

## Q&amp;A

## MATERIALS SCIENCE

# Nanotube composites

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**A carbon revolution has occurred — carbon atoms can be coaxed into several topologies to make materials with unique properties. Nanotubes are the vanguard of this innovation, and are on the cusp of commercial exploitation as the multifunctional components of the next generation of composite materials.**

## Why do we need composite materials?

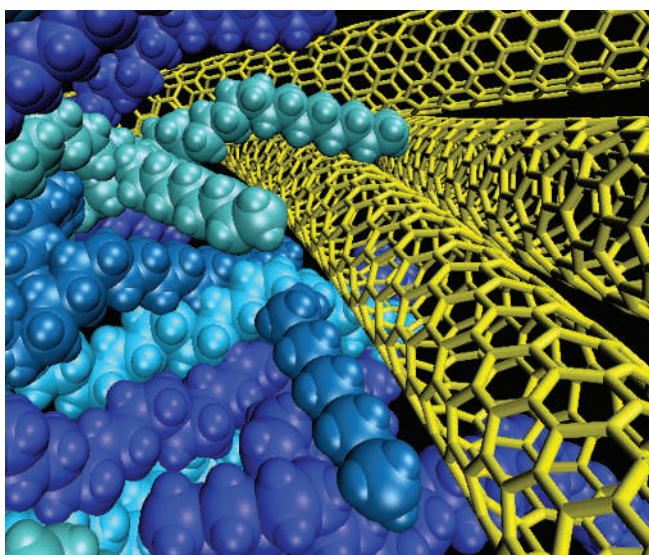
Composites, which are formed from two or more distinct materials, have desirable combinations of properties that aren't found in the individual components. For example, fibre-reinforced composites are engineered structures that commonly comprise a soft matrix — typically a polymer — encapsulating a stiffer, load-bearing filler in the form of fibres or particles. For high-strength composites, the fibres should be stiff and have a high aspect ratio (length-to-width ratio). This allows a good transfer of load from the matrix to the filler when the composite is put under mechanical stress, in much the same way that steel bars reinforce concrete.

## What makes carbon nanotubes special compared with other reinforcing fibres?

It's the combination of their small size and particular physical properties. Nanotubes have molecular dimensions, and consist of perfect graphite sheets rolled into hollow cylinders. There are two types: single-walled (with diameters of about 0.5–2 nanometres) and multiple-walled (which have diameters of 2–50 nm). In many respects they resemble the polymer chains used as composite matrices — both have covalently bonded structures, similar dimensions and mechanical flexibility. This makes nanotubes entirely different from traditional fibres such as carbon or glass, which are relatively large (with diameters on the scale of micrometres) and brittle. The basic mechanical properties (such as strength) of nanotubes greatly exceed those of other fibres, yet this strength is combined with a low mass density, making them extremely light. Furthermore, nanotubes can conduct heat and electricity down their long axes as efficiently as metals — a great improvement on traditional fibres (Box 1).

## How do nanotubes affect the properties of composites?

Nanotubes in plastic composites — which are anticipated to be the largest bulk application of these reinforcers — would serve to increase



**Figure 1 | Slippery interfaces.** This computer-generated image shows how single-walled nanotubes (yellow) bundle together when used as the reinforcing element of a composite material. The nanotubes are depicted at the interface with the polymer polyethylene (individual polymer molecules are shown in different shades of blue). The surfaces of nanotubes are atomically smooth, so their interactions with the polymer matrix are weak.

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stiffness, strength and toughness, and provide other properties such as electrical and thermal conductivity. Because, at present, nanotubes can be manufactured only at lengths up to the submillimetre scale (so falling into the short-fibre category), for the foreseeable future their dominant role in composites is likely to remain as matrix modifiers and providers of multifunctional attributes. But once nanotubes can be efficiently assembled on a macroscopic scale, they could become serious competition for the continuous carbon fibres that are woven and stacked to form load-bearing elements in structural composites used in the building and engineering industries.

## Are nanotube composites easy to make?

Unfortunately not. The biggest challenge is to fully disperse individual nanotubes in the matrices, because nanotubes tend to form clusters and bundles. These aggregates persist unless high shear forces are applied, for example by vigorous mixing of the polymer. But such mixing often damages nanotube structures, compromising their properties. Another issue is that the polymer–nanotube mixtures are highly viscous (owing to the large surface area of nanotubes). This creates engineering

problems, because the composites don't flow easily and are difficult to mould. Processing is also rendered difficult by the poor solubility of nanotubes in most solvents and polymers. Nevertheless, several approaches have been successfully adopted to obtain intimate mixing of nanotubes with polymer phases, including dry powder mixing, melt mixing, polymerization of monomers onto nanotube surfaces, and surfactant-assisted mixing.

## Does a nanotube's small size directly affect the properties of nanotube composites?

Certainly. The reinforcement effect of a filler should improve markedly as its fibres get smaller, because of the increased surface area (per volume of filler) available for interaction with the matrix. For example, nanotubes of about 10 nm in diameter have an interfacial area with matrices that is almost 1,000 times greater than that of 10-micrometre fibres of the same volume. This intimate contact can influence the properties of the polymer matrix, affecting its chain entanglements, its morphology and even its crystallinity. Therefore, the resulting composite can be much tougher and stronger than would be expected

**Box 1 | Nanotubes — a unique reinforcer**

Unlike traditional micrometre-sized reinforcements, such as carbon fibres, nanotubes are truly molecular in size — comparable in lateral dimensions and aspect ratio to polymer chains. But there the comparison ends. In most polymers, cleavage of one bond is sufficient to sever the polymer strand. But nanotubes can require 10–50 carbon-carbon bonds per repeat unit to be broken for rupture to occur. As the carbon-carbon bond is one of the strongest found in nature, it is unlikely that there will ever be a polymer chain stronger than a nanotube.

The deformation characteristics of nanotubes are also intriguing. Carbon fibres are stiff and brittle, and act as rigid rods, whereas nanotubes are elastic and can be easily bent, buckled, twisted, flattened or tangled without breaking (see panel). So although nanotubes have much higher stiffness and tensile strength than carbon fibres, they are much more flexible: the bending of carbon fibres in composites leads to their



fracture, whereas long nanotubes bow, remaining in arbitrary shapes.

This difference results from the way that nanotubes and carbon fibres are formed from two-dimensional sheets of graphite (known as graphene layers). A single-walled nanotube can be thought of as an individual graphene sheet rolled up to make a defect-free, hollow structure just one atom thick — distinctly different from the randomly stacked graphene layers found in carbon fibres. The skinny carbon-shell structure of nanotubes makes

them strong in tension but easily bent; enables them to withstand large strains before failing; and provides a super-low-density framework.

The combination of high local stiffness with elasticity at larger scales determines the 'persistence length' of nanotubes — the characteristic distance from one end of the tube at which thermal energy becomes sufficient to introduce significant bending. The persistence lengths of single-walled nanotubes are expected to be in the order of tens to hundreds

of micrometres. For multiwalled nanotubes, or bundles of single-walled tubes, the persistence lengths could be substantially higher, becoming comparable to the maximum lengths of nanotubes that can currently be prepared. In these cases, the nanotubes behave like short, stiff carbon fibres. The load-bearing and conducting properties of nanotubes are bolstered by the unusual persistence lengths of these structures and by the varied, stable conformations that they adopt.

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on the basis of the properties of the isolated filler. Furthermore, nanotubes with aspect ratios of tens of thousands to one can percolate — that is, form an inter-nanotube connective pathway — throughout the matrix at exceedingly small volume fractions, strengthening the composite and making it electrically conductive.

### Why aren't nanotube composites already widely available?

Because there are still a few manufacturing problems to be overcome. Initial attempts to make these materials often yielded lacklustre results, mostly because of the poor interfaces that formed between the nanotubes and the surrounding matrix (Fig. 1) — strong bridges between the polymer and the nanotubes are necessary for good load transfer between the two. Such difficulties are not new, and also arose in the early days of carbon-fibre composites. However, the problem is more acute for nanotubes, both because their surfaces are atomically smooth (which results in poor matrix adhesion) and because the interfacial area for such tiny filler particles is huge.

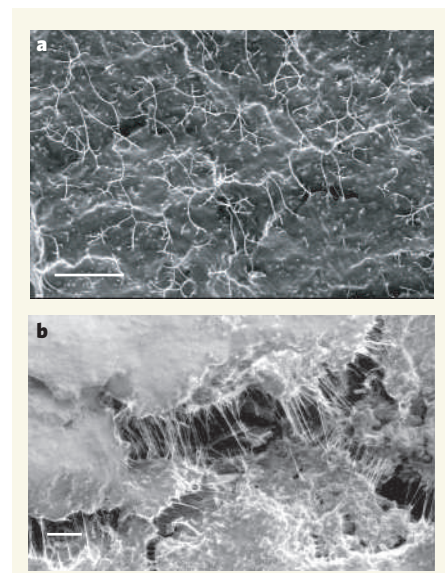
### Are there any other manufacturing issues?

Poor dispersion of nanotubes in the matrix is also a problem — large aggregates of nanotubes initiate cracks in composites, rather than reinforcing them. Bundle structures — comprising many parallel nanotubes held together

by weak bonds (Fig. 1) — also tend to form. Under stress, the nanotubes in the bundles can slip past each other, splitting off in layers from the host and weakening the composite. Examining the fracture surfaces of polymer-nanotube composites can help determine whether proper load transfer is occurring in the material (Fig. 2). If the matrix-filler interface is strong, the nanotubes break under stress. But for poorly fastened interfaces, nanotubes are pulled out of the matrix as a result of interfacial slippage.

### What has been done to enhance the interfacial properties of nanotubes?

Several methods have been used to modify nanotube surfaces chemically (Fig. 3, overleaf). One approach is to attach chemical groups covalently. Unfortunately, this strategy creates defects in the nanotube lattice, which can lower the electrical and thermal conductivity of the nanotubes and compromise their mechanical properties. Alternatively, non-covalent interactions can be used to either wrap surfactants or polymers around nanotubes, or to adsorb aromatic structures to the side-walls. These surface-modification methods are milder than the covalent approach, and usually cause little disruption to the structure or conductivity of the nanotubes. The idea of chemically modifying fillers to increase their interfacial strength isn't new — the surfaces of carbon fibres are also modified before use. But the near-perfect structures of nanotubes make the process more



**Figure 2 | Fractured composites.** The reinforcing effect of nanotubes in composites can be undermined by weak interfacial contacts between nanotubes and the surrounding polymer matrix. **a**, In this scanning electron microscope (SEM) image of the fracture surface of a nanotube-epoxy composite, the fibres (seen in white contrast) are single-walled nanotubes that have been pulled out of the matrix and have then fallen back onto the fracture surface. **b**, This SEM image shows a crack in a nanotube-epoxy composite. Bundles of single-walled nanotubes (strands with pale contrast) are exposed and stretched between cracks in the composite. Scale bars, 1 µm.

challenging, as there are no defects upon which to anchor a pendent group, and nanotubes are chemically quite inert. Nevertheless, recent work in this area shows that nanotube-surface modification is cleaner and more controllable than carbon-fibre modification.

### Couldn't the interfacial slippage be exploited?

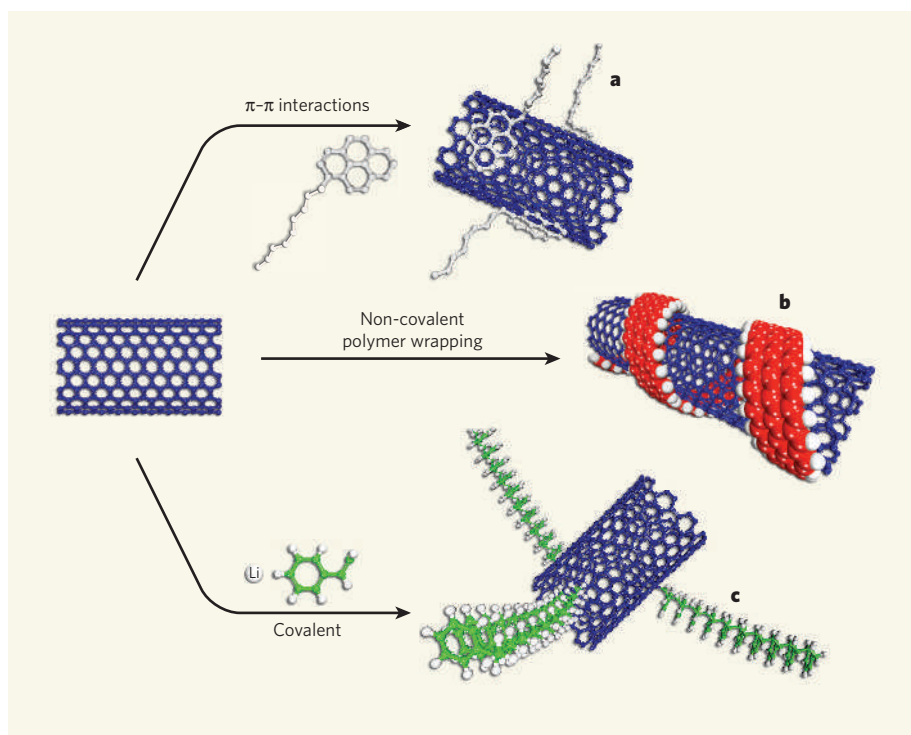
Although interfacial shear is detrimental to stiffness and strength, it could produce high mechanical damping, as the large number of nanotube-polymer interfaces involved in nanotube slippage creates a lot of friction and energy dissipation. Viscoelastic behaviour at the interfaces causes this effect. Such damping is vital for many commercial applications, such as isolating objects from vibration. Once again, good dispersion of nanotubes in the matrices is essential to optimize this effect.

### Is it possible to order the arrangement of nanotubes in composites?

Certainly. Nanotubes have been aligned in composites using magnetic fields, but this is unlikely to be especially useful because of the very high field strengths required. The best way to orient nanotubes is to put them under shear, for example by extrusion. Moving from randomly aligned mixtures of nanotubes in composites to well-ordered arrays can enhance the resulting material's performance under stress, and improve its electrical and thermal conductivities (conductivity in nanotubes is directional, being much better down their long axes). Such alignment also minimizes the number of nanotubes required to exert their effects. Perhaps most impressively, it is possible to incorporate aligned arrays of nanotubes into 'three-dimensional' composites. Traditional fibre-reinforced composites consist of stacked panels in which the fibres lie in plane; these materials have excellent in-plane properties, but fare poorly along the through-thickness direction. Inter-laminar nanotube arrays, aligned perpendicular to the stack panels, provide enhanced properties along the thickness direction. The arrays do this by fastening adjacent fibre stacks together — acting almost like Velcro between them.

### We've seen that nanotube composites combine strength and conductivity — what else can they do?

With their wide range of excellent properties, nanotubes could act as fillers in diverse multifunctional composites. For example, the strength and damping properties of these materials might be increased if the nanotube-polymer interfaces can be suitably engineered. Adding nanotubes to plastics provides materials that could be used to shield microelectronics from electromagnetic interference. Similarly, experiments show that the microwave-absorbing capability of nanotubes could be exploited to heat temporary housing structures, and may have applications in space



**Figure 3 | Chemical modification of carbon nanotubes.** Carbon nanotubes have poor solubility in most solvents and polymers, but this problem can be overcome by chemically modifying their surfaces. At present, three methods are used for this purpose. **a**, Aromatic molecules can be appended to nanotubes using certain non-covalent interactions (known as  $\pi$ - $\pi$  interactions). Groups emanating from these molecules interact with the surrounding solvent or matrix. **b**, Non-covalent interactions (including  $\pi$ - $\pi$  interactions, van der Waals forces and charge-transfer interactions) can be used to wrap polymers around nanotubes. **c**, Chemical groups can be covalently attached to nanotubes. In this case, lithium (Li) forms anions on the nanotube, which react with styrene monomers to form polystyrene chains covalently attached to the nanotube walls.

exploration. Furthermore, applying mechanical stress to nanotubes modulates their electrical conductivity. This effect could be exploited in advanced materials that have embedded sensors and actuators made of nanotubes, which could be used for real-time monitoring of stress distribution and to actively control the composite structures. Finally, thin nanotube layers might also be used in transparent conducting composites.

### How will we see nanotube composites used in the future?

At present, the most widespread use is in electrostatic-discharge components, in which multiple-walled nanotubes slightly enhance the electrical conductivity of plastics. Some manufacturers of high-end sporting goods, such as tennis rackets, also claim to make their products from nanotube composites, so delivering superior performance. In the short term, the biggest markets for nanotube composites will undoubtedly be for high-value applications that can absorb the added costs — sectors such as aerospace (which needs lightweight, high-strength, high-temperature-resistant composites) and energy (for example, in nanotube-reinforced rubber seals for large oil-recovery platforms). Aerospace composites that have the required properties are already being developed. Once the cost of nanotubes

becomes comparable to that of carbon fibres (or even to that of the much cheaper reinforcer, carbon black), commodities such as nanotube-filled rubber tyres could become a reality. These are exciting times for nanotube composites. With strategies falling into place to solve the problems of their manufacture, commercial success for these materials — at least in select, value-added applications — is finally on the horizon. ■

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