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Umar Khan[1], Ian O'Connor[2], Yurii K Gun'ko[2] and Jonathan N Coleman[1,3*]

[1] *School of Physics, Trinity College Dublin, University of Dublin, Dublin 2, Ireland.*

[2]*School of Chemistry, Trinity College Dublin, University of Dublin, Dublin 2, Ireland.*

[3]*Centre for Research on Adaptive Nanostructures & Nanodevices, Trinity College Dublin, University of Dublin, Dublin 2, Ireland.*

We have prepared mixed dispersions of single walled nanotubes and nano-graphite / graphene in the solvent N-methyl pyrrolidone. This allows the deposition of hybrid films by vacuum filtration. Scanning electron microscopy shows the components to be well mixed with little sign of phase separation. Although dominated by nano-graphite, Raman spectroscopy shows the presence of some graphene flakes with <5 layers. Mechanical measurements show the hybrids to be stronger and stiffer than nanotube or graphene-only films, reaching strengths and stiffnesses of 38 MPa and 4.8 GPa respectively for the sample with 20wt% graphene. In addition the hybrid films were more electrically conductive than the nanotube-only or graphitic films reaching a DC conductivity of 2×10^4 S/m for the 70wt% nano-graphite / graphene sample.

* Corresponding Author. Fax: +35316711759. E-mail address: colemaj@tcd.ie (JN Coleman)

1. Introduction

The excellent mechanical[1] and electrical[2] properties of carbon nanotubes have been well known for many years. Nanotubes have been used to prepare paper-like sheets[3], reinforced polymer based composites[4, 5], fibers[6] and conductive composites[7] and films[8]. More recently, it has become apparent that graphene displays properties every bit as fascinating as nanotubes. Graphene sheets have unique electronic properties[9] and have recently been shown to be the strongest material known to man[10]. In this work we have combined these materials to form graphene-nanotube hybrids. These hybrids are stronger, stiffer and more conductive than films of either component alone.

As in the early days of nanotubes, graphene has proved difficult to process. The most common solution has been to extensively oxidize graphite, rendering it polar. This makes it easy to exfoliate in water resulting in aqueous dispersions of graphene oxide[11]. This was a significant breakthrough, as these dispersions could then be easily processed into polymer-based composites[12-14] and sheets[15, 16].

The range of possibilities for new nanostructured materials based on composites or hybrid mixtures is extremely large. However, this field has been dominated by polymer-nanotube composites[4]. However, other composite types such as hybrids are possible. For example, films prepared from mixtures of singlewalled nanotubes (SWCNTs) and multiwalled nanotubes[17, 18] and from mixtures of SWCNTs and carbon fibers[18] have been demonstrated. In each case, these films have displayed novel properties. More recently, films prepared from mixtures of oxidized nanotubes and graphene oxide have been reported[19]. In this work, oxidized materials were used to facilitate materials processing. However, we believe it would be more interesting and potentially more rewarding to study mixtures of

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pristine nanotubes and pristine graphene. This would allow the study of the effects of the intrinsic properties of graphitic nanostructures on the mixture.

A recent breakthrough has made this possible. It has long been known that nanotubes can be dispersed and exfoliated in solvents such as N-methyl pyrrolidone (NMP)[20-23]. However, we have recently shown that graphite can be exfoliated to give defect-free graphene (rather than chemically modified graphene) at reasonable yield in NMP or similar solvents[24]. As nanotubes and graphene can both be dispersed in NMP, it is possible to prepare mixed dispersions and so nanotube-graphene hybrid films. In this work we have prepared such films at a range of nanotube / graphene mass ratios. We have characterized these films by scanning electron microscopy and Raman spectroscopy. We find that hybrid films are mechanically better and electrically more conductive than nanotube or graphene-only films.

2. Experimental

Purified HIPCO SWCNTs were purchased from Unidym (www.cnanotech.com, Lot number: P0288) and used as received. The graphite powder used in all experiments was purchased from Sigma Aldrich (product number 332461). N-methyl pyrrolidone (product number 42799) was purchased from Sigma-Aldrich and used as received. SWCNT powder was dispersed in NMP at concentration 0.5 mg/ml by high energy ultrasonication using a sonic tip for 10 min at a true power output of 9.3 W (measured by heating water, VibraCellCVX, nominal power 20%×750W). Various masses of graphite flakes were dispersed in 250ml NMP by low energy ultrasonication for 18 hrs in sonic bath (Branson 1510E-MT bath sonicator). The graphite and SWCNT dispersions were mixed in a round bottom flask (750 ml) in varying ratios such that ~80 mg of solid was dispersed in 250ml NMP by low energy ultrasonication for 18 hrs in sonic bath (Branson 1510E-MT bath sonicator). No centrifugation was carried

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out at any stage. The mixture was further sonicated for three hrs in low power sonic bath. This was followed by the filtration of the resultant mixed dispersion through a microporous PVDF membrane with pore size ~0.45 μm (Millipore). The films were not rinsed to avoid reaggregation. After filtration, the SWCNT/graphite coated membrane was dried at room temperature for 24 hrs then carefully peeled off. The free standing films were then dried at 60 ^{o}C for 24 hrs followed by further drying at 100 ^{o}C under vacuum for 24 hrs to remove any trapped solvent. Film thicknesses varied from ~100-500μm. The dried films were cut into strips using a die cutter. The strip dimensions were measured using digital micrometer to be 2.25×20 mm. Mechanical properties of the strips were measured using a tensile tester Zwick Roell with 100 N load cell at a strain rate of 0.5 mm/min. Measurements were made on at least 4 strips for each mass fraction. The modulus, strength and strain at break were all calculated for each strip and the results averaged. Electrical measurements were made by using a source meter (Kiethley 2004) which was interfaced with computer using I-V 0001 software. Scanning electron microscopy measurements were made using a Hitachi S-4300 field emission Raman measurements were made using Horiba Jobin Yvon LabRAM-HR. We note that mechanical, electrical and SEM characterization were all carried out on the same samples.

3. Results and Discussion

As mentioned above, preparing mixed dispersions of graphene and SWCNTs in NMP has allowed the fabrication of SWCNT-graphene hybrid films. While nanotube-only films were prepared for comparison, it proved impossible to prepare a graphene only film as they tended to break up on the filter paper. However, we found that hybrid films consisting of 95%SWCNT:5% graphene were robust enough to form free-standing films. The films prepared in this work typically had thicknesses from 10-500μm.

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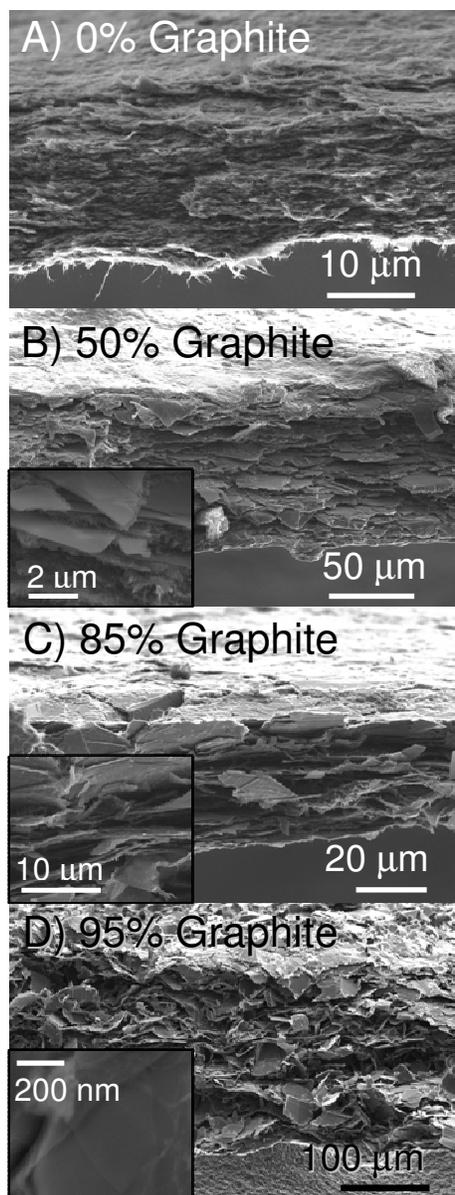
Figure 1: SEM images of fracture surfaces of various SWCNT/graphite hybrids with various nano-graphite mass fractions; A) 0wt%, B) 50wt%, C) 85wt%, D) 95wt%.

In order to investigate the morphology of these hybrid films, we have carried out extensive SEM investigations both on the top and bottom surfaces of the films but also on internal surfaces formed by tensile fracture. Representative images of fracture surfaces are shown in figure 1 A-D for different films with varying graphite content: 0wt%, 50wt%, 85wt% and

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95wt%. Figure 1A shows a SWCNT-only film which looks very like previously published images of "Buckypaper". Shown in figure 1B and C are two hybrid films with 50wt% and 85wt% graphite respectively. Here, flakes of graphite appear to be embedded in a matrix of carbon nanotubes (figure 1B, inset). These flakes can be as thick as ~2μm but generally vary in thickness from a many 10s of nm down to below 10 nm. As such, they can be considered (at least in part) to be nano-graphite. As the graphitic content increases, the flakes are not so much embedded in a nanotube matrix as coated with a sparse layer of SWCNTs (figure 1C, inset). Even in the 95wt% graphite sample illustrated in figure 1D, we see flakes with partial coatings of SWCNTs. Interestingly, these nanotubes often bridge adjacent graphite flakes. It is also worth noting that we have observed extremely thin flakes which appear to be semi-transparent to the electron beam (figure 1D, inset). We associate these flakes with few-layer graphene. In addition we note that, in all cases, the graphite is uniformly distributed and in most cases orientated parallel to the plane of the film. The exception was in case of the 95% graphite sample. Here the graphite was much more disordered, reminiscent of a jammed system. Similar behaviour has been observed for thin films of graphene deposited from NMP[24].

We explore the aggregation state of the graphite further using Raman spectroscopy (λ=633nm). Here the shape of the 2D band around 2700 cm^{-1} gives information about the number of layers in thin graphite flakes[25]. We found that the 2D region of the Raman spectra of all films, except the 95wt% film, were dominated by an intense nanotube peak around 2600 cm^{-1}. Three representative Raman spectra, collected from different regions of a 95wt% film are shown in figure 2C-E. Raman spectra for SWCNTs and graphite powder are shown for comparison in figures 2A and B respectively. It is clear that the spectrum in figure 2C is dominated by SWCNTs. In addition, the spectrum in figure 2D appears to have contributions from SWCNTs and graphite. These type of spectra are most commonly

observed. However in 10-12% of cases we see spectra such as that in figure 2E. The shape of

the 2D band in this spectrum is typical of graphene flakes with 2-5 layers*[25]*. That such thin

flakes are observed, even in the 95% graphite sample, shows not only that graphene was

present in the initial graphite dispersions, but that some few-layer graphene has survived the

inevitable re-aggregation associated with film formation. In addition the lack of a D band

($\sim$1300cm^{-1}) shows this few layer graphene flake to be relatively defect free.
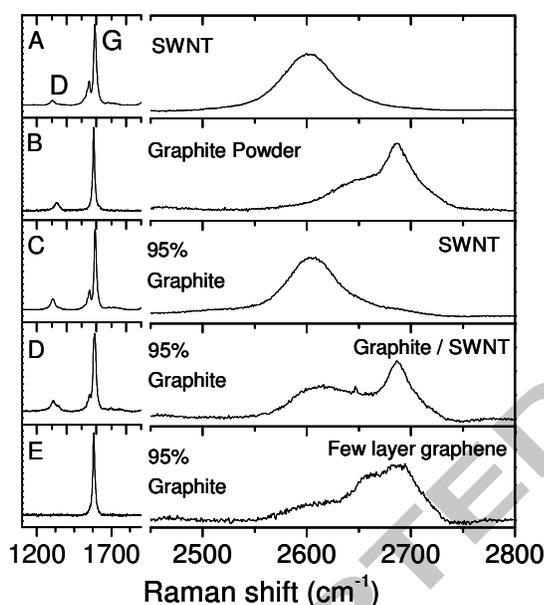
Figure 2: Raman spectra taken at different positions on a 95wt% graphite film. Also shown are

the spectra for SWCNTs (A) and graphite powder (B) for comparison. NB In each case, the

curves to the right side of the break have been upscaled by a factor of 4.

We have also characterized these hybrids in terms of their mechanical and electrical

properties. Shown in figure 3A are typical stress-strain curves for the films prepared in this

work. In all cases, the curve shapes were similar with the stress increasing sub-linearly with

strain. From these curves, we have measured the Youngs modulus, Y, the tensile strength, σ_B,

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and the strain at break (ductility), ε_B. These parameters are shown as a function of graphene/graphite content in figures 3A, B and C. The nanotube-only film had modulus, strength and ductility values of; Y=2.0 GPa, σ_B=22 MPa and ε_B=1.5%. These values are similar to values recently reported for Buckypapers made from a range of nanotube types prepared in our lab[26]. However, we recognize that better mechanical properties for nanotube films have been observed by a number of other groups[17, 27].

However, more interestingly, when graphene/nanographite is added to the nanotubes to form a hybrid, both stiffness and strength increase significantly to 4.8 GPa and 38 MPa respectively for 20wt% graphite. These values are typical for brittle polymers such as polystyrene[28]. As more graphite is added, the modulus and strength tend to fall off, but in both cases remain above the value for the nanotube only film up to graphite contents of 90wt% and 65wt% respectively. However, the 95wt% graphite film displayed stiffness and strength values of 1GPa and 1.6 MPa, significantly below the nanotube-only film. In contrast, the ductility falls steadily with increasing graphite content, reaching 0.5% for the 95wt% graphite film. It has been proposed that nanotube films relax under applied stress by the motion of inter-tube or inter-bundle junctions[26]. At a certain applied stress, the junctions begin to rupture, causing failure. It is possible that the addition of small quantities of graphite impedes the deformation of the network and hinders junction motion. This would mean greater stress would be required to cause a given amount of junction motion resulting in an increased modulus. In addition it is likely that stress would build at the jammed junctions. Thus, failure would tend to occur at higher stresses and lower strains resulting in increased strengths and reduced ductilities, as observed.
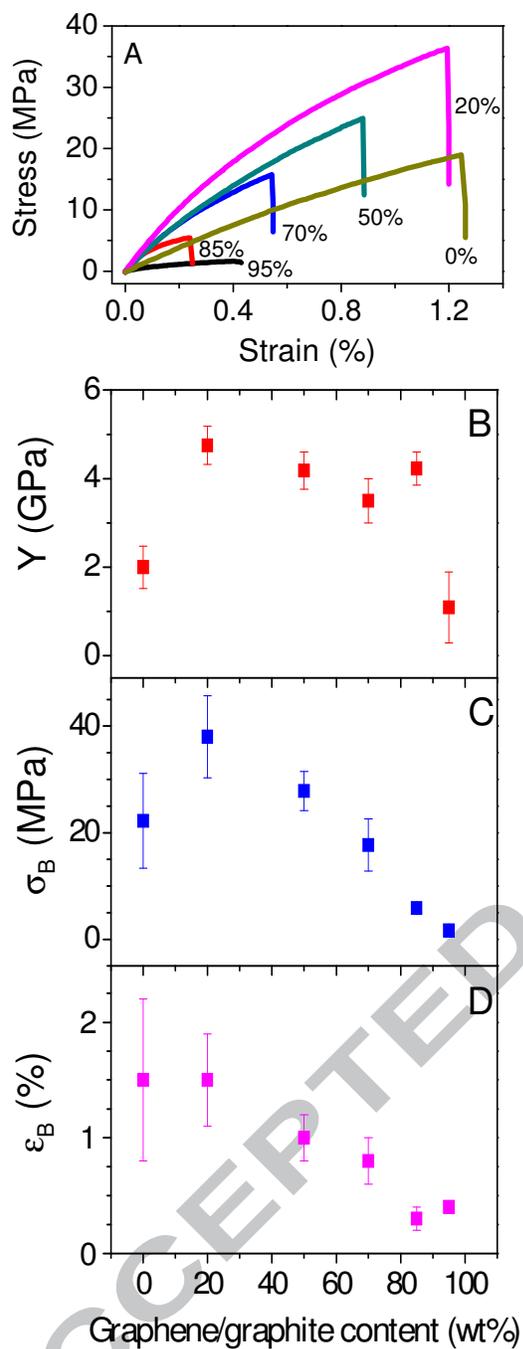
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Figure 3: Mechanical properties of nanotube / graphene hybrids. A) Representative stress strain curves for the films used in this work. B) Young's modulus, C) tensile strength and D) strain at break (ductility) as a function of graphene mass fraction. The errors represent standard deviations calculated from 5 measurements.

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We note that these mechanical properties are far below those achieved for films of graphene oxide*[15, 16]* or reduced graphene oxide[29] which routine display moduli and strengths as high as 30 GPa and 120 MPa respectively*[15]*. However, it is thought that the presence of oxides and adsorbed water*[15]* play a significant role in the inter-sheet stress transfer in such materials. By contrast, the nanotubes and graphene*[24]* used in the current work are almost defect free and can interact only via London interactions. This results in lower stress transfer and correspondingly lower mechanical properties. In addition, trapped NMP may act to reduce stress transfer at junctions and interfaces, further limiting the mechanical properties.[30] Due to the high NMP/graphene binding energy, it is very difficult to remove this residual NMP.[24]
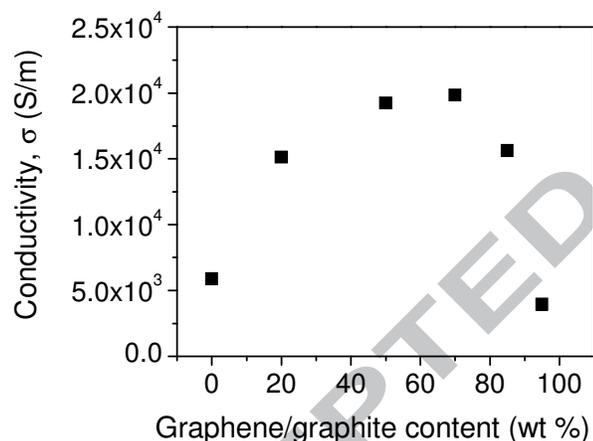
Figure 4: Direct current conductivity as a function of graphene mass fraction for the films used in this work.

We also made in-plane DC electrical measurements on these films. The nanotube-only film displayed a DC conductivity of σ_{DC}=5000 S/m. This is in line with previous measurements made on similar mats of HIPCO nanotubes made in our lab[31] but is low compared to other measurements made on thin films (~100nm) of the same tubes[32]. However, like the mechanical properties, the DC conductivity increases significantly with

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graphite content, reaching a maximum of 20,000 S/m for the 75wt% sample. At higher graphite contents, the conductivity falls off, reaching σ_{DC}=3000 S/m for the 95wt% sample. This data compares with NMP deposited, graphene/graphite-only films which displayed conductivity of 6500 S/m[24] (measured on a filter paper). We note that the maximum value observed is only an order of magnitude below the maximum observed DC conductivity for undoped nanotube films which is approximately 2-2.5×10^5 S/m as observed by a number of groups[8, 33-35]. In addition, this maximum value is close to the highest observed conductivities for reduced graphene oxide films which vary from 5,000 S/m[29] to 10^5 S/m[36] with a number of values within this range[37]. However, we note that before reduction, graphene oxide films are poorly conductive. Thus, the results just quoted could only be achieved after chemical treatment[29, 36] or by annealing, in some cases at temperatures as high as 1100C[36]. In contrast, our films consist of pristine nanotubes and graphene and have experienced no chemical or thermal treatment (except during the manufacturers purification step for the SWCNTs).

While both SWCNTs and graphene are highly conductive, we suggest that graphene films should be more conductive for two reasons. Firstly, their two-dimensional nature should result in better connectivity and so a greater choice of conductive paths for current to flow through. In addition, their planar nature should allow them to pack more closely than nanotubes, giving lower porosity. This is known to be a factor in the conductivity of nanotube films[31]. However, the data presented in figure 4 shows the opposite; that nanotube films are more conductive then the films with the highest graphite content. We believe that this is due to relative differences in the effective resistance of inter-sheet versus inter-tube junctions. Junction resistances determine the conductivity of nanotube films[31] and also, we expect, graphene films. As shown in figure 1, the packing of graphite sheets achieved by vacuum

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filtration is sub-optimal such that the inter-sheet junctions are of poor electrical quality. In addition, it is possible that nanotube-graphite junctions have lower resistance than poor quality intersheet junctions. Thus, added nanotubes would act as interconnects between graphene sheets, increasing the conductivity. However, at very high nanotube contents, reduced connectivity and higher porosity would cause the conductivity to fall as observed.

We note that these films are far from optomised. Unlike graphene oxide, where the sheets repel each other due to the presence of dipoles, solvent dispersed graphene can aggregate during film formation[24]. Thus, the hybrids used in this work are dominated by multilayer-graphene and nano-graphite rather than monolayer or few-layer graphene. We anticipate that advances in the dispersion process will result in better quality hybrid films which consist of mainly monolayer graphene and highly exfoliated SWCNTs. In addition, films of both nanotubes and graphene have been produced by spraying, opening the door for production of large area thin films of SWCNT/ graphene hybrids. The reasonably high conductivity and good mechanical properties of such films will make them suitable for application as conductive coatings. In addition, the extremely low cost of graphite, coupled with the ease of processing compared with that of reduced graphene oxide, will make these materials increasingly attractive in the future.

4. Conclusion

We have prepared hybrids of single walled carbon nanotubes and pristine, un-oxidised graphene. The graphite is generally well dispersed with no large-scale aggregation. In addition there is both SEM and Raman evidence of the presence of very thin graphene flakes in addition to nano-graphite and graphite. For certain mass fractions, these hybrids display mechanical and electrical properties that are better than those of either nanotube-only or graphene-only films. These properties mean that such hybrids have the potential to replace

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carbon nanotube films in a number of areas which require electrical conductivity of mechanical robustness. Not only would addition of graphene improve the physical properties of such materials but it would significantly reduce cost.

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Figure captions

Figure 1: SEM images of fracture surfaces of various SWCNT/graphite hybrids with various graphite mass fractions; A) 0wt%, B) 50wt%, C) 85wt%, D) 95wt%.

Figure 2: Raman spectra taken at different positions on a 95wt% graphite film. Also shown are the spectra for SWCNTs (A) and graphite powder (B) for comparison. NB In each case, the curves to the right side of the break have been upscaled by a factor of 4.

Figure 3: Mechanical properties of nanotube / graphene hybrids. A) Representative stress strain curves for the films used in this work. B) Young's modulus, C) tensile strength and D) strain at break (ductility) as a function of graphene mass fraction. The errors represent standard deviations calculated from 5 measurements.

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