

Carbon Nanotube Composites: Benefits and precautions

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SUMMARY

Firstly, the potential of carbon nanotubes as composite reinforcements has been studied through Raman analysis of an ideal double-walled nanotube system. Secondly, preliminary studies have shown that the potential health hazards from nanotube powders depends on the nanotubes' morphology, giving the possibility that the risks can be minimised through design.

Keywords: Carbon nanotubes, polymer, Raman spectroscopy, reinforcement, toxicology

INTRODUCTION

Carbon nanotubes have attracted significant attention due to their intriguing combination of high strength, high modulus, good thermal conductivity and their range of electrical behaviour. Recently the production of carbon nanotubes has been commercialised with kilogram and even tonne quantities being made available. The price of nanotubes has fallen dramatically as a consequence. However, multi-walled nanotubes (MWNTs) still remain much cheaper than single-walled nanotubes (SWNTs) due to the difficulty in producing the latter. It also remains a significant challenge to translate the excellent properties of the individual nanotubes into bulk, high performance materials. The incorporation of nanotubes into a polymer matrix is one method to realise such bulk materials [1]. In general, nanotube-polymer composite research has focussed on two main applications; (i) the use of nanotubes as a matrix modifier to change the electrical conductivity of the polymer matrix and (ii) the use of nanotubes as a structural reinforcement.

Previous research has shown that nanotubes have significant potential as matrix modifiers within polymer composites. The high aspect ratio of nanotubes means that they can form electrically conductive percolated networks very efficiently. For example, percolation thresholds can be achieved at loadings of only 0.0025 wt% [2]. The percolation threshold and conductivity of these networks is very dependent on the ability to disperse the as-produced nanotubes used into individual tubes. Chemical or

physical treatment of the as-produced nanotubes may therefore be required to remove physical entanglements in order to achieve low percolation thresholds [3]. It is also important to control the processing conditions as the shear forces used can cause the nanotubes to aggregate, destroying the percolated network being formed [4].

The use of nanotubes as structural reinforcements has proven a more difficult application to realise. In particular, the application has been limited by difficulties in achieving sufficiently high loadings, good dispersion and strong interfacial properties. Furthermore, it has been shown theoretically that the effective modulus of MWNTs reduces significantly if the stress transfer between the layers of the nanotube is poor [5]. This reduced effective modulus is an issue for nanotube composites as MWNTs are preferable in terms of cost, availability and ease of dispersion for commercial applications. Therefore, determining the level to which stress is transferred between the different layers of a MWNT is significant on whether future composite work will have to focus on the more expensive narrow MWNTs and SWNTs for useful reinforcement.

Raman spectroscopy can be used to measure the stress within a material since the vibrational energy of a molecular bond, and hence its Raman band, changes as a force is applied to it. We have used previously Raman spectroscopy to measure the stress within nanotubes in a polymer-nanotube composite [6]. These measurements enable both the polymer-nanotube interface and the modulus of the nanotubes to be calculated. In large diameter MWNTs, the Raman spectra collected is an average of all the walls in the nanotubes making it impossible to distinguish the contribution to the band shift from the individual layers. Recently, Dresselhaus and co-workers have demonstrated that the G' band Raman spectra in double-walled nanotubes (DWNTs) is split into 2 components due to curvature effects; the lower component, G_1' is from the inner wall and the higher component, G_2' , is from the outer wall [7]. We have taken advantage of this splitting to use Raman spectroscopy to measure the stress in both the inner and outer walls of DWNTs within an epoxy-nanotube composite, enabling the stress transfer efficiency between the walls, k_i , to be calculated [9].

Finally, there is concern over the potential health risks to composite manufacturers and research scientists associated with handling nanotubes powders. A pilot study on the potential health hazard to the lungs from nanotubes will be presented and the results related to the aspect ratio of the nanotubes and their aggregates [8].

NANOTUBES AS COMPOSITE REINFORCEMENTS

Preparation and characterization of the DWNTs

Well-characterized double-walled nanotubes (DWNT) were prepared from single walled nanotubes (SWNT) using the peapod route (Figure 1). In brief, SWNTs from NANOCARBLAB were purified and opened by oxidative treatment. The open tubes were then filled with C_{60} through sublimation to form peapods. Finally the encapsulated fullerenes were coalesced by annealing at 1300 °C under a primary dynamic vacuum for 48 hours to form DWNTs [9,10]. Raman spectra were collected from the starting SWNT and the resultant DWNTs using a 1.96 eV excitation laser (Figure 2a-c). The SWNT spectrum showed radial breathing modes (RBMs) at

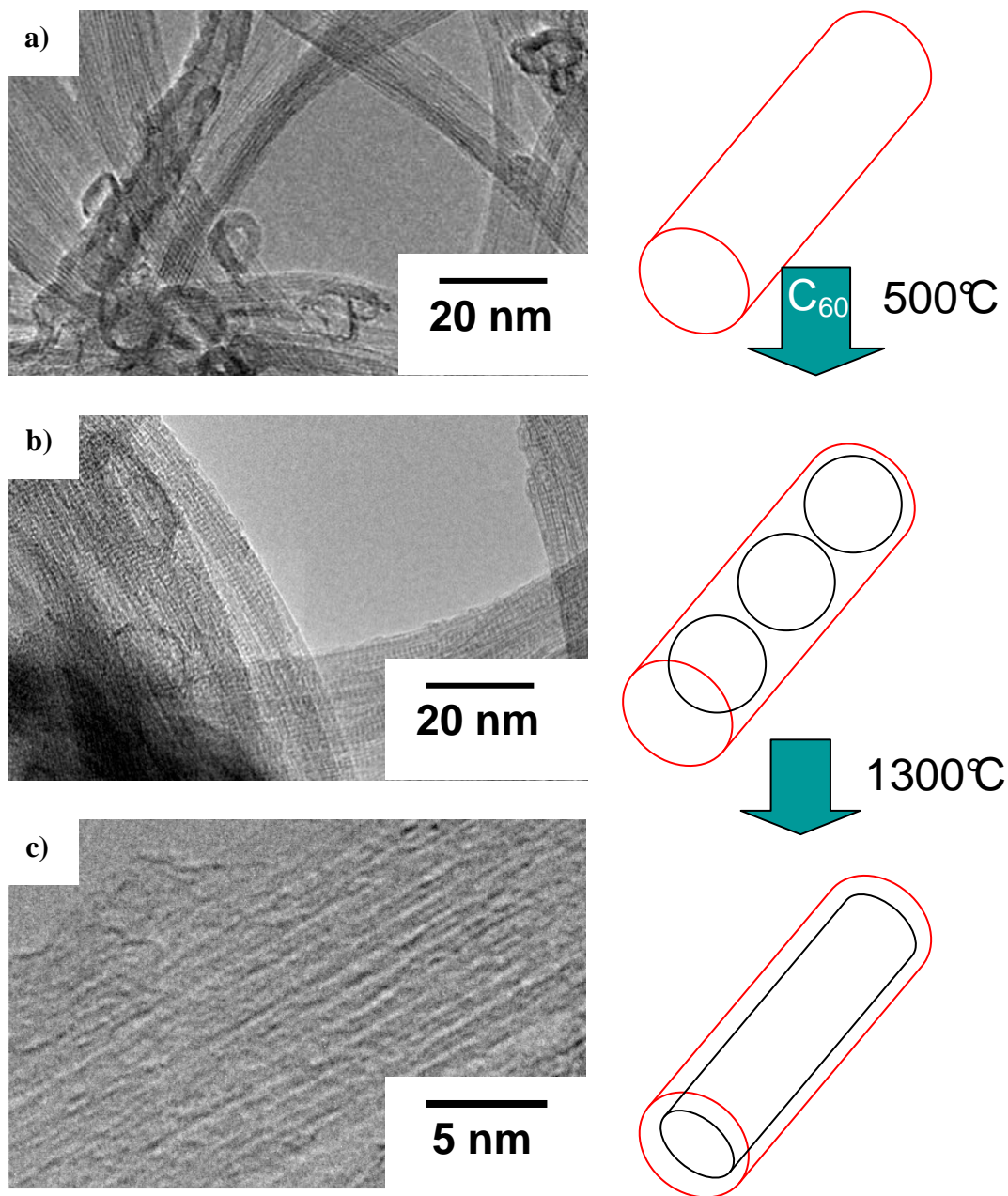


Figure 1: Transmission electro microscopy (TEM) images of the a) single-walled nanotubes, b) the peapods and c) double-walled nanotubes formed by annealing the peapods. The schematic on the right hand side summarises the production conditions.

wavenumbers under 250 cm^{-1} , which are inversely proportional to the diameter of the nanotubes. The SWNTs also had a G' (or 2^{nd} D) band which is well-described by one component. In contrast the G' band for the DWNTs consisted of two components, one at lower wavenumbers (G_1') and one at higher wavenumbers (G_2'). Also the DWNTs possessed addition bands in the RBMs. Comparison of the two spectra allowed the bands associated with the outer walls (i.e. the bands in the original SWNT spectra) and the inner walls (i.e. the new bands in the DWNT spectra) to be identified. Thus, the lower wavenumber RBMs and the G_2' band were from the outer walls and the higher wavenumber RBMs and the G_1' band were from the inner walls.

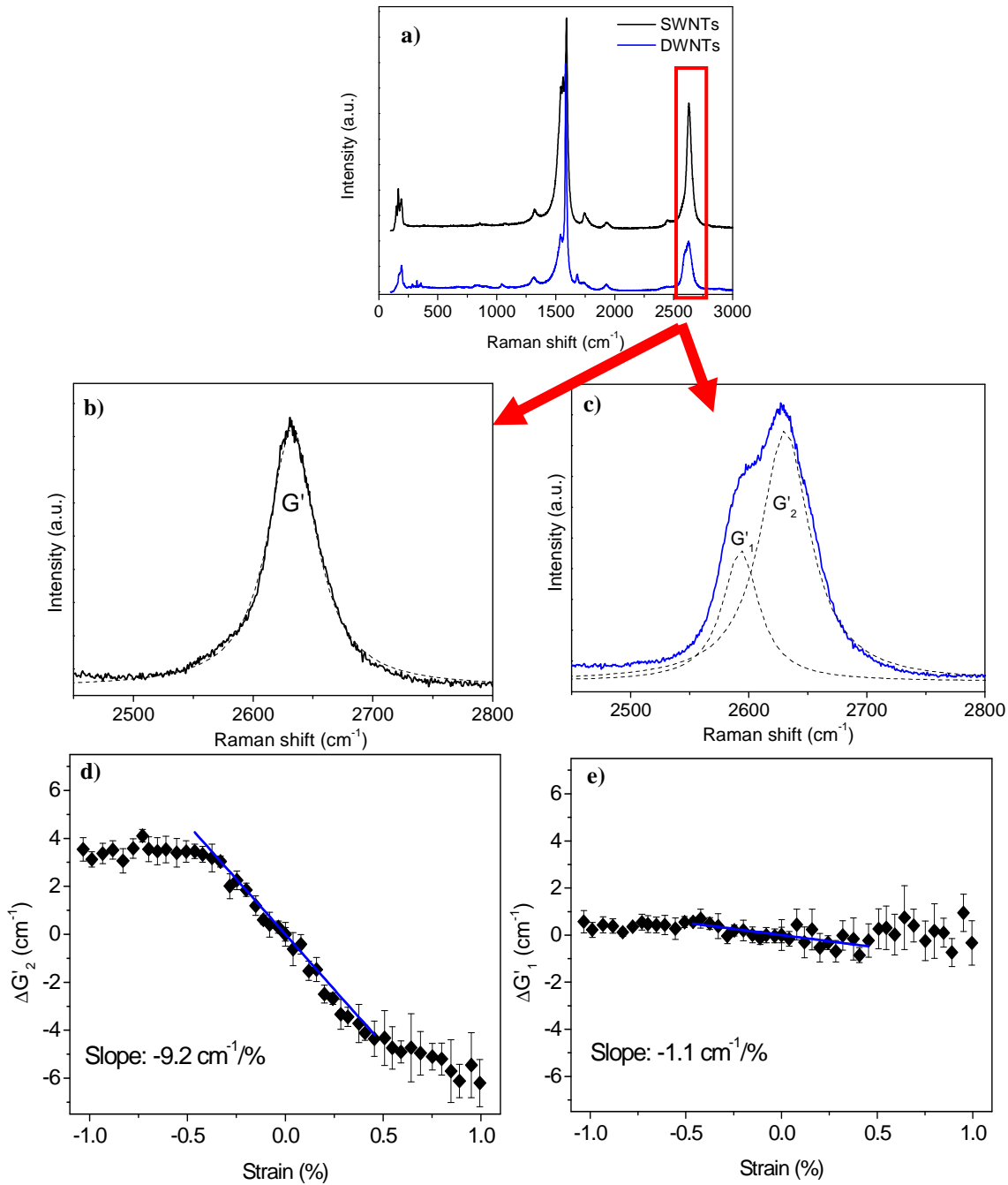


Figure 2: Raman spectra from the SWNT (a) and DWNT samples using a 1.96 eV excitation laser. (b) and (c) show details of the G' band for the SWNT and DWNT spectra respectively. The shift in the position of the G' position band as a function of strain for (e) the outer walls of the DWNTs and (f) the inner walls of the DWNTs [9].

Preparation and characterization of the composites

The DWNT composites were made using a two part epoxy system consisting of a hardener (Araldite HY 5052) and a resin (Araldite LY 5052). This epoxy system was chosen due to its low fluorescence. The nanotubes were initially dispersed in the hardener with the aid of ultrasonication and the resin was then added. Thin films of the nanotube-epoxy mixture were cast onto the surface of epoxy beams and left to cure at room temperature. The coated beams were tested in 4-point bending under a Raman

spectrometer so that the Raman spectra could be collected as function of strain. The shift in the G' position was then plotted as a function of strain for the components from the inner (G₁') and outer (G₂') walls of the DWNTs (Figure 2e-f). The G₂' component was found to shift significantly with applied strain at a rate of -9.2 cm⁻¹/%, which is typical for a nanotube composite with a moderate polymer-nanotube interface and degree of dispersion. The polymer-outer wall interface failed at 0.5 % strain, leading to little further increase in stress within the nanotubes with further increases in strain in the polymer matrix. The G₁' band position was found to be approximately constant for all the applied strain such that the inner walls in the DWNTs were virtually unstressed during both tensile and compressive deformation. We can define the stress transfer efficiency of the wall-wall interface, k_i, as the ratio of the gradients of the G₁' and G₂' plots [9], where k_i = 0 for no stress transfer and k_i =1 for a perfect interface. k_i was found to be 0.05 ± 0.04 for the DWNTs showing that little stress was transferred across the interface, reducing the specific modulus of the overall nanotube. The implication of this result is that the anticipated levels of reinforcement by MWNTs in composites cannot be achieved through interlayer shear forces alone. However, the interfacial efficiency may possible increased in the future through defects or functionalisation cross-linking the layers.

HEALTH HAZARDS ASSOCIATED WITH CARBON NANOTUBES

There has been much discussion over the last decade on potential health hazards of carbon nanotubes due to the *long fibre paradigm*. This paradigm states that an inhaled fibre is considered hazardous if the fibre is thinner than 3 µm, longer than ~ 20 µm and biopersistent in the lungs, in other words it does not dissolve or break into shorter fibres. Above all, for there to be any adverse effect, the numbers of such fibres must reach a sufficient level to cause chronic activation of inflammatory cells, genotoxicity, fibrosis and cancer in the target tissue. A pilot study has assessed the potential of nanotubes to cause mesothelioma by using a previously established protocol involving the direct exposure of nanotubes and then looking for changes associated with the development of the disease [8]. The results indicated that long, individually dispersed nanotubes do obey the long fibre paradigm whereas short and/or entangled nanotubes showed low potency. It should be noted that the study has not investigated exposure and evaluated whether workers would be exposed to threshold doses within the workplace. However, the single published study on nanotubes in workplace air (Maynard *et al.*) found that the airborne particles resembled the tangled MWNT samples shown here to have low potency [11].

CONCLUSIONS

The interwall shear forces in DWNTs in composites has been found to be poor, such that the inner walls are virtually unstressed during both tensile and compressive deformation. Therefore, the effective Young's modulus MWNTs in composites will be relatively low. A useful focus of future research would be to develop techniques to modify the MWNTs to increase the resistance of their walls to the easy shear process with, for example, the introduction of internal defects. Preliminary studies have suggested that long, individually dispersed nanotubes do obey the long fibre paradigm whereas short and/or entangled nanotubes showed low potency, giving the possibility that the risks can be minimised through design.

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