young's modulus of up to 50 GPa was reported suggesting the orientation of PAN molecular chains as evidenced by X-ray diffraction study. In a study by Bellan *et al.* [104], the average Young's modulus of electrospun poly (ethylene oxide) (PEO) nanofibres measured by AFM technique was reported to be 7.0 GPa, which was significantly larger than that of PEO bulk materials. While electrospinning induced molecular orientation was attributed to the high stiffness of the nanofibre, no data on the molecular orientation of single nanofibre was provided. Lee *et al.*[103] reported that the Young's modulus of PVP nanofibres containing TiO_2 nanoparticles was only 0.9 GPa, which was measured with an AFM using the three point bending method.

4. Electrospun carbon nanotube/polymer composite nanofibres

CNT/polymer composites have been fabricated by a number of processing methods including melt processing, solution processing and *in situ* polymerisation [105]. However, it is difficult to control the orientation of CNTs within the polymer matrix. This is particularly important for the reinforcement of polymers and for meeting the expectation for nanocomposites with significantly enhanced mechanical properties.

It has been established that electrospinning a polymer solution containing well-dispersed carbon nanotubes leads to nanocomposite fibres with the embedded carbon nanotubes orienting parallel to the nanofibre axis due to large shear forces in a fast fibre-drawing process [106]. It has been demonstrated that electrospinning is a potential method for aligning and debundling CNTs [107]. The improved CNT alignment within the fibres plus low cost and fairly simple spinning process has made this technique promising for producing CNT/polymer composite nanofibres.

The reported electrospun CNT/polymer composites including corresponding solvent and CNT concentration are listed in table 1. While CNTs have potential to be embedded into various polymer matrices, some polymers cannot be easily electrospun into nanofibres.

a. Carbon nanotube dispersion

A common method for preparing CNT/polymer solution for electrospinning involves making nanotube dispersion and polymer solution separately and then mixing them together. In general, interest has been focused on achieving homogenous nanotube dispersion in a polymer solution, which will affect the orientation and distribution of CNTs in the resultant nanofibres.

Polymers	Solvents	CNTs	CNTs (wt%)	Diameter (nm)	Tensile strength* (MPa) (Modulus, MPa)	Ref
PAN	--------	SWNTs/ MWNTs	1	180	--------	[108]
PAN	DMF	MWNTs	1-20	50~300	285~312 (6.4~14.5GPa)	[109]
PAN	DMF	MWNTs	1.5,7	20~140	------	[110]
PAN	DMF	SWNTs	1-10	50~400	20~30	[111]
PAN	DMF	MWNTs	1	200~2000	--------	[112]
PAN	DMF	SWNTs	1~4	50~200	(140 GPa)	[45]
PAN	DMF	MWNTs	2-20	100-300	37-80 (2-4.4GPa)	[113]
PVA	Water	MWNTs	4.5	295~429	4.2~12.9	[114]
PVA	Water	SWNTs	10	315~447	5.9~6.0	[115]
PEO	Ethanol/Water	SWNTs	3	----	(0.7~1.7GPa)	[116]
Polymethyl methacrylate	Chloroform	MWNTs	0.5-2	200~6000	------	[117]
Polymethyl methacrylate	DMF	MWNTs	1-5	100~800	------	[118]
Polyurethane	DMF	SWNTs	1	50~100	10~15	[119]
Polycaprolactone	Chloroform/ Methanol	MWNTs	7-15	100~550	--------	[120]
Polylactic acid	DMF	SWNTs	1-5	1000	-------	[121]
Regenerated silk fibroin	Formic acid	SWNTs	0.5-5	147	2.8-7.4 (180~705)	[122]
Regenerated silk	Formic acid	SWNTs	1	147~153	13.9~58.0 (633.8~6549.3)	[123]
Polybutylene terephthalate	1,1,1,3,3,3 Hexafluoro-2-propanol	MWNTs	5	250~3500	(1.79 GPa)	[124]
Polycarbonate	Chloroform	MWNTs	4	350	------	[125]
Nylon 6,6	Formic acid	MWNTs	2-20	150~200	-------	[126]
Polystyrene	DMF/ tetrahydrofuran	MWNTs	0.8,1.6	300,4500	----	[127]

Polyvinyl alcohol (PVA); Dimethylformamide (DMF); * Unit for modulus values is MPa unless otherwise stated.

Table 1. Electrospun CNT/polymer composite nanofibres and their mechanical strength

The stable dispersion of CNTs can be achieved by using surfactants (e.g. sodium dodecyl sulphate), large amphiphilic polymers (e.g. polyvinyl pyrrolidone) and natural macromolecules (e.g. polysaccharide, Gum Arabic) which can be adsorbed onto the hydrophobic nanotubes [116][128]. Nevertheless, the most common method for dispersing individual nanotubes is ultrasonication treatment. While ultrasonication is a valuable technique to overcome the entanglement of nanotubes and break up the agglomerates, it could also introduce defects and irregularity into the CNTs [128].

Purity is also an important factor affecting the composite quality. CNTs are typically purified by chemical methods to remove amorphous carbon and metal catalyst. The

purification treatment also facilitates the dispersion of the CNTs in solvents as well as improves the nanotube-matrix interaction [15]. It was demonstrated that the caps of SWNTs could be removed by treatment with hot nitric acid due to the formation of carboxylic acid and hydroxyl groups at the nanotube ends [129][130]. Apart from this, the purified CNTs can be functionalised to get better dispersability and additional functions [131]. There are several approaches to chemical functionalisation of nanotubes [105][132]. Although functionalised CNTs showed improved dispersion, the electronic and photonic properties of nanotubes would be altered as well [133].

b. Structure and morphology

Alignment of individual nanotubes within the host polymer is a crucial step, in particular with the applications for reinforcement. Electrospinning is expected to make CNTs align with the fibre axis during the fibre formation process because of the high stretching ratio. Strategies to make the best use of this capability have been employed to improve the dispersion of CNTs in polymer solution using surface functionalised CNTs and ultrasonication treatment.

Salalha *et al.* [134] proposed a theoretical model for the behaviour of rodlike particles in the electrospinning jet and predicted the possibility for CNTs to be aligned along the streamlines of an electrospun jet. They fabricated electrospun MWNT/PEO nanocomposite fibres [25].They found that PEO crystals were highly aligned along the fibre axis during the electrospinning process. The MWNTs were individually embedded in the nanofibres, mostly aligned along the fibre axis. Nevertheless, twisted, bent and non-uniform nanotubes were also observed (Figure 3a). By comparing the MWNT dispersions with the raw nanotubes under TEM, they suggested that over-sonication of nanotubes for dispersion might damage nanotubes, preventing them from being well orientated. This finding is consistent with what Kearns and Shambaugh reported [135].

In other similar studies [116][134], well dispersed SWNTs were incorporated into PEO nanofibres by electrospinning. It was shown that nanotube alignment within the nanofibres depended strongly on the quality of the initial dispersion. Ko *et al*. [45] also found that a better alignment of CNTs was formed in polyacrylonitrile (PAN) than in polylactic acid (PLA) nanofibres, indicating the matrix dependency of nanotube alignment (Figure 3b). The improved orientation also resulted in a better distribution of carbon nanotubes within nanofibres. Vibration electrospinning employing in-built ultrasonic generator has also been used to align CNTs in nanofibres [136].

There have been several studies on controlling the spatial orientation of electrospun CNT/polymer composite nanofibres [109] [137] [138] [139] [140]. Modification of electrospinning setup has been a common approach to produce aligned electrospun composite nanofibres. This includes employing rotating collectors such as a disk or mandrel to collect nanofibres aligned in the rotating direction.

Ge *et al*. [109] developed aligned electrospun MWNT/PAN composite nanofibre sheets by collecting the nanofibres onto a winder with a surface velocity larger than the velocity of electrospun nanofibres. They observed highly oriented CNTs within the nanofibres and attributed this to the structural formation during the electrospinning process and the slow relaxation of CNTs [109]. Using a similar setup, Jose *et al.* [137] also fabricated aligned electrospun Nylon-6 nanofibres containing surface modified MWNTs. The MWNTs showed high degree of alignment in the nanofibres. They also demonstrated that MWNT/nylon-6
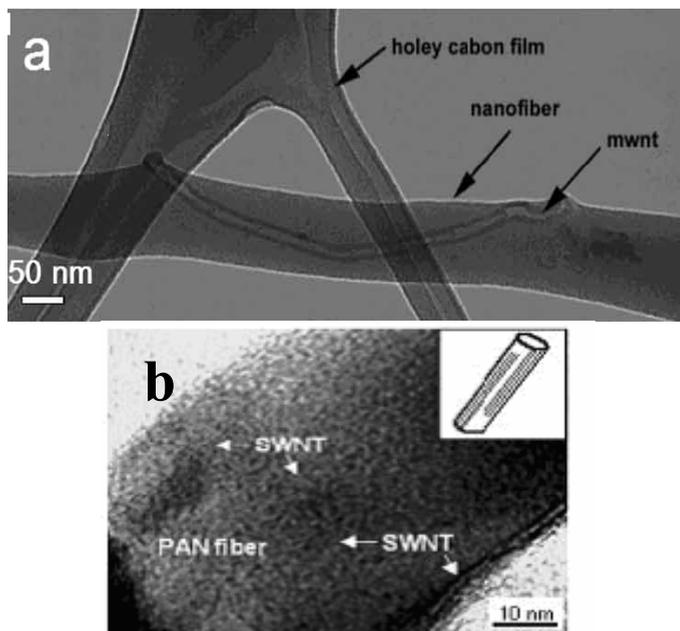
Fig. 3. a) TEM image of protrusion of MWNTs from the fibre [128] [Copyright ACS]. b) High resolution TEM image showing a uniform distribution and alignment of SWNTs in PAN fibre with the diameter of about 50nm [45] [Copyright Wiley-VCH].

nanofibres had significantly smaller diameter, ranging from 250 nm to 750 nm, than the neat nylon-6 fibres and the fibre diameter reduced with the increase in the concentration of CNTs. This is consistent with what Ra *et al.* reported for electrospun MWNT/PAN nanofibres [141].

Huang *et al.* [142] used a modified rotating disk collector including two separate, parallel aluminium plates with sharp edges to fabricate CNTs/polyvinylidene difluoride (PVDF). They found that the interfacial interaction between SWNTs and PVDF and the application of extensional forces had a strong synergistic effect on crystalline structures of PVDF inducing highly oriented crystallites at only 0.01 wt% of nanotubes. However, the effect of the MWNTs on crystal orientation was low and was attributed to the detrimental effect of the MWNTs on the preferred orientation of PVDF chains.

Zhang *et al.* [138] fabricated uniaxially aligned electrospun nanofibres of PAN and Triton X-100 grafted MWNTs using two collectors including i) parallel copper sheets [143] and ii) a slowly rotating drum with multi electrodes [144]. While large scale aligned MWNT/PAN can be produced using the multi-electrode drum at a slow rate of 1 rpm no aligned nanofibres were observed at high rate of drum rotation, i.e. 600 rpm. This was attributed to lack of enough time for nanofibres to be attracted across the axes of the drum at higher rotation rate.

Yee *et al.* [139] modified the design of a disk by using two separate parallel aluminium electrodes attached to a rotating disk to collect well-aligned MWNT/PVDF nanofibres where both electric field and mechanical force contributed to nanofibre alignment. It was found that the alignment of nanofibres collected by the modified disk was about the same as

that by the conventional disk. However, nanofibres collected by modified rotating disk showed a uniform lateral distribution across a relatively larger distance. This was mainly because the specific electric field distribution created by aluminium electrodes coupled with the repelling force from the residual charges on the electrospun nanofibres. Aligned MWNT/nylon-6 nanofibres were also electrospun using perpendicular rotating disks [140]. In addition to rotating collectors, a secondary collector plate (as simple as a cardboard) was found to be an effective way of fabricating aligned electrospun SWNT/regenerated silk nanofibres of less than100 nm in diameter [123].

c. Mechanical properties

Most studies on CNT/polymer composites have been driven by improving the mechanical strength. This is of particular importance for electrospun nanofibres, because the relatively low bulk mechanical properties hinder their applications in some areas. Due to the small size, measuring the tensile properties for individual electrospun nanofibres is difficult. A few experimental investigations on mechanical properties of electrospun CNT/polymer nanofibres have been reported [45][124][145][146]. In these studies, atomic force microscopy (AFM) has been used as a tool to study the mechanical behaviour of single electrospun composite nanofibres.

Ko *et al.* [45] were among the first to study the mechanical properties of CNT reinforced electrospun nanofibres. They measured the elastic modulus of electrospun SWNT/PAN nanofibres. The fibre modulus obtained was 140 GPa which was well beyond the value of 60 GPa measured for PAN fibres [45]. Nevertheless, other mechanical properties such as strength and strain at break have not been measured. Liu *et al*. [145] studied the stress-strain behaviour of electrospun MWNT/ poly (methyl methacrylates) (PMMT) single nanofibres. Using AFM and environmental scanning electron microscope, tensile strength as high as 80 MPa and Young's modulus of 267 MPa were reported for composite nanofibres, which are significantly higher than that of pure PMMA nanofibres. The significant improvement in modulus and strength was due to the good dispersion and orientation of nanotubes within the polymer and to the strong interfacial adhesion due to the nanotube surface modification. Recently, Almecija *et al.* [146] developed a method to deposit electrospun nanofibres across pre-prepared trenches on silicon substrates. Measuring both force and displacement on SWNT/PVA strained nanofibres. They then developed a model in which the tensile properties of single nanofibres were generated using force-displacement data. The maximum strength and modulus obtained by this method was 2.6 and 85 GPa, respectively.

A novel method to study the mechanical deformation of electrospun composite nanofibres has been described by Kim *et al.* [125]. They performed *in-situ* tensile tests on single electrospun composite nanofibres by electron beam induced thermal stress under TEM. In this method, the bombardment of electron beam onto the fibres resulted in local thermal expansion and hence initiated tensile deformation. The strain rate can be controlled by adjusting the electron beam flux on the fibres [26] [147]. As the strain increased, the fibre elongated and with further increase of strain the necking occurred mainly at the end of a MWNT embedded into fibre. This was due to the slippage of the MWNTs in the direction of the applied tensile stress taking place beyond a certain critical stress value. A combination between CNT slippage mechanism and stress concentration (provided by the nanopores on the fibre surface), as well as the transfer of mechanical load from polymer matrix to MWNTs (due to highly aligned nanotubes along the fibre axis) were considered to be the main reason for the enhancement of the critical fracture strain and the toughening the electrospun

composite nanofibre [125]. More recently Singh and co-workers [148] developed a novel characterisation device for testing individual electrospun polymer nanofibres. The tool consists of a nano manipulator, a transducer and associated probes and is operated inside a scanning electron microscope (Figure 4a). The three-plate capacitive transducer independently measures forces and displacement with a resolution of micronewton and nanometre, respectively. The tensile test of an electrospun polyaniline fibre (diameter ~1 μm) demonstrated the capabilities of the system. Engineering stress versus strain curves exhibited two distinct regions (Figure 4b); the Young's modulus of the latter region was approximately 5.9 GPa. Failure at the probe-specimen weld occurred at ~67 MPa, suggesting a higher yield stress for polyaniline microfibres when compared with the bulk counterpart.

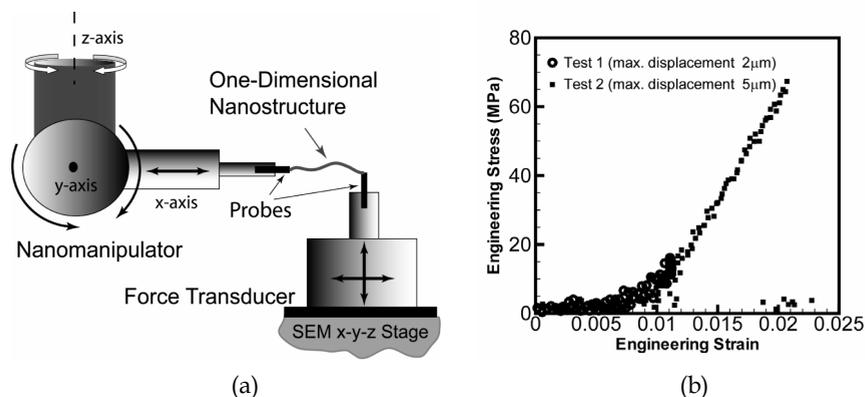(a)   (b)

Fig. 4. (a) Schematic of the nano mechanical characterisation device showing the magnified view of the fibre specimen between two probes and the available degrees of freedom. (b) Engineering stress and strain for *test 1* (circles) and *test 2* (squares); the latter experiment involved loading the specimen to a maximum displacement of 5 μm; failure at the probe-specimen weld occurred prior to reaching maximum displacement [148] [Copyright AIP].

Ye *et al*. [147] used TEM to study the reinforcement and rupture behaviour of SWNT/PAN and MWNT/PAN nanofibres. Under tension, two-stage rupture behaviour of the composite nanofibres including crazing of polymer matrix and pulling-out of carbon nanotubes was observed. The involved mechanism was explained by the fact that CNTs reinforce the polymer fibres by hindering crazing extension, hence reducing the stress concentration and dissipating the energy. Two major factors, the distribution of CNTs in the polymer matrix and interfacial adhesion between nanotubes and polymers, determine the reinforcement effect of CNTs in polymer fibres.

Elastic deformation of MWNTs in electrospun MWNTs/PEO and MWNTs/PVA nanofibres were studied by Zhou and co-workers [149]. The degree of elastic deformation was found to increase as the modulus of the polymer matrix increased. A simplified model was also proposed to estimate the elastic modulus ratio of MWNTs and polymers. To confirm the validity of the model, the results were compared with that from AFM measurement.

As for CNT reinforced electrospun nanofibre mats, several research groups studied the mechanical behaviour of electrospun nanofibre membranes. These studies have demonstrated that CNTs improve the mechanical properties of electrospun polymer nanofibres as long as they are well dispersed into the polymer matrix. For example stress-

strain analysis showed that the tensile strength of SWNT reinforced polyurethane (PU) nanofibre membrane was enhanced by 46% compared to pure PU nanofibre mat [119]. However, this value was further increased by 104% for PU membranes containing ester-functionalized SWNTs. This improvement in the mechanical strength was attributed to improved dispersion of the SWNTs as well as enhanced interfacial interaction of nanotubes with the PU matrix because of modified nanotube surface [119]. Recently, Yoon *et al.* [150] reported enhancement in mechanical strength of CNT reinforced nanofibres caused by better nanotube-polymer adhesion and good dispersion of SWNT because of the plasma treatment of nanotubes. Uniform dispersion of amino functionalised MWNTs and nanotube alignment in nylon 6 led to increased mechanical properties of electrospun MWNT/nylon-6 nanofibre mat [137] [151].

The upper limit of CNT concentration in electrospun nanofibres is also confined by the extent of CNT dispersion. Hou *et al.* [113] reported thick sheets of electrospun PAN nanofibres containing well-aligned MWNTs with concentrations from 0 to 35 wt%. It was shown that the presence of MWNTs improved the modulus and tensile strength of the composite nanofibre sheet. The tensile modulus increased with increasing the concentration of MWNTs in nanofibres. However, the tensile strength of nanofibres increased with an increase in the concentration of MWNTs up to 5wt% and then started to reduce for higher MWNTs content. This was attributed to poor dispersion of the MWNTs and poor interfacial cohesion between the MWNTs and the polymer matrix at higher concentrations. Meanwhile, strain to break reduced with increasing the MWNT concentration. Similar findings have also been reported by other research groups [152] [153].

The importance of fibre alignment on the mechanical properties has been well established. In a study by Jeong et al. [154], aligned electrospun MWNT/PVA membranes have been reported. The tensile strength of these membranes increased from 5.8 MPa to 12.9 MPa by adding 1wt% of MWNTs. In a recent study, however, Blond et al. [155] achieved a higher level of reinforcement. They produced aligned SWNT/PVA nanofibre membrane with the strength of up to 40 MPa using a rotating drum collector followed by mechanical stretching.

It has been demonstrated that CNTs nucleate crystallisation in CNT/polymer composite films [50][57][66][67]. The presences of crystalline polymer coating around the nanotubes significantly enhance the stress transfer and therefore the mechanical properties of composites [42]. It is normally believed that crystallisation of polymers is a slow process involving orientation of polymer molecules and solidification. Therefore, nucleate crystallisation of polymer should occur mainly in composite films that normally take a long time for evaporation of solvent during the film casting process, and a fast drying and solidification process, such as in electrospinning, could hinder the nucleation crystallisation because the polymer molecules have not sufficient time to orient around nanotubes. In a recent study, Naebe *et al.* [114] revealed that the nucleation crystallisation indeed happened in CNT reinforced electrospun PVA nanofibres. They demonstrated that the increased PVA crystallinity due to the presence of CNTs resulted in considerable improvement in the strength of composite nanofibres. Later, other researchers [123] also demonstrated the occurrence of nucleation crystallisation in other CNT-polymer systems with improved in tensile properties.

Post-electrospinning treatment, using methanol for instance, was found to be an effective way to increase the mechanical properties of electrospun PVA nanofibres [156]. Naebe *et al.* [114] performed a series of post-spinning treatments on MWNT/PVA composite nanofibres including soaking in methanol and crosslinking with glutaric dialdehyde. These treatments

induced the crystallinity of nanofibres as well as established a crosslinked PVA network. They showed that the tensile strength of MWNT/PVA composite nanofibres was significantly improved by applying post–electrospinning treatments. This was attributed to the increased polymer crystallinity due to the combined effect of post-spinning and nucleation crystallization of polymer matrix induced by the nanotubes. Similar results were found for SWNT reinforced PVA electrospun nanofibres [115]. In a similar study, Gandhi *et al*. [123] showed that post-spinning treatment with methanol and stretching significantly increased the strength and toughness of electrospun silk nanofibres containing only 1% CNTs. Methanol increased the polymer crystalline structure whereas stretching assisted in aligning them in the nanofibres.

d. Influence of polymer types

Different types of polymers, including semi-crystalline, amorphous and elastomeric polymers, have been used to fabricate CNT-containing composite nanofibres [119] [125] [127] [128] [145]. It was revealed that flow-induced crystallisation might have occurred during electrospinning of semi-crystalline polymers, and the polymer crystals were oriented along the fibre axis [128] [134]. On the other hand, it was shown that nanotubes aligned well during electrospinning of CNT/polymer nanofibres. Since the presence of oriented polymer crystals has a significant influence on mechanical properties, it is complicated to evaluate the real contribution of CNTs regarding the improvement in the mechanical performance of electrospun composite nanofibres.

With the amorphous polymers, only a few studies on CNT/polymer nanofibres have been reported [125] [127] [145]. Although enhanced mechanical properties were reported for the nanofibres, the role played by polymer morphologies (i.e. crystalline, amorphous, and rigid) was not fully understood.

e. Influence of carbon nanotube types

SWNTs and MWNTs differ from one another in their size and dispersability in solution and polymer matrix as well as in mechanical and electrical properties [3]. However, few papers have reported on the influence of CNT types on the structure-property relationship of electrospun nanofibres.

Dror et al. [128] and Salalha et al. [134] studied the effect of SWNTs and MWNTs on the formation of electrospun PEO nanofibres. On the basis of X-ray diffraction, it was demonstrated that while the PEO crystal orientation in electrospun nanofibres was not affected by the inclusion of SWNTs, the incorporation of MWNTs into PEO matrix had a detrimental effect on the degree of the crystal orientation. Nevertheless, no data on mechanical properties of CNT/PEO nanofibres was reported. Electrospun MWNT/PVA and SWNT/PVA nanofibres have been reported [114] [115]. It was observed that the SWNTs and MWNTs induced different crystal phases in the PVA. With the same CNT concentration, the tensile strength of MWNT/PVA nanofibres showed no significant difference to that of SWNT/PVA ones.

f. Electric and thermal properties

The formation of electrospun CNT/polymer nanofibres has been explored for possible improvement in the electrical and thermal properties of polymer. As for electrical conductivity, most polymers possess a very low conductivity and the presence of CNTs

provides a platform for inherently conducting polymer nanofibres suitable for many applications. Incorporation of CNTs into polymer nanofibres was found to increase the electrical conductivity of composite nanofibres [109]. The electrical properties of electrospun MWNT/PAN composite fibres were investigated by two independent groups [109] [141]. Ge *et al.* [109] developed highly orientated PAN nanofibre mats containing MWNTs. At a concentration of 10 wt% MWNTs, the composite nanofibres started to form the percolating network. Due to highly anisotropic orientation of the composite nanofibre structure, the electrical conductivity enhanced to ~1.0 S/cm at a concentration of 20 wt% MWNTs. Ra *et al.* [141] achieved a rather high conductivity with carbonised MWNT/PAN nanofibres. While carbonised PAN nanofibres without CNTs did not reveal anisotropy in electrical conductivity, a high anisotropy in electrical conductivity was observed for the carbonised MWNT/PAN nanofibres. The conductivity parallel to the spinning direction was about three times higher than that perpendicular to the spinning direction at only 2.5 wt% of MWNT. The authors claimed that the direction dependency of conductivity is an indication of CNT alignment along the nanofibre axis, which was further supported by the TEM observation.

Electrospun MWNT/nylon composite nanofibres were also prepared and the electrical properties were examined as a function of the filler concentration [126]. The MWNT/nylon nanofibres were electrospun on the ITO coated glass and a metal coated glass electrode was placed on the composite fibre sheet. The filler concentration was varied from 0 to 20 wt% and the I~V characteristics were examined. As shown in Figure 5, the I~V curve indicates a non-ohmic behaviour, which changed with the filler concentration. Similar electrical behaviour was also reported for SWNT/PVDF [157] and MWNT/PEO [158] composite nanofibres.
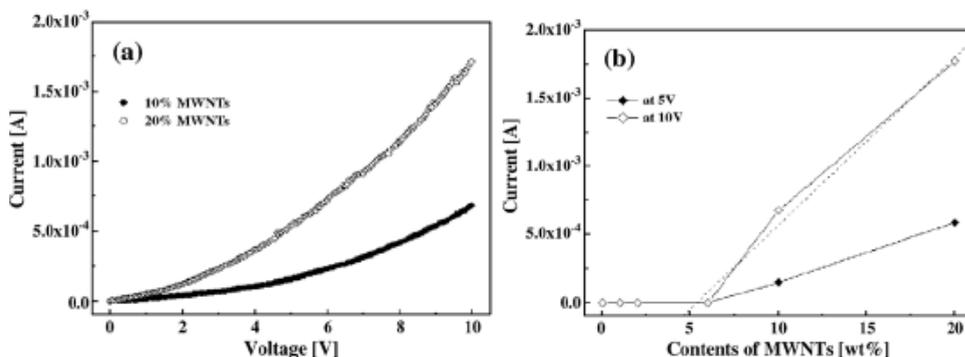

Fig. 5. (a) I~V characteristics for the nylon electrospun nanofibres loaded with 10 and 20 wt% CNTs. (b) Plot of the current as a function of the CNTs wt.% at 5 and 10 V [126] [Copyright Elsevier Science].

In an attempt to define the parameters that determine the conductivity of the nanofibre mats, McCullen *et al.* [152] performed a study on electrospun MWNT/PEO nanofibre. Electrical conductivity measurements of the randomly deposited nanofibre mats showed that by increasing the concentration of MWNTs the electrical conductivity increased remarkably. Above a percolation threshold of about 0.35 % of MWNTs in PEO, the conductivity increased by a factor of 10^{12} and then became approximately constant as the

concentration of MWNTs was further increased. Maximum conductivity was obtained at about 1 wt % loading of MWNTs. The addition of only 1 % CNTs to silk nanofibres was found to increase the conductivity of nanofibres mat significantly [123].

In a rather different approach to studying the electrical conductivity of polymer nanofibres, Kang *et al.* [159] prepared MWNT/silk protein nanofibre mat. The electrical conductivity of the electrospun mat was found to be significantly higher than the plain silk protein nanofibres (from ~10^{-15} to ~10^{-4} S/cm) regardless of the dip-coating time. It was hypothesised that CNTs not only deposited on the surface of electrospun mat but also adsorbed by nanofibres due to strong interaction between the oxidised MWNTs and the peptide groups of silk protein.

Sundaray and co-workers [117] described the electrical conductivity of single electrospun MWNT/PMMA composite nanofibres. Alignment of MWNTs in the direction of the fibre axis was confirmed by bright field TEM images. The room temperature DC electrical conductivity of an electrospun MWNT/PMMA fibre showed a ten-orders increase compared to pure PMMA fibre. Percolation threshold of the composite nanofibre was well below the 0.05% w/w of CNTs loading and the conductivity increased with increase in MWNT concentration.

Not many papers reported on the thermal properties of electrospun CNT/polymer composite nanofibres. Thermal analysis has been carried out on the electrospun composite nanofibres to understand the relationship between the presence of carbon nanotubes and thermal properties. It was indicated that the presence of CNTs enhanced the thermal stability of polymer nanofibres.

The effect of heat treatment on SWNT/PAN composite fibres was investigated using TEM by Ko *et al.* [45]. SWNT/PAN was found to keep its shape but its microstructure changed significantly after the heat treatment. PAN lost hydrogen and oxygen during heat treatment and the shrinkage led to SWNTs sticking out of the fibres. Thermal properties of MWNT/PAN was investigated by Ge *et al.* [109] using thermal gravimetric analysis (TGA) and thermal mechanical analysis (TMA). They found that the thermal stability of MWNT/PAN nanofibres increased when compared to pure PAN nanofibres. It was attributed to the structural changes occurred in the nanofibres due to the presence of the carbon nanotubes, although the driving force behind the structural change has yet to be determined. An increased Tg was also found for MWNT/PAN composite nanofibres due to the formation of charge-transfer complexes which restricted molecular segment motions at the interface between the nanotube and PAN. The thermal expansion coefficient (CTE) of the MWNT/PAN composite nanofibres also increased [109]. A similar trend in thermal stability was also reported for MWNT reinforced polybutylene terephthalate (PBT) [124], PVA [114] and nylon-6 [151] composite nanofibres.

g. Applications

Electrospun nanofibres have a broad range of applications due to the combination of simplicity of fabrication process and their unique features. While several reviews on polymer nanofibre applications have been published [99][100][101][160], the works on CNT/polymer nanofibres have been mainly focused on developing a fundamental understanding of the fibre structure property relationships. Conducting electrospun CNT/polymer nanofibres have been demonstrated to be attractive for a large variety of potential applications, such as in optoelectronic and sensor devices [161]. For example,

electrochemical biosensors were fabricated using electrospun MWNT/polymer composite nanofibres [162] [163]. In a recent study, the electrospun MWNT/poly(acrylonitrile-co-acrylic acid) nanofibres were found to enhance the maximum current of glucose oxide electrode and the enzyme electrode could be used several times without significant decrease in current [162]. Electrospun PVA nanofibres containing chitosan grafted MWNTs also exhibited sensory ability to hydrogen peroxide and potassium ferricyanide [163]. This nanofibre-based sensor demonstrated more sensitive response and intense current as well as faster electric charge transport than those of film-based sensors. Other potential applications of electrospun CNTs/polymer nanofibres include tissue engineering scaffolds, composite reinforcement, drug carriers for controlled release and energy storage. Given the advantages of CNT/polymer nanofibres in mentioned fields above, the number of investigations on these topics is very small.

5. Concluding remarks

The use of the electrospinning technique to incorporate carbon nanotubes (CNTs) into polymer nanofibres has been shown to induce alignment of the nanotubes within the polymer matrix, leading to significant improvements in fibre strength, modulus and electrical conductivity. To realise their commercial applications, considerable work is still required. This includes a thorough understanding of the structure–property relationship for various electrospun polymer nanofibres, the effective incorporation of carbon nanotubes into polymer fibres with a high loading content, and large scale production of composite nanofibres of consistent and high quality but at a low cost [164] [165] [166]. Core-shell CNT/polymer nanofibres are also a subject that warrant further research [167].

6. References

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