Adapting carbon nanotubes for fine composite structures

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ABSTRACT

Although defective, commercially-available, CVD-grown, multi-walled carbon nanotubes are widely used for polymer nanocomposites due to their availability and low cost. However, to use these materials effectively, they must be disentangled, and chemically modified in order to produce high quality composites. This paper shows that such nanotubes can be disentangled by cutting; abrupt, repeated exposures to oxidising conditions in air is a clean, convenient and efficient means of producing material with open ends, moderate functionalisation, and enhanced solvent dispersibility; the surface character can easily be tuned to acidic or basic. These approaches could be deliberately integrated into conventional CVD processes, but also have implications for existing products. Matrix-filler interactions can be quantified by examining the contact angle of individual polymer droplets on single nanotubes, and correlated to the mechanical performance of corresponding macroscopic nanocomposites.

Keywords: nanotubes, nanocomposites, surface modification, cutting, wetting, CVD synthesis

1 INTRODUCTION

There is enormous interest in the use of carbon nanotubes as fillers in composite materials. The intrinsic properties of individual carbon nanotubes are remarkable; they have unmatched strength and thermal conductivity, as well as high stiffness and electrical conductivity, all at low density. In addition, their high surface area enables an intimate interaction with polymer matrices, potentially influencing matrix characteristics such as glass transition temperature and crystallinity, as well as functional properties inducing operating temperature, solvent resistance, and tribology. Although encouraging results have been obtained for nanotube-filled polymers, significant improvements over conventional fillers have proved elusive (a recent review summarises progress in this area [1]). A critical factor is the reliance on CVD-grown material, which is available in large quantity at reasonable purity, but defective and often entangled. However, a range of steps can be taken to improve the applicability of such materials, and to employ them in situations where they can provide a unique benefit. Although the intrinsic properties of nanotubes grown by other techniques, such as arc or laser evaporation are better, these methods only produce gram-scale yields, often with intractable carbonaceous by-products. In contrast, the annual production capacity for CVD nanotubes is now measured in thousands of tonnes; scalable methods for improving the usability of these materials are therefore of great interest.

One promising avenue is to exploit CVD nanotubes in fine structures where other reinforcements cannot be accommodated; examples include fibres [2][3], foams [4][5][6] and the matrices of conventional fibre composites [7]. Although nanotubes tend to raise viscosity, thereby introducing processing difficulties, in certain circumstances, the change in rheology can be beneficial even enabling [6]. In these cases, the nanofiller can simultaneously aid processing and improve properties.

2 CUTTING

Multiwall carbon nanotubes grown by CVD are usually inherently entangled, which hinders efforts to produce composites containing the well-dispersed nano-reinforcement that is required for effective stress transfer. Most nanotube composite manufacturing, therefore, includes either an explicit cutting step, or implicitly involves breakage during shear or ultrasonic processing. Explicit cutting is more reliable, but most methods both cause damage to the nanotubes, and involve a length work-up procedure; examples include mechanical ball-milling or grinding, and sonication or irradiation in aggressive acidic environments. In our work [8], the use of abrupt, repeated exposure to thermally oxidising conditions proved to be an efficient means of producing material with open ends, moderate levels of functionalisation, and, most importantly, enhanced dispersibility in organic solvents.

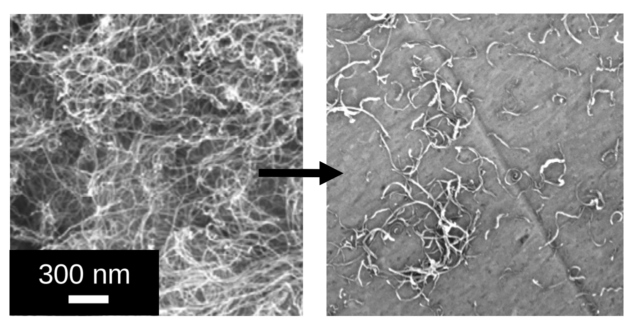

Figure 1:Scanning electron micrograph showing the effect of cutting the original entangled nanotubes (left) into shorter fragments (right)

The key is to cycle the oxidation conditions rapidly and repeatedly in order to localize the reaction at defect sites, to encourage cutting rather than the thinning process usually associated with gas phase oxidation. In our experiments, cycling was achieved by moving the sample between room temperature and a furnace at 600°C; but an alternative strategy would be to control the supply of oxygen in short bursts. After treatment the material is much more readily dispersed in solvents, such as DMF.

Figure 2: Photographs of dispersions of carbon nanotubes in DMF after 5 min of mild sonication and settling overnight. Left to right: as-grown nanotubes, 3 cycles of thermal cutting, 6 cycles of thermal cutting.

Interestingly, heating the nanotubes to 800°C in an inert atmosphere and cooling to room temperature before exposing them to air, changes the surface chemistry. The oxygen-containing surface groups switch from acid character (carboxylic acids, phenols etc) to basic groups (pyrones), as confirmed by XPS. The nanotubes with acidic character disperse best in solvents with Lewis base character (eg DMF), whilst the nanotubes with basic character disperse best in solvents with Lewis acid character (eg chloroform). It is worth noting that this type of change in character may happen inadvertently if the procedure for removing nanotubes from the original growth furnace is not standardized. It may also go unnoticed, as typical quality control techniques (EM, Raman, TGA) do not reveal the nature of the surface chemistry. Such effects may help to explain apparent variability in performance between nanotube batches. On the other hand, by using these effects deliberately, nanotubes can be adjusted for different applications. The basic equipment for these cutting and modification processes is similar or identical to typical CVD growth equipment. There is, therefore, considerable scope for integrating such processes into production facilities.

3 WETTING

The surface interactions of (modified) carbon nanotubes with a given polymer matrix has an important role in determining composite performance. Characterization of wetting and adhesion interactions at the nanoscale is challenging. However, we have developed a new methodology to create polymer droplets on individual nanotubes which allows quantitative determination of contact angle. The contact angle can be directly correlated to the mechanical effectiveness of the filler; the lower the angle the greater the stiffness. This methodology allows the surface modification of the nanotube to be linked to the interaction with the polymer, and hence to the performance of the macroscopic composite. Optimizing these factors is a crucial step to improving nanocomposite performance.

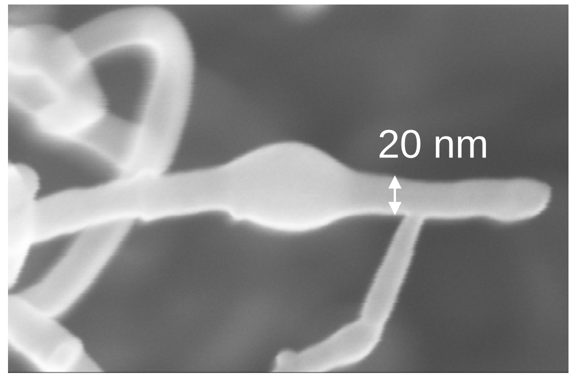

Figure 3: Scanning electron micrograph of a polymer droplet on a carbon nanotube. The shape of the droplet can be used to calculate the contact angle.

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