Direct Synthesis of CNT Yarns and Sheets

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ABSTRACT

We have developed an automated CVD process based on gas phase pyrolysis for the synthesis of CNT based yarns and sheets. The materials may be single-walled or dual-walled. Sheet material is now being fabricated in 3 foot by 6 foot panels. Yarns over 1000 m have also been produced at a rate of 150 m/hour per spin system. These products potentially enable a variety of applications which make use of their specific strength, flexibility, and electronic properties. Post processing of the yarns can improve uniformity and a controlled pitch angle of 15 degrees improves properties. Prepregnated composites of the textiles with strengths of about 1.8 GPa have been demonstrated. Applications include: very light weight electrical conductors to replace copper wire in some applications, composites, sandwich structures, hybrid batteries, fire resistant coatings, and thermoelectric devices.

Keywords: SWCNT, DWCNT, MWCNTS, Yarns, Wires, Sheets, EMI, Strength, Conductivity, Ballistics

1 INTRODUCTION

Carbon nanotubes are generally blended with various matrix materials at volume fractions of about 1 to 5% [1-3] or as minor constituents of battery electrodes [4]. A number of investigators [5, 6] have synthesized yarns mostly pulled from forests grown on silicon substrates. For the most part these have been multi-walled nanotubes. The notable exception was the research done at Cambridge by Professor Alan Windle and colleagues dealing with direct multiwall yarn synthesis also using a CVD process. Windle produces a dual-walled yarn of very light weight (0.04 g/1000 m) [7]. We describe in this paper a means of forming relatively thick yarns directly from SWCNT tube bundles and further a means to post process these nanotube yarns to yield very high strength yarns spun directly from the CVD furnace. The formation of CNT sheets can also be accomplished by drawing tubes from forests as shown by Baughman and colleagues [8]. Alternatively, CNT Bucky papers have been produced: formed from surfactant suspensions of CNTs in water that are subsequently filtered [9, 10].

2 EXPERIMENT

Carbon nanotubes are synthesized using a gas phase pyrolysis process [7, 11-16] whereby a metal organic compound is added to a carbon based fuel in the CVD process. The catalyst particles formed in the furnace are allowed to grow to a certain size then stopped. The carbon decomposition reaction is followed by tube growth throughout the transit time in the reaction chamber. Sometime during the growth process the nanotubes are electrostatically attracted to each other to form bundles [17, 18]. These bundles form a cloud of nanotubes which exit the furnace as a large coherent tube which can be manipulated to form yarns or alternatively to form sheets. Yarns are formed by causing this cloud of nanotube bundles to impinge on an anchor or substrate from which they can be pulled off by a yarn spinning device. An example of how this works is shown in Figure 1.

Figure 1. The formation of ~ 1 nm, SWCNT yarns by spinning from a rotating anchor. The CNTs are coming from the furnace on the right and the spinning system is out of the photograph on the top left.

The resultant yarn is then post process into a tightly woven wire whose pitch angle is set to about 10 degrees. A reel of 1 km of this yarn is shown in Figure 2.

Figure 2. A reel of 1 km, 3 tex, SWCNT yarn.
Sheets of either single-walled or dual-walled CNTs, determined by fuel composition and run conditions, are formed in the apparatus of Figure 3.

Figure 3. Apparatus to synthesize DWCNT sheets is shown above. The sheets are formed by nanotubes exiting the reactor not shown, and impinging on the belt located within the large box enclosed within the exhaust hood. The Allen Bradley controller is also not shown.

The output of this box is a CNT textile which is removed from the box by cutting. An example of a typical product is shown in Figure 4.

Figure 4. A >6 foot, DWCNT textile compared with a standardized “furnace operator” for scale.

2.1 Growth

The growth of carbon nanotubes is not fully understood. Our concept involves creation of the catalyst in a pre-chamber. In this pre-chamber both the carbon source such as ethanol is blended with an organometallic catalyst such as nickelocene, cobaltocene or ferrocene, and a sulfur containing compound such as thiophene. The function of this pre-chamber is to provide sufficient energy to vaporize the fuel and its constituents, induce the thermal decomposition of the organometallic molecules to create catalyst clusters and allow these catalyst clusters to grow to the desired size. Finally at the end of this pre-chamber, sulfur reacts with the clusters to stop the growth process. No nanotube growth occurs in this portion of the reactor. The catalyst clusters then are injected into the furnace where they catalytically react with the fuel to cause its decomposition. At this point the fuel source may be quite different from the raw ethanol due to decomposition cascade reactions. Growth appears to be initially very fast and to then slow down as the reactants are consumed. Detail models of this growth process will be presented in the future.

2.2 Mechanical Properties

Mechanical properties of both sheets and yarns are determined by tensile testing in a vibration isolated tensile testing instrument. The gauge length is fixed at 10 mm for all samples and the cross head rate is set at 5 mm/minute. Most of our measurements are made without an extensometer so that strain rates reflect system compliance, and even slippage in the grips. No adhesives are used as they seem to diffuse down the specimen.

The tensile strength for a typical yarn is shown in Figure 5.

Figure 5. Breaking strength characteristics for SWCNT yarns. Breaking strength is in N/tex shown on the left axis and in GPa on the right axis. Gauge length is 10 mm for all of these samples. These samples have the catalysts retained within the structure and have not been heat treated.

2.3 Electronic Properties

Carbon nanotubes and presumably yarns and sheets made of CNTs, conduct electricity quite differently than copper. High frequency effects are also quite different in copper wires electrons are caused to diffuse the skin of the conductor and therefore proximity effects are also very high. Because of the high radial mobility, external magnetic fields, for example those existing in coils, solenoids, electric motors, can affect electron mobility especially at high frequency. Since axial mobility of electrons in CNTs is restricted by the requirement than they have to overcome $1/G^2$ at every junction HF effects are minimal until the frequencies exceed 30 GHz.

Sheets made of CNTs are often compared with Bucky paper. Bucky paper however, is made quite differently, generally by suspending CNTs with the help of a surfactant in a water solution and then filtering out the CNTs (coated with surfactant) to make a thin film resembling paper. A comparison between the best Bucky paper and our dual-walled nanotube sheets is shown in Table 1.
Table I. Difference between Nanocomp’s sheet or ribbon conductors and Bucky Paper.

<table>
<thead>
<tr>
<th>Property</th>
<th>Bucky Paper</th>
<th>DWCNT Sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>74 MPa</td>
<td>&gt;1000 MPa</td>
</tr>
<tr>
<td>Modulus</td>
<td>8 GPa</td>
<td>&gt;30 GPa</td>
</tr>
<tr>
<td>Resistivity</td>
<td>5 x 10^{-2} Ω-cm^2</td>
<td>2.6 x 10^{-4} Ω-cm (ambient)</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>40 (magnetically aligned)</td>
<td>60 Watts/m²-K^2</td>
</tr>
<tr>
<td>Seebeck Coefficient</td>
<td>NA</td>
<td>&gt;70 μV/K</td>
</tr>
</tbody>
</table>

DC Electrical Characteristics

Electrical characteristics at ambient temperature were measured using the four point contact method at ambient and at elevated temperatures.

Sample temperatures were measured with a calibrated optical technique. The data shown in Figure 6 suggests that even though the CNT conductors under dc conditions can carry more power, they heat up faster under the same conditions as copper. Under some cases the temperature increase can be designed for in the applications especially where other factors such as stress or fatigue are an issue for conductors.

AC Electrical Characteristics

High frequency behavior of CNTs has been studied by a number of investigators [22-24]. The mean free path of electrons in copper is 0.04 microns whereas the mean free path in CNT ranges from 1 to 60 microns [25]. At high frequency the impedance is controlled by skin effects, eddy currents and proximity effects. Since electron transport in CNT is said to be ballistic, such that the electrons are surface confined, the driving force to cause electron transport to the outer surface of the wire is much higher than for copper, therefore this effect is “pushed” to very high frequencies. Ballistic conduction has been reported for multi-wall nanotubes as well [26]. An example of this remarkable behavior is shown in Figure 7 comparing Litz wire of two different diameters with a CNT wire and a copper wire. The resistance has been normalized for this comparison.

Figure 7. The high frequency response of CNT wire compared with single strand copper and litz wire of two different diameters.

3 SUMMARY

3.1. Carbon nanotube sheets and yarns exhibit dc conductivity worse than copper but at moderate frequency may outperform copper for some applications.

3.2. Strength of CNT yarns is starting to approach that of graphite and if adsorbed species and the catalyst weight is taken into account they already will.
3.3. A continuous process to produce CNT yarn has been developed and production rates exceeding 150 m/hr have been demonstrated.

3.4. A process for producing very large CNT sheets which can be single wall or dual wall has been demonstrated and sheets larger than 3 feet by 6 feet have been produced.

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REFERENCES

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