

# Carbon nanotube composites

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Carbon nanotubes are molecular-scale tubes of graphitic carbon with outstanding properties. They are among the stiffest and strongest fibres known, with Young's moduli as high as 1 TPa and tensile strengths of up to 63 GPa. They also have remarkable electronic properties and can be metallic or semiconducting depending on their structure and diameter. There is currently great interest in exploiting these properties by incorporating carbon nanotubes into some form of matrix. A wide range of polymer matrices have been employed, and there is growing interest in nanotube/ceramic and nanotube/metal composites. This review outlines the properties of carbon nanotubes and describes the preparation and properties of carbon nanotube composites. The prospects for commercial exploitation of these materials are discussed.

**Keywords:** Nanotubes, Composite materials, Nanotube/polymer composites

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## Introduction

Carbon nanotubes are among the most exciting new materials to have been discovered in the past 30 years.<sup>1</sup> Their remarkable properties have attracted intense interest from the scientific community, as well as from industry, and nanotubes are currently the subject of around 7 papers per day. The explosion of interest in carbon nanotubes can be traced back to a 1991 *Nature* paper by Sumio Iijima.<sup>2</sup> Iijima was using high resolution transmission electron microscopy (HRTEM) to examine carbon produced by the arc evaporation of graphite in an atmosphere of helium. About a year earlier, it had been shown that this method could be used to produce C<sub>60</sub> and other fullerenes in high yield,<sup>3</sup> so it seemed likely that other novel forms of carbon might be formed at the same time. It was while studying the hard deposit which formed on the graphite cathode following arc evaporation that Iijima made his discovery: the central part of the deposit contained large numbers of tiny tubules of graphitic carbon, consisting of concentric graphene cylinders, typically about 10 nm in diameter, with fullerene-like end-caps. Although tubes of carbon, produced catalytically, had been known for decades, the structures discovered by Iijima were far more perfect than any that had been seen before, and promised to have exceptional properties. In subsequent work, two groups showed that single-walled nanotubes could be produced in a similar apparatus in which one or both electrodes contained cobalt, nickel, or some other metal.<sup>4,5</sup> These single-walled tubes generally have smaller diameters than the multiwalled nanotubes (typically of the order of 1–2 nm dia.). It was shown in 1996 that single-walled nanotubes, like multiwalled nanotubes, can be produced catalytically.<sup>6</sup>

There is now abundant experimental evidence of the outstanding properties of carbon nanotubes. Their

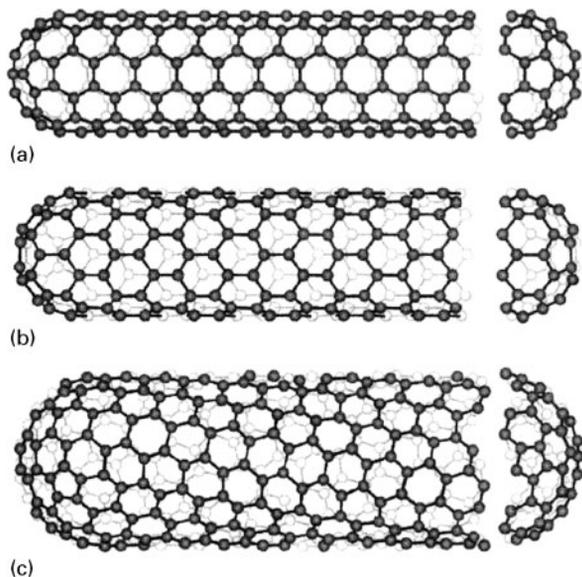
stiffness and strength are phenomenal. Measurements using *in situ* transmission electron microscopy (TEM), and atomic force microscopy (AFM) have produced estimates for the Young's modulus of the order of 1 TPa.<sup>7,8</sup> For comparison, the stiffest conventional carbon fibres have Young's moduli of approximately 800 GPa, while glass fibres typically have moduli of about 70 GPa. Direct measurements on individual nanotubes using atomic force microscopy have shown that they can accommodate extreme deformations without fracturing;<sup>9</sup> they also have the extraordinary capability of returning to their original, straight, structure following deformation. In addition, carbon nanotubes are excellent electrical conductors,<sup>10</sup> with current densities of up to 10<sup>11</sup> A m<sup>-2</sup>, and have very high thermal conductivities.<sup>11</sup>

Many of these outstanding properties can be best exploited by incorporating the nanotubes into some form of matrix, and the preparation of nanotube containing composite materials is now a rapidly growing subject.<sup>12,13</sup> In many cases, these composites have employed polymer matrices, but there is also interest in other matrix materials, such as ceramics and metals. The aim of this paper is to review recent work on carbon nanotube composites, and to assess how successful this work has been in exploiting the full potential of nanotubes. To begin, a brief introduction is given to the science of carbon nanotubes.

## Structure and properties of carbon nanotubes

The nanotubes discovered by Iijima have structures closely related to those of fullerenes. This can be most clearly illustrated by considering the two 'archetypal' carbon nanotubes which can be formed by cutting a C<sub>60</sub> molecule in half and placing a graphene cylinder between the two halves. Dividing C<sub>60</sub> along one of the five-fold axes produces the 'armchair' nanotube shown in Fig. 1a, while bisecting C<sub>60</sub> parallel to one of the three-fold axes results in the 'zigzag' nanotube shown in

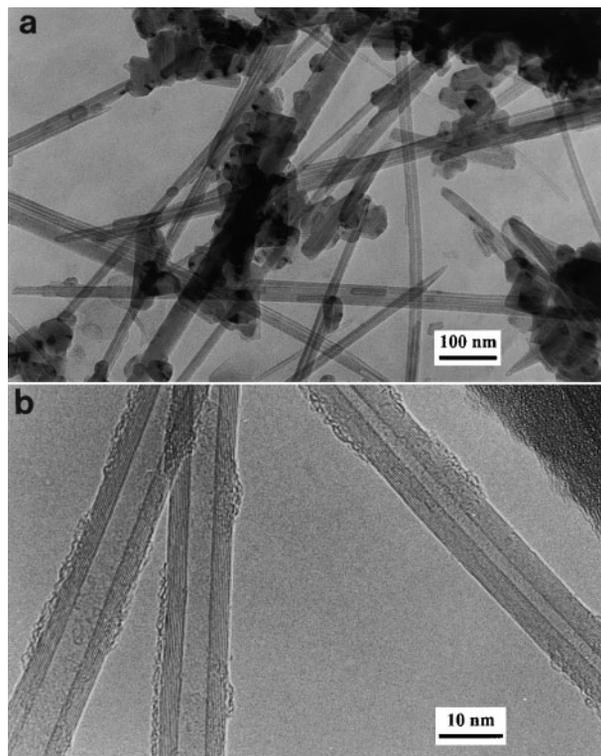
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a armchair  $(n, m)=(5, 5)$ ; b zigzag  $(n, m)=(9, 0)$ ; c chiral  $(n, m)=(10, 5)$

### 1 Three classes of carbon nanotube structure

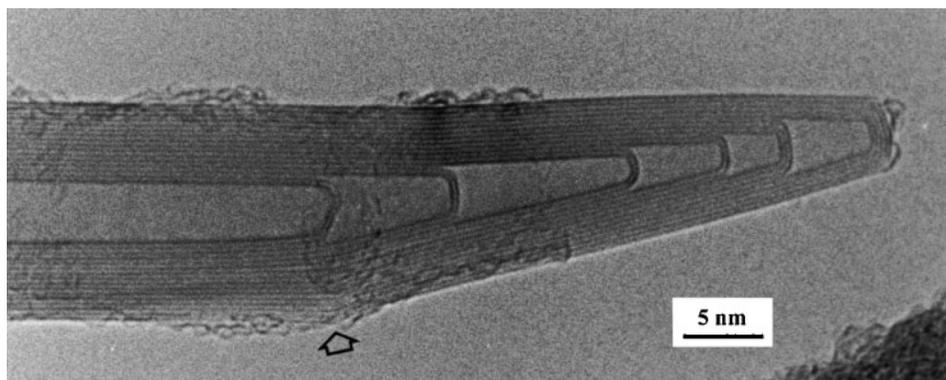
Fig. 1b. The terms 'zigzag' and 'armchair' refer to the arrangement of hexagons around the circumference. There is a third class of structure, 'chiral', in which the hexagons are arranged helically around the tube axis, as shown in Fig. 1c. Experimentally, the tubes are generally less perfect than the idealised versions shown in Fig. 1 and, as already noted, may be either multiwalled or single-walled. The abbreviations MWNT and SWNT are commonly used for multiwalled and single-walled nanotubes respectively. Figure 2a shows a typical sample of MWNT-containing cathodic soot at moderate magnification. As can be seen, the nanotubes are accompanied by other material, including nanoparticles (hollow, fullerene-related structures) and some disordered carbon. At high resolution, the individual layers making up the concentric tubes can be clearly imaged, as in Fig. 2b. The multiwalled tubes range in length from a few tens of nanometres to several micrometres, and in outer diameter from about 2.5 to 30 nm. The end-caps of the tubes are sometimes symmetrical in shape, but more often asymmetric. Conical structures of the type shown in Fig. 3 are commonly observed. This type of structure is believed to result from the presence of a single pentagon (at the position indicated by the arrow) with five further pentagons at the apex of the cone.



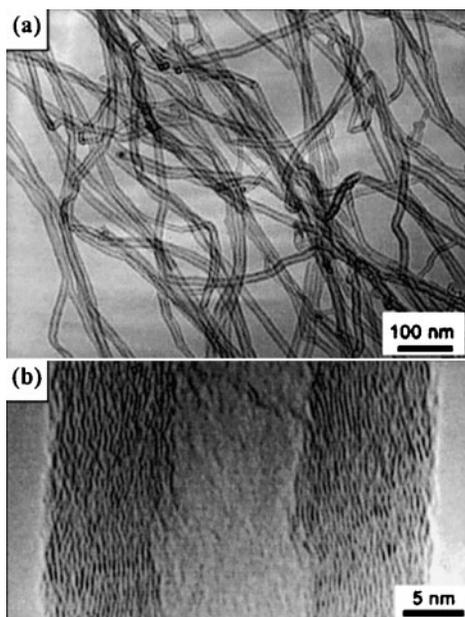
2 a TEM image of nanotube-containing soot and b higher magnification image of individual tubes

Multiwalled tubes produced by catalytic methods are generally much more defective than those made by arc evaporation, as can be seen in Fig. 4.<sup>14</sup> However, their properties can be improved by high temperature heat treatment.<sup>15</sup> Some typical micrographs of SWNTs can be seen in Fig. 5.<sup>16</sup> As a result of their very small diameters, the tubes are much more flexible than MWNTs, and are therefore often observed to be curled and looped rather than straight. Because SWNTs frequently have a narrow range of diameters, they tend to cluster together to form 'ropes'.

There have been a large number of studies, both theoretical and experimental, of the mechanical properties of carbon nanotubes. The first measurements of stiffness were made in 1996 by Treacy *et al.*,<sup>7</sup> who carried out *in situ* measurements of the intrinsic thermal vibrations of multiwalled carbon nanotubes in a TEM. These indicated that the tubes had extremely high elastic moduli, but the error on the measurements was large: estimates for the Young's modulus ranged from



3 Image of typical multiwalled nanotube (MWNT) cap, with arrow indicating approximate position of pentagonal ring

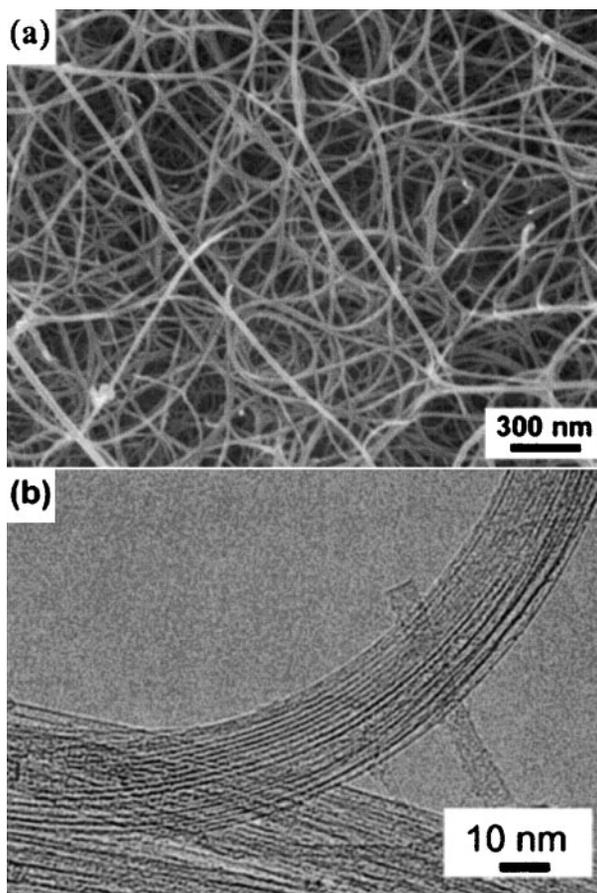


a low magnification TEM image; b HRTEM image of typical nanotube

**4 TEM images of multiwalled carbon nanotubes synthesised by decomposition of  $C_2H_2$  at  $850^\circ C$  over cobalt catalyst<sup>14</sup>**

410 GPa to 4.15 TPa, with an average of 1.8 TPa. Rather more accurate measurements were made using a 'nanostressing stage' inside a scanning electron microscope (SEM).<sup>17</sup> These experiments indicated that the Young's modulus of the outermost layers of multiwalled carbon nanotubes varied from 270 to 950 GPa. The tensile strengths of individual nanotubes were also determined in this work, and values ranging from 11 to 63 GPa were found. Measurements of Young's modulus have also been carried out using atomic force microscopy. Wong *et al.*<sup>8</sup> described a method of fixing nanotubes at one end, and then determining the bending force  $F$  of the fibres as a function of displacement  $d$ . For small deflections, linear  $F-d$  curves were observed, and the results implied a value of  $\sim 1.28$  TPa for the Young's modulus. However, for deflections larger than  $10^\circ$  an abrupt change in the slope of the  $F-d$  curve was seen. This was attributed to elastic buckling of the tubes. In TEM studies of nanotubes, buckled tubes are quite often seen, as a result of stresses imposed by the way the tubes are supported on the grid. In some cases, the buckles are regularly spaced, as shown in Fig. 6.<sup>18</sup> It has been demonstrated that when the stress constraining a tube is released, the tube can return to its original straight form. This behaviour sets nanotubes apart from conventional carbon fibres, and all other currently known fibres, which are much more susceptible to fracture when subject to stress beyond the elastic limit. It also raises the fascinating possibility that composites could be produced which would snap back into place following deformation.

As already noted, catalytically produced MWNTs are much less perfect in structure than arc grown tubes, and are therefore considerably less stiff. Salvetat *et al.* used atomic force microscopy to record force-displacement curves for nanotubes prepared by the catalytic decomposition of acetylene.<sup>19</sup> This produced an average value for the Young's modulus of 27 GPa. The tensile



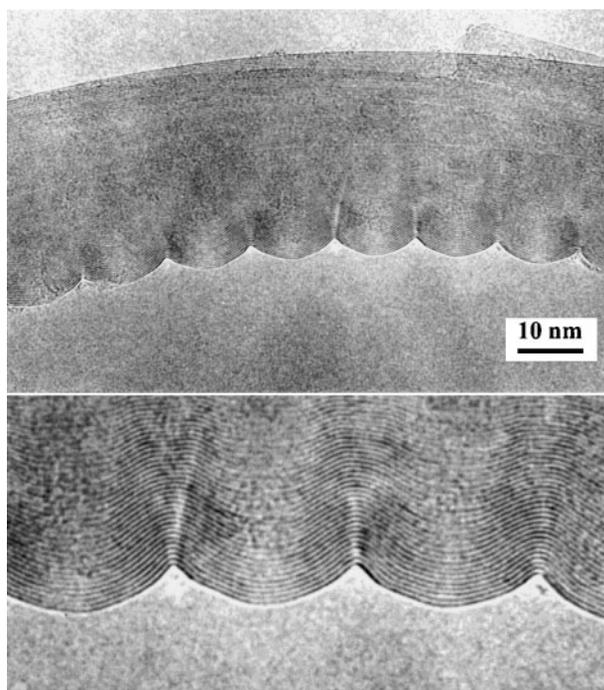
a low magnification SEM image; b high magnification TEM image

**5 Images of single-walled carbon nanotubes prepared by decomposition of  $C_2H_2$  at  $950^\circ C$  over  $FeMo/Al_2O_3$  catalyst<sup>16</sup>**

strengths of catalytically produced MWNTs have not yet been measured. However, it is possible that these might be relatively high: the defects in these imperfect structures might be expected to assist stress transfer between layers.

Determining the mechanical properties of SWNTs presents an even greater challenge than for MWNTs. However, some measurements have been made using a nanostressing stage.<sup>20</sup> These produced values for the Young's modulus in the range 320–1470 GPa (mean 1002 GPa) and an average breaking strength of 30 GPa.

There have also been a substantial number of studies of the electronic properties of carbon nanotubes.<sup>1,21</sup> Early theoretical work showed that nanotubes could be metallic or semiconducting depending on their structure and diameter.<sup>22–24</sup> Ebbesen *et al.* confirmed experimentally that the electronic properties of nanotubes could vary widely from tube to tube.<sup>25</sup> Both semiconducting and metallic behaviour has been observed. Measured resistivities fall into the approximate range  $0.05 \mu\Omega m$ – $10 m\Omega m$ . This compares with a value of approximately  $0.4 \mu\Omega m$  for high quality single crystal graphite (parallel to the  $c$  axis) and  $0.017 \mu\Omega m$  for copper. The resistivities of catalytically produced nanotubes are likely to be similar to those of disordered carbons, i.e. of the order of  $10$ – $100 \mu\Omega m$ , but experimental measurements on this type of tube have not yet been carried out. The thermal and optical properties of carbon nanotubes



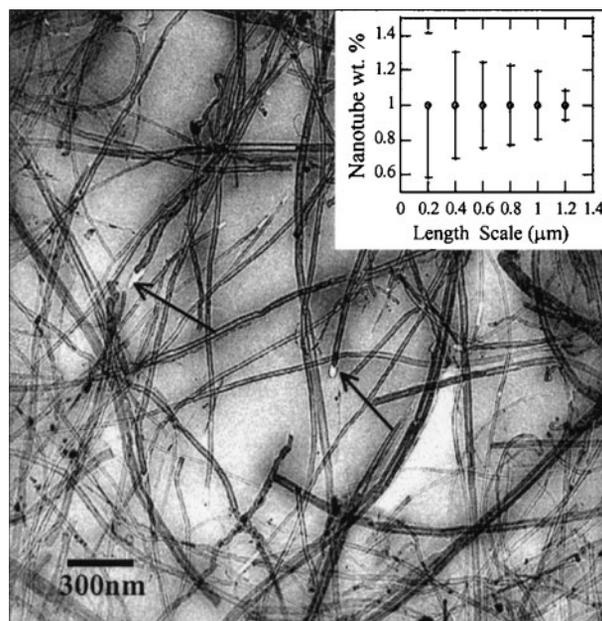
6 High resolution TEM image of deformed nanotube showing periodic buckling<sup>18</sup>

have been studied less intensively than the electronic properties, but some interesting results have been obtained. The high thermal conductivities of nanotubes have already been mentioned.<sup>11</sup> It has also been reported that carbon nanotube suspensions have non-linear optical properties, suggesting possible applications as optical limiters.<sup>26</sup>

Another area which has been the subject of much research is the chemical modification of carbon nanotubes. Chemical treatments of nanotubes were first carried out in an attempt to selectively remove the end-caps and use them as molecular containers. It was demonstrated in 1994 that nanotube caps could be removed by treatment with hot nitric acid, apparently as a result of selective oxidation at the pentagonal rings.<sup>27</sup> In subsequent work, it was demonstrated by acid-base titration and by temperature programmed decomposition that this acid treatment resulted in the formation of surface carboxylic acid and other groups on the tube surfaces.<sup>28</sup> These surface acid groups can then be further modified in a variety of ways.<sup>29</sup> Functionalisation has been widely used to facilitate the dispersion of nanotubes in solvents as a prelude to the preparation of composite materials, and can also help to improve bonding between tubes and matrix.<sup>30</sup>

## Preparation of carbon nanotube/polymer composites

A commonly used method for preparing nanotube/polymer composites has involved mixing nanotube dispersions with solutions of the polymer and then evaporating the solvents in a controlled way. As noted in the previous section, the nanotubes are often pretreated chemically to facilitate solubilisation. Shaffer *et al.*, for example, have demonstrated that acid treatments enable stable aqueous solutions of catalytically produced MWNTs to be prepared.<sup>31</sup> These workers then showed that a nanotube/PVA (polyvinyl alcohol) composite could be



7 TEM image of MWNT/polystyrene thin film (arrows indicate regions of polymer shrinkage): inset shows distribution of nanotube lengths<sup>34</sup>

prepared simply by mixing one of these aqueous nanotube dispersions with an aqueous solution of the polymer and then casting the mixtures as films and evaporating the water.<sup>32</sup> Solution based methods have also been used to produce nanotube/polystyrene composites. Thus, Hill *et al.* have solubilised both SWNTs and MWNTs by functionalising with a polystyrene copolymer.<sup>33</sup> This was achieved by first acid treating the tubes and then carrying out esterification of the surface-bound carboxylic acids. The polymer-modified carbon nanotubes were shown to be soluble in common organic solvents. To prepare composites, polystyrene was dissolved in the nanotube solution, and nanotube/polystyrene thin films prepared using wet casting. Functionalisation of the nanotubes is not always necessary in order to prepare a polymer composite. Qian *et al.* used a high energy ultrasonic probe to disperse MWNTs in toluene and then mixed the dispersed suspension with a dilute solution of polystyrene in toluene, again with ultrasonic agitation.<sup>34</sup> The low viscosity of the polymer solution allowed the nanotubes to move freely through the matrix. The mixture was cast on glass and the solvent removed to yield MWNT-doped films. Specimens of the composite were prepared for TEM by placing drops of the mixed solution on copper TEM grids. On evaporation of the toluene, a thin film of the composite was left suspended across the grid bars. A micrograph of one of these films is shown in Fig. 7, and this illustrates the excellent dispersion that was achieved. Note that *in situ* polymerisation has also been used to prepare nanotube/polystyrene composites, as is discussed below.

The solution mixing approach is limited to polymers that freely dissolve in common solvents. An alternative is to use thermoplastic polymers (i.e. polymers that soften and melt when heated), and then apply melt processing techniques. Thus, shear mixing can be used to produce a homogeneous dispersion of nanotubes and extrusion to produce nanotube alignment or to fabricate artefacts in the required form by injection moulding.



**8 Alignment of nanotubes in polymer matrix following cutting with microtome: arrows indicate buckled nanotubes<sup>39</sup>**

Andrews *et al.* used shear mixing to disperse catalytically-produced nanotubes in a range of polymers including high impact polystyrene, acrylonitrile butadiene styrene, and polypropylene.<sup>35</sup> The dispersion of nanotubes was determined as a function of mixing energy and temperature and the composites were formed into fibres and thin films. Haggemueller *et al.* used a combination of solvent casting and melt mixing methods to disperse SWNTs in polymethylmethacrylate (PMMA).<sup>36</sup> Composite fibres with a high degree of nanotube orientation were produced by melt spinning.

Polycarbonate is another thermoplastic polymer that has been used as a matrix for nanotube composites.<sup>37,38</sup> Sennet *et al.* have used melt processing techniques to disperse and align carbon nanotubes in polycarbonate.<sup>38</sup> Dispersion was achieved by mixing the catalytically produced MWNTs and SWNTs with polycarbonate resin in a conical twin-screw extruder and alignment was carried out using a fibre spinning apparatus. By optimising mixing time and fibre draw rates, excellent dispersion and alignment were accomplished.

Nanotube/epoxy composites have also been prepared by a number of groups.<sup>39-43</sup> The earliest work in this area was carried out by Ajayan *et al.*<sup>39</sup> In 1994, this group described a study in which purified tubes were embedded into an epoxy resin which was then cut into thin slices with a diamond knife. Their initial aim in doing this was not to produce a composite material, but to obtain thin TEM specimens which it was hoped would contain cross-sectional images of nanotubes. However, no cross-sections were observed following sectioning; instead, the nanotubes were found to have become aligned in the direction of the knife movement, as shown in Fig. 8. According to Ajayan *et al.*, the alignment is primarily a consequence of extensional or shear flow of the matrix produced by the cutting. Of course, alignment can be much more readily achieved when the epoxy is in a liquid state. Xu *et al.* showed that some alignment of nanotubes in nanotube/epoxy composites can be achieved by using spin coating methods.<sup>42</sup> The cure reaction of a SWNT/

epoxy resin composite has been analysed using thermal analysis and Raman spectroscopy.<sup>43</sup> The SWNTs were found to have a catalysing effect on the cure reaction.

An alternative method for preparing nanotube/polymer composites is to use the monomer rather than the polymer as a starting material, and then carry out *in situ* polymerisation. Cochet *et al.* were among the first to use this method, to prepare a MWNT/polyaniline composite.<sup>44</sup> Nanotubes prepared by arc evaporation were used, and were sonicated in a solution of HCl to achieve a dispersion. The aniline monomer, again in HCl, was added to the suspension and a solution of an oxidant was slowly added with constant sonication and cooling. Sonication was continued in an ice bath for 2 h, and the composite was then obtained by filtering, rinsing, and drying. In this way, it was possible to prepare composites with high MWNT loadings (up to 50 wt-%). Transport measurements on the composite revealed major changes in the electronic behaviour, confirming strong interaction between nanotubes and polymer, as discussed below. A number of other nanotube/polymer composites have been prepared using *in situ* polymerisation, including MWNT/polystyrene<sup>45</sup> and SWNT/polyimide.<sup>46</sup> Several groups have used electrochemical polymerisation to grow porous composite films of MWNT and polypyrrole for use as supercapacitors.<sup>47,48</sup>

In the techniques described so far, the aim has been to produce composites in which the nanotubes are distributed evenly throughout the polymer (either randomly oriented or aligned). For some applications, however, a layered arrangement is advantageous. Photovoltaic devices containing layers of nanotubes or nanotube/polymer composites have been prepared, as discussed in the section 'Electrical and optical properties of carbon nanotube/polymer composites' below. The preparation of multilayer SWNT/polymer composites with excellent mechanical properties has also been described.<sup>49</sup> The method involved the layer-by-layer deposition of SWNTs and polymer onto a substrate, followed by crosslinking. In this way, composites with SWNT loadings as high as

50 wt-% could be obtained. Coating was carried out by alternate dipping of a glass slide or silicon wafer into dispersions of SWNTs (stabilised by acid treatment) and polymer solutions. The layers were held together by van der Waals forces and by electrostatic attraction between the negatively charged SWNTs and a positively charged polyelectrolyte, such as branched polyethyleneimine (PEI). Coatings containing up to 50 SWNT/PEI bilayers could be built up in this way. When the procedure was complete, the multilayer films were heated to 120°C to promote crosslinking. The films could then be lifted off the substrate to obtain uniform free-standing membranes. A rather similar method was used to synthesise multilayer composite films of the polyelectrolyte polydiallyldimethylammonium chloride and SWNTs.<sup>50</sup>

Before proceeding to discuss the properties of carbon nanotube/polymer composites in detail, it is worth briefly considering the effect that the inclusion of nanotubes can have on polymer microstructure. Although this topic has not yet been widely studied, a number of groups have demonstrated that the crystallisation and morphology of the polymers can be strongly affected by small additions of nanotubes. For example, Lozano and Barrera<sup>51</sup> showed that the addition of catalytically grown carbon nanofibres can promote nucleation of polypropylene. Similar observations were made by Valentini *et al.*<sup>52</sup> The crystallinity of a polymer has also been shown to increase with the addition of carbon nanofibres.<sup>53,54</sup> Changes in the crystal structure of polymers can also be induced by nanotubes.<sup>55</sup> More work on these effects would be welcome.

## Mechanical properties of carbon nanotube/polymer composites

Much of the work on the preparation of nanotube/polymer composites has been driven by a desire to exploit the tubes' stiffness and strength. Even where the interest has been focused on other properties, the ability of nanotubes to improve the mechanical characteristics of a polymer has often been a valuable added benefit. In early work, the measured properties were often disappointing, but such studies were of value in understanding the reasons for composite failure, and in identifying the critical issues which need to be addressed.

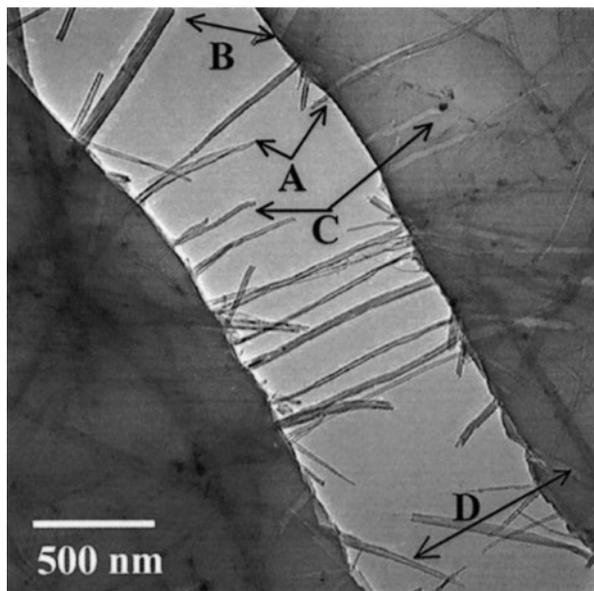
Shaffer and Windle were among the first to carry out a systematic study of the mechanical properties of nanotube/polymer composites. Their technique for preparing MWNT/PVA composites was described in the previous section.<sup>32</sup> The tensile elastic moduli of the composite films were assessed in a dynamic mechanical thermal analyser as a function of nanotube loading and temperature. The stiffness of the composites at room temperature was relatively low. From the theory developed for short-fibre composites, a nanotube elastic modulus of 150 MPa was obtained from the room temperature experimental data. This value is well below the values reported for isolated nanotubes: even defective catalytically grown tubes have measured stiffness of the order of 30 GPa.<sup>19</sup> The low value may have more to do with poor stress transfer than with the weakness of the nanotubes themselves. Above the glass transition temperature of the polymer (~85°C), the nanotubes had a more significant effect on the properties of the composite.

Cadek *et al.* achieved rather better results in 2002 with composites made from PVA and arc produced MWNTs.<sup>56</sup> The composites were prepared by solution mixing, and films were formed on glass substrates by drop casting. The presence of 1 wt-% nanotubes increased the Young's modulus and hardness of the PVA by factors of 1.8 and 1.6 respectively. This improvement over the early results of Shaffer and Windle reflects both the superior quality of the tubes and stronger interfacial bonding. Evidence for the latter was provided by TEM studies.

The mechanical properties of nanotube/polystyrene composites were studied by Qian and co-workers.<sup>34,35</sup> Two samples of catalytically produced MWNTs were used, one with an average length of ~15 µm, the other with an average length of ~50 µm. With the addition of 1 wt-% nanotubes they achieved a 36 and 42% increase in the elastic stiffness of the polymer for short and long tubes respectively (the neat polymer modulus was ~1.2 GPa). In both cases, a 25% increase in the tensile strength was observed. Theoretical calculations, carried out assuming a nanotube modulus of 450 GPa, produced increases of a 48 and 62% in the stiffness of the polymer for short and long tubes respectively. The close agreement, within ~10%, between the experimental and theoretically predicted composite moduli indicated that the external tensile loads were successfully transmitted to the nanotubes across the tube/polymer interface. At higher nanotube concentrations, the changes in the mechanical properties of the composites were more pronounced.<sup>35</sup> For MWNT/polystyrene composites containing from 2.5 to 25 vol.-% nanotubes, Young's modulus increased progressively from 1.9 to 4.5 GPa, with the major increases occurring when the MWNT content was at or above about 10 vol.-%. However, the dependence of tensile strength on nanotube concentration was more complex. At the lower concentrations (≤10 vol.-%), the tensile strength *decreased* from the neat polymer value of ~40 MPa, only exceeding it when the MWNT content was above 15 vol.-%.

In an attempt to understand the tensile fracture mechanisms of the nanotube/polystyrene composites, Qian *et al.* performed deformation studies inside a TEM.<sup>34</sup> Their elegant method of preparing TEM specimens has been described above. Focusing the electron beam onto the thin film resulted in local thermal stresses which initiated cracks in the composite. The propagation speed of the crack could be controlled by varying the beam flux onto the sample. These *in situ* TEM observations showed that the cracks tended to nucleate at low nanotube density areas, then propagate along weak nanotube/polymer interfaces or relatively low nanotube density regions. The nanotubes became aligned perpendicular to the crack direction and bridged the crack faces in the wake, as shown in Fig. 9. When the crack opening displacement exceeded ~800 nm, the nanotubes began to break and/or pull out of the matrix. The fact that some of the pulled-out tubes do not appear to be coated with polymer suggests that there is room for improvement in nanotube-polymer bonding.

Watts and Hsu have also used TEM to study the fracture behaviour of a nanotube/polymer composite.<sup>57</sup> Their composite consisted of arc grown MWNTs embedded in a diblock copolymer known as MPC-DEA. To prepare specimens of the composite for TEM,



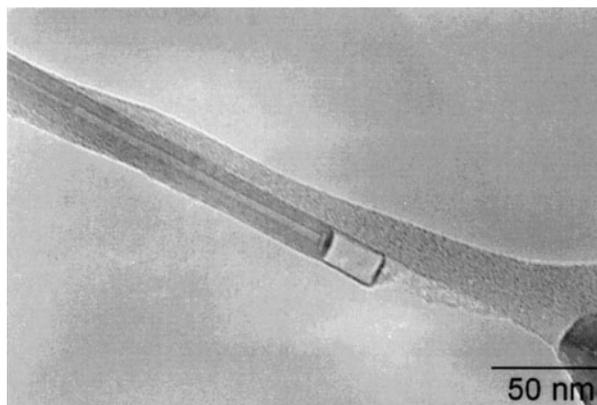
9 TEM image of crack in MWNT/polystyrene thin film induced by thermal stresses<sup>34</sup>

the tubes were mixed with the polymer in an acidified aqueous solution and drops of this were applied to TEM grids which were then dried in vacuum. As in the work of Qian *et al.*, cracks were produced in the material by irradiation with an electron beam, but a low accelerating voltage (75 kV) was used to avoid massive disruption of the thin composite film. Individual tubes and bundles of tubes were observed to become stretched as the cracks grew wider, and pull-out was often seen. In contrast to the work of Qian *et al.*, however, the tubes did not break. This was probably because high quality arc grown nanotubes were used, rather than catalytically produced tubes.

The early work on nanotube/epoxy composites by Ajayan *et al.* has been described in the previous section.<sup>39</sup> In 1998, Ajayan and co-workers described a study of the mechanical behaviour of MWNT/epoxy composites in both tension and compression.<sup>58</sup> It was found that the compression modulus was higher than the tensile modulus, indicating that load transfer to the nanotubes in the composite was much higher in compression. The authors suggested that during load transfer to MWNTs, only the outer layers are stressed in tension, whereas all the layers respond in compression.

Nanotube/epoxy thin films prepared by Xu *et al.* showed excellent mechanical properties.<sup>42</sup> Compared to neat resin thin films, for which the elastic modulus was 4.2 GPa, a 20% increase in modulus was seen when 0.1 wt-% MWNTs were added. This was attributed to partial alignment of the MWNTs induced by spin coating. Fracture behaviour of the films was investigated by SEM, and showed that pulled-out tubes were often covered with polymer, suggesting strong interfacial adhesion. Similar results were reported by Gojny *et al.*<sup>59</sup> This group showed that functionalising arc produced MWNTs with amine groups greatly enhanced bonding with the epoxy matrix. As a result, the outer shells of the tubes often remained embedded in the matrix following pull-out, as shown in Fig. 10.

All of the work described so far in this section has involved multiwalled carbon nanotubes. Ajayan *et al.*



10 Image of epoxy coated MWNT subject to tensile stress as result of electron irradiation: telescopic pull-out of outer tube layer has occurred<sup>59</sup>

have described a study of SWNT-containing composites.<sup>60</sup> Two types of composite were prepared, first an SWNT/epoxy composite and second a pressed pellet containing SWNTs and carbonaceous soot material formed during nanotube synthesis. The SWNTs were used as-prepared, i.e. generally grouped into bundles rather than separated into individual tubes. The composites were loaded axially in tension until failure occurred and the fracture surfaces were then examined in detail using SEM. In some cases, the tube bundles were found to have been pulled out of the matrix during the deformation and fracture of the composites, while in other cases the nanotubes were not entirely pulled out but were stretched between two fracture surfaces. The authors believed that during pull-out the nanotubes were sliding axially within the ropes and that the failure observed at large crack distances was not failure of individual tubes, but the bundles pulling apart. Studies by micro-Raman spectroscopy supported this hypothesis. It was found that little shift in the second order  $A_{1g}$  band occurred as a result of the application of axial tension, showing that the individual nanotubes were not being significantly stretched. To take full advantage of the high Young's modulus of SWNTs in polymer composites, it is clear that load must be transferred effectively from the matrix to the nanotubes. Ajayan *et al.* suggested that load transfer could be improved by breaking bundles down into individual tube fragments before dispersing in the matrix. Alternatively, the bundles themselves could be reinforced by crosslinking the tubes within bundles (e.g. by chemical treatments or irradiation).

Single-walled nanotube/epoxy composites have also been prepared by Biercuk *et al.*<sup>61</sup> The Vickers hardness of the polymer was found to increase monotonically with addition of SWNTs, up to a factor of 3.5 at 2 wt-% nanotube loading. Greatly enhanced thermal conductivities were also observed. Thus, samples loaded with 1 wt-% unpurified SWNT material showed a 70% increase in thermal conductivity at 40 K, rising to 125% at room temperature.

The preparation of SWNT/polyelectrolyte composites by the layer-by-layer method has been described in the previous section.<sup>49</sup> The films produced in this way were shown to have exceptional mechanical properties. Thus, the average ultimate tensile strength of the films was found to be 220 MPa, with some measurements as high as 325 MPa. This is several orders of magnitude greater

than the tensile strength of strong industrial plastics, and indicates that the layer-by-layer method has great promise for the production of strong nanotube-containing composites.

## Electrical and optical properties of carbon nanotube/polymer composites

The effect of adding nanotubes on the electrical properties of polymers has been studied by many groups. These studies fall into a number of distinct categories. In some cases, the nanotubes have been used to increase the conductivity of relatively low cost polymers, as an alternative to currently used fillers such as carbon black. Other studies have involved the incorporation of nanotubes into conducting polymers such as polyaniline. Still further work has been aimed at specific applications such as photovoltaic devices or supercapacitors. In many cases, improved mechanical properties have been a valuable by-product of the inclusion of nanotubes. The addition of nanotubes to low cost, bulk polymers is considered first.

### Electrostatic dissipation

Improving the electrical conductivity of bulk polymers is important in a number of applications. For example, in some aircraft components, enhanced conductivity is required to provide electrostatic discharge and electromagnetic radio frequency interference protection. Static electrical dissipation is also needed in other applications, including computer housings and exterior automotive parts. With these types of application in mind, Sandler *et al.* investigated the electrical properties of nanotube/epoxy composites.<sup>40</sup> Matrix resistivities of about 100  $\Omega$  m with filler volume fractions as low as 0.1 vol.-% were achieved. These figures represented an advance on the best conductivity values previously obtained with carbon black in the same epoxy matrix.

Lozano and co-workers prepared composites of catalytically grown carbon nanofibres in a polypropylene matrix.<sup>51,62</sup> The nanofibres were purified and functionalised to facilitate bonding with the matrix, and high shear processing was used to disperse the fibres in the polymer matrix. Rheological and microscopic analysis showed that a homogeneous dispersion of nanofibres was formed, and a percolation threshold for electrical conduction of 9–18 wt-% was observed.

These and other published studies suggest that carbon nanotubes have great promise in reducing electrostatic charging of bulk polymers. Nanotubes also have other advantages over conventional fillers, such as carbon black and carbon fibres, in that they are more amenable to processing and can be more easily dispersed throughout the matrix. In addition to the studies available in the open literature, there is undoubtedly a great deal of commercial work being carried out on the use of nanotubes to reduce the electrostatic charging of plastics. In fact, nanotube containing plastics are already being used in commercial products.<sup>63</sup> These include fuel lines in automobiles, where the nanotubes help to dissipate any dangerous charge which may build up. Thermoplastic polymers containing nanotubes are also used in some exterior automobile parts, so that they can be earthed during electrostatic painting.

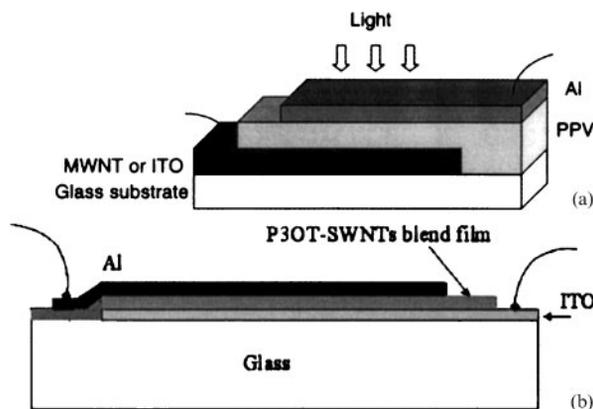
## Conducting polymer composites

Polyaniline is a conducting polymer with many attractive characteristics such as processability and environmental stability. There has been interest in adding nanotubes to this polymer, to provide both enhanced conductivity and improved mechanical properties. As mentioned above in the section 'Preparation of carbon nanotube/polymer composites', Cochet *et al.* have prepared a MWNT/polyaniline composite by *in situ* polymerisation.<sup>44</sup> The nanotubes were found to have a strong influence on the transport properties of the polymer. Thus, the room temperature resistivity of the composite was found to be an order of magnitude lower than that of pure polyaniline, while the low temperature resistivity was much smaller than that of either polyaniline or of MWNTs. The temperature dependence of resistivity was also weaker than that of polyaniline alone. These observations were explained by assuming that *in situ* polymerisation favours charge transfer between polyaniline and MWNTs resulting in an overall material which is more conducting than the starting components. Raman studies indicated that these charge transfer processes involved a site-selective interaction between the quinoid ring of the polymer and the MWNTs. Other groups have also demonstrated excellent conductivity in MWNT/polyaniline composites,<sup>64,65</sup> while a group from DuPont have shown that SWNT/polyaniline composites can be used as printable conductors for organic electronics devices.<sup>66</sup>

### Optoelectronic properties

Several groups have prepared nanotube composites using the conjugated polymer poly(*p*-phenylene vinylene) (PPV) and its derivatives. Polymers of this class have electroluminescent properties, and are widely used in light-emitting diodes. They are also used in photovoltaic devices. In an early study, workers from Ireland and the USA described the synthesis of a composite material containing arc produced MWNTs in a PPV derivative, PmPV.<sup>67</sup> The composite was prepared using a solution mixing method, and good wetting of the tubes by the polymer was achieved. One of the aims of adding nanotubes to the polymer was to increase its electrical conductivity. Previous attempts to achieve this by doping had resulted in degradation of the optical properties of the polymer. In the case of nanotubes, an increase in the electrical conductivity of the polymer by up to eight orders of magnitude was seen, with no concomitant degradation of optical properties. This was apparently because the tubes acted as nanometric heat sinks, preventing the build up of large thermal effects, which damage these conjugated systems. It was also shown in this work that the composite could be used as the emissive layer in an organic light-emitting diode (LED).

As mentioned above, several groups have been interested in using nanotube/polymer composites in photovoltaic devices. The photovoltaic effect involves the generation of electron and hole pairs and their subsequent collection at opposite electrodes. In organic materials, the photon absorption excites an electron into the conduction band, which leads to a generation of bound electron-hole pairs, or excitons. These excitons have to dissociate into free charges in order to be transported to the electrodes. Exciton dissociation can occur at a junction between a polymer and an electron acceptor



ITO=indium-tin oxide; PPV=poly(*p*-phenylene vinylene); P3OT=poly(3-octylthiophene)

11 **a** Illustration of photovoltaic device fabricated by Ago *et al.*<sup>71</sup> and **b** photovoltaic device fabricated by Kymakis and Amaratunga<sup>72</sup>

molecule. This allows the preferential transfer of the electrons into the electron acceptor molecule while leaving the holes to be preferentially transported through the polymer, a process known as photoinduced charge transfer. In 1992, photoinduced charge transfer from a conducting polymer to  $C_{60}$  was discovered,<sup>68</sup> and this has led to the fabrication of several efficient photovoltaic systems using fullerene/polymer combinations.<sup>69</sup> Photovoltaic devices based on nanotube/polymer combinations have now been fabricated by several groups, and this work will now be summarised.

The earliest attempt to fabricate a nanotube/polymer photovoltaic device appears to be the 1996 work of Romero *et al.*<sup>70</sup> In this work, a layer of MWNTs was deposited on Teflon, and a PPV derivative was cast onto this, with a thin aluminium layer on top. The device displayed clear diode behaviour, but only a small photocurrent was observed when the junction was irradiated with light from a He-Ne laser. This may have been due to the relatively thick PPV active layer. Ago *et al.* fabricated a nanotube containing photovoltaic device by depositing a layer of PPV onto a glass-supported MWNT film.<sup>71</sup> The interaction between MWNTs and PPV was investigated by means of photoluminescence (PL) measurements. The photoluminescence efficiency of the PPV was found to be markedly reduced by the presence of the MWNT layer. Since photoluminescence is a result of radiative recombination, a reduction may imply improved exciton separation, which is what one wishes to achieve in a photovoltaic device. The device fabricated by Ago *et al.* is illustrated in Fig. 11a. This showed a clear diode characteristic in the dark, and upon illumination through the aluminium electrode, a photocurrent was observed. A quantum efficiency approximately twice that of the standard indium-tin oxide device was reported.

Kymakis and Amaratunga used a slightly different approach to prepare a nanotube/conjugated polymer photovoltaic device.<sup>72</sup> In this work, composite SWNT/poly(3-octylthiophene) films were drop or spin cast from a solution onto indium-tin oxide (ITO) and quartz substrates to produce the arrangement shown in Fig. 11b. Devices were also prepared using the pure P3OT polymer. A considerable enhancement of the photovoltaic

effect was observed with the P3OT/SWNTs blend device compared with the pure polymer device.

## Non-linear optical properties

As mentioned above in the section 'Structure and properties of carbon nanotubes', it has been demonstrated that suspensions of both SWNTs and MWNTs have non-linear optical properties. Nanotube/polymer composites may therefore have applications in optical devices. To date, however, there has been little work on the optical limiting properties of nanotube containing composites. In one of the first studies in this area, Chen *et al.* demonstrated third order optical non-linearity in a SWNT/polyimide composite.<sup>73</sup> Recently, O'Flaherty *et al.* prepared a composite in which MWNTs were dispersed in the polymer poly(9,9-di-*n*-octylfluorenyl-2,7'-diyl) (PFO).<sup>74</sup> Suspensions of the nanotube/PFO composite in toluene were prepared, and the optical limiting properties of the solutions were measured using nanosecond laser pulses. Maximum optical limiting was observed at carbon nanotube loadings in excess of 3.8 wt-%, relative to the polymer.

## Carbon nanotube/ceramic composites

Ceramics have high stiffnesses and thermal stabilities, but relatively low breaking strengths. Incorporating carbon nanotubes into a ceramic matrix might be expected to produce a composite with both toughness and high temperature stability. However, achieving a homogeneous dispersion of tubes in an oxide, with strong bonding between tubes and matrix presents rather more of a challenge than incorporating tubes into a polymer. Various approaches have been adopted for incorporating nanotubes into oxides such as alumina and silica, and these will now be summarised.

Peigney and co-workers have been among the pioneers in the synthesis of nanotube/oxide composites.<sup>75-77</sup> They have developed an ingenious technique which involves the use of catalysts such as iron-containing  $\alpha$ -alumina. Passing a  $CH_4$ - $H_2$  mixture over the catalysts resulted in the *in situ* growth of nanotubes on iron particles, producing the precursor for a nanotube/oxide composite. The resulting powders can then be hot pressed to form the final composite material. The mechanical properties of these composites were initially disappointing.<sup>72</sup> Thus, the fracture strengths of the nanotube/Fe- $Al_2O_3$  composites were only marginally higher than that of  $Al_2O_3$  and were generally markedly lower than those of the carbon-free Fe- $Al_2O_3$  composites. The fracture toughness values were lower than or similar to that of  $Al_2O_3$ . However, SEM observations of composite fractures indicate that the nanotube bundles, which are very flexible, could dissipate some fracture energy. A similar method was used by An and Lim to prepare nanotube/ $Al_2O_3$  composites, in this case using  $C_2H_2$  as the carbon source.<sup>78</sup> Nanotube contents of up to 12.5 wt-% were achieved and a significant reinforcement effect was reported.

Achieving alignment of nanotubes in a ceramic matrix is much more difficult than in a polymer, since ceramics do not lend themselves so easily to processing. However, a number of groups have shown that aligned nanotube/metal oxide composites can indeed be produced. Peigney

*et al.* exploited the fact that, when their grains are maintained at sufficiently low sizes (less than about 1  $\mu\text{m}$ ), many polycrystalline ceramics become superplastic, allowing the use of thermomechanical processing for the forming of these materials. A series of cobalt and iron containing oxide catalysts were prepared.<sup>77</sup> The primary grain size in the powders was smaller than 100 nm, but in some of them the as produced primary grains were strongly aggregated and required ball milling in order to reduce aggregate size to less than 1  $\mu\text{m}$ . Nanotubes were then prepared *in situ*, as described above, and the powders were then extruded at high temperatures in a graphite die under vacuum. The best results were achieved with nanotubes incorporated into Fe–Al<sub>2</sub>O<sub>3</sub> and Fe/Co–MgAl<sub>2</sub>O<sub>4</sub> matrices. In both cases, the nanotubes were not damaged by the processing and alignment of the nanotubes was clearly observed. In fact, the presence of the nanotubes seemed to facilitate the superplastic forming by inhibiting grain growth and acting as lubricating agents. It was demonstrated that the aligned nanotube/metal oxide composites showed an anisotropy of electrical conductivity, which could be adjusted by controlling the nanotube content.

One of the first studies of a SWNT/ceramic composite was described by Zhan *et al.*<sup>79</sup> This group used the technique of spark plasma sintering (SPS) to prepare Al<sub>2</sub>O<sub>3</sub> composites containing 10 vol.-% SWNTs. The advantage of spark plasma sintering is that it allows ceramic powders to be annealed at lower temperatures and for much shorter times than other sintering processes, leading to the fabrication of fully dense ceramics or composites with nanocrystalline microstructures under mild conditions. Unlike some of the other processes used to prepare nanotube/oxide composites, spark plasma sintering does not damage the nanotubes and the nanotube bundles could be seen to be located mainly at the boundaries of the Al<sub>2</sub>O<sub>3</sub> grains, in good contact with the Al<sub>2</sub>O<sub>3</sub> matrix. Before sintering, the powders had been mixed by ball milling, which produced a reasonably homogeneous dispersion, again without damaging the nanotubes. The fracture toughnesses of the final composites were remarkable – about twice that of the fully densified but unreinforced Al<sub>2</sub>O<sub>3</sub> matrix. In contrast to previous work on nanotube/ceramic composites, the fracture toughness was found to increase with nanotube density. This is thought to be due to the formation of entangled networks of single-walled carbon nanotubes, which may inhibit crack propagation. A subsequent study of the nanotube/Al<sub>2</sub>O<sub>3</sub> composites showed that they had high electrical conductivities.<sup>80</sup>

Various techniques have been used to prepare carbon nanotube/silica composites. Seeger *et al.* described a method which involved preparing a composite gel of MWNTs with tetraethoxysilane (TEOS) and then sintering this at 1150°C in argon.<sup>81</sup> A drawback of this technique was that the sintering process led to a partial crystallisation of the SiO<sub>2</sub> resulting in a very inhomogeneous matrix. An alternative method which avoids these problems has been developed.<sup>82</sup> This involves using a Nd:YAG laser to rapidly heat a TEOS/nanotube mixture, resulting in partial melting of the matrix. This produced an amorphous silica matrix, with no crystallisation.

A novel nanotube/silica composite material with potentially useful optical properties has recently been

described by Han *et al.*<sup>83</sup> These workers synthesised films consisting of silica spheres with diameters ranging from 200 to 650 nm. Molybdenum/cobalt catalyst particles were then deposited onto the silica spheres and used to catalyse the growth of SWNTs. Since SWNTs are highly non-linear and fast-switching materials, they can be incorporated into an optically confining environment to achieve these characteristics at relatively low levels of laser intensities.

There have been a few studies on preparing nanotube composites using oxides other than alumina and silica. Vincent *et al.* reported the production of nanotube/TiO<sub>2</sub> composites using sol–gel methods.<sup>84</sup> Possible applications of the composites included optical non-linear wave guides and unidimensional conductive films. Sol–gel methods were also used by Sakamoto and Dunn to prepare SWNT/V<sub>2</sub>O<sub>5</sub> composites for use as electrodes in secondary lithium batteries.<sup>85</sup> Little work has been carried out so far on incorporating nanotubes into non-oxide ceramics. In one of the few published studies, Ma *et al.* fabricated nanotube/silicon carbide composites by mixing SiC nanoparticles with 10 wt.-% MWNTs and hot pressing at 2000°C.<sup>86</sup> They found that the nanotubes played a strengthening and toughening role in the composite: both bend strength and fracture toughness increased by about 10%, compared to monolithic SiC. There have also been some initial studies on carbon nanotube/carbon fibre composites.<sup>87,88</sup>

## Carbon nanotube/metal composites

Composite materials containing conventional carbon fibres in a metal matrix, such as aluminium or magnesium, are used in a number of specialist applications.<sup>89,90</sup> Such composites combine low density with high strength and modulus, making them particularly attractive to the aerospace industry. There is growing interest in the addition of carbon nanotubes to metal matrices, although only a small number of studies have been published to date. Kuzumaki *et al.* described the preparation of a nanotube/aluminium composite in 1998.<sup>91</sup> Their method involved mixing a nanotube sample with a fine aluminium powder, mounting the mixture in a 6 mm silver sheath, and then drawing and heating the wire at 700°C in a vacuum furnace. The result was a composite wire in which the nanotubes were partially aligned along the axial direction. The tensile strengths of the as prepared composite wires were comparable to that of pure aluminium, but the composite wires retained this strength after prolonged annealing at 600°C, while the strength of pure aluminium decreased by about 50% after this treatment. The same group subsequently prepared nanotube/titanium composites which showed a large increase in hardness and modulus compared to pure titanium.<sup>92</sup>

Chen *et al.* prepared nanotube/nickel/phosphorus composite coatings on stainless steel substrates using an electroless plating method.<sup>93</sup> The coatings exhibited higher wear resistance and lower friction coefficients than SiC/Ni/P and graphite/Ni/P composite coatings. The same group prepared nanotube/copper composites by a powder metallurgy technique, and showed that the presence of the nanotubes again resulted in improved wear rates and friction coefficients. These results suggest that nanotube/

metal composites may have potential in tribological applications.

## Discussion

The subject of carbon nanotube composites has grown rapidly over the past 5 years or so into a vibrant and exciting area of research. It is important to recognise, however, that this is still a new subject, and the work carried out so far may have hardly scratched the surface of what is possible. For example, the great majority of the studies that have been published to date have involved the use of polymer matrices; there is great scope for more work on incorporating nanotubes into ceramics, metals, and other forms of carbon. Also, most of the work up to now has been aimed at exploiting the mechanical properties of carbon nanotubes rather than their electronic or optical properties, although interest in those is growing.

When considering the mechanical performance of carbon nanotube composites, it is clear that these depend strongly on whether arc grown tubes or catalytically produced tubes have been used. In considering the characteristics of the two types of tube it is instructive to compare the work of Qian *et al.*<sup>34</sup> with that of Watts and Hsu.<sup>57</sup> Both incorporated the nanotubes into polymers and then used TEM to characterise the composites and study their fracture behaviour. Qian *et al.* used catalytically produced tubes, and these were found to be well dispersed throughout the polymer matrix, with no clustering together of tubes. However, during composite fracture the tubes were often observed to break, suggesting that they have relatively poor strength. Watts and Hsu, on the other hand, employed much more perfect nanotubes produced by arc evaporation, and TEM studies revealed superior mechanical properties, with no observed breaking. However, the nanotubes tended to cluster together so that during crack growth the tubes could quite easily slide past one another. Thus, while it is clear that the best mechanical performance will be achieved with arc grown nanotubes, it is important that the tubes be well dispersed throughout the matrix in order fully to exploit their properties.

Equally important is achieving good bonding between nanotubes and matrix. Many studies have shown that this interfacial bonding can be enhanced by functionalising the nanotubes before embedding them in the matrix. The effect of this can be seen in Fig. 10, from the work of Gojny *et al.*,<sup>59</sup> where bonding between MWNTs and an epoxy matrix is so strong that the outer shells of the tube remain embedded in the matrix following pull-out. A possible disadvantage of functionalisation is that it could weaken the nanotubes by disrupting the perfect cylindrical structure. This might be expected to be a particular problem with single-walled tubes. However, functionalisation of the nanotubes may not be necessary to produce bonding with a polymer matrix. Liao and Li have modelled the interfacial characteristics of a nanotube/polystyrene composite, assuming no covalent bonding between the tubes and the matrix.<sup>94</sup> It was found that electrostatic and van der Waals interactions contributed significantly to the interfacial stress transfer. A nanotube pull-out simulation suggested that the interfacial shear stress of the nanotube/polystyrene system is about 160 MPa, significantly higher than for most carbon fibre reinforced polymer composite systems. It is also worth

mentioning recent work by Star and co-workers<sup>95,96</sup> in which it was demonstrated that poly{(5-alkoxy-*m*-phenylenevinylene)-co-[(2,5-dioctyloxy-*p*-phenylene)vinylene]} (PAmPV) derivatives could be induced to wrap around SWNTs, forming strong non-covalent bonds.

The quality of the nanotubes and the nature of the interfacial bonding also has a strong influence on the electrical properties of nanotube/polymer composites. Arc grown tubes can have resistivities lower than that of single crystal graphite but, as already discussed, their electronic properties depend on their precise structure. At present we do not have a reliable method of separating metallic and semiconducting tubes, so it is not possible to exploit their full potential. Catalytically produced tubes are likely to be poorer conductors than metallic arc-grown tubes owing to their relatively disordered structure. Nevertheless, catalytically grown tubes are sufficiently conducting to be useful in some commercial applications, such as electrically conductive paints. The influence of interfacial bonding on electronic properties was demonstrated in the work of Cochet *et al.*<sup>44</sup> These workers prepared a MWNT/polyaniline composite by *in situ* polymerisation and found it to have excellent electrical transport properties. This was attributed to strong interaction between tubes and polymer.

As has been shown in this review, the possible applications of carbon nanotube composites range widely, from electrically conductive paints to optical devices. Only a relatively small number of these new materials have been used commercially, however, and there are still many problems to overcome before the full potential of nanotube containing composites can be realised. Not least of these problems is the high cost of good quality carbon nanotubes. Currently, the commercial price of unpurified arc-grown MWNTs is approximately \$100-00/g, while purified MWNTs cost around \$300-00/g. Catalytically grown MWNTs are much cheaper but, as emphasised throughout this review, have generally inferior properties. As far as SWNTs are concerned, unpurified samples cost around \$50-00/g, while purified SWNTs are \$500-00/g. As a comparison, the price of gold is currently about \$12-00/g! The development of new techniques for the low cost synthesis of high quality nanotubes is clearly essential. This might be achieved through improved catalytic processes, and there is currently a large amount of work being carried out towards this end. Alternatively, it may be possible to develop new non-catalytic techniques for the synthesis of fullerene-related nanotubes. In this connection it is interesting to note that nanotubes can be produced by the high temperature heat treatment of conventional carbons such as microporous non-graphitising carbons<sup>97,98</sup> or carbon black.<sup>99,100</sup> Further work in this area would be of value.

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