Micro Fabrication of CNT based fibers

Manjunath E B
Department of Mechanical Engineering, Center for P G Studies, Bangalore Institute Of Technology, K.R.Road, V.V.Puram, Banglore-560004
Aravind V
Department of Mechanical Engineering, Bangalore Institute of Technology, K.R.Road, .V.V.Puram, Bangalore-560004
Somanna M Y
Department of Mechanical Engineering, Bangalore Institute of Technology, K.R.Road, .V.V.Puram, Bangalore-560004

Abstract

The discovery of carbon nano tubes (CNTs) was a major breakthrough on a technological front. But, these CNTs have largely failed to relate to the real world problems because of the difficult material synthesis and laborious processing. These multifunctional carbon nanotubes (CNT) fibers combine the specific strength, stiffness, and thermal conductivity of carbon fibers with the specific electrical conductivity of metals. But realizing these excellences in practical applications needs to assemble individual CNTs into larger scale products. In this paper, we review some key spinning techniques like spinning from a vertical aligned CNT arrays, Electrophoretic spinning, spinning from CNT aerogel and solution spinning techniques include surfactant based spinning, liquid crystal based solution spinning. The methods and limitations and recent progress of each technique have been addressed.

INTRODUCTION

Carbon nanotubes (CNTs) are the stiffest (Young‘s modulus) and strongest (yield strength) materials as yet measured. Their tensile strength is about 11–63 GPa for individual multiwalled CNTs (MWNTs) and 13–52 GPa for individual single-walled CNTs (SWNTs) [1–3]. They are also good conductors of electricity and heat [4–8]. These extraordinary properties make them attractive for advanced applications. In order to fully utilize their superior properties at practical scale, CNTs need to be prepared into larger size assemblies, such as micro scale CNT fibers. Recent progresses [9–12] in neat CNT fibers demonstrate the possibility of retaining CNT‘s excellent properties at larger-scale and more practical level. The CNT fibers have been reported to have tensile strength of 1~3GPa, Young‘s modulus of 100~260 GPa, toughness of 100~900 J·g−1, and density of 0.2 g·cm^{-3} [9]. These progresses motivate further study of lightweight and high-strength composites for possible structural applications.

Numerous methods have been developed to assemble CNTs into fiber. [13] Generally, these techniques could be divided Into two groups: solution-spinning methods [14–18] and solid-spinning techniques. In solution-based spinning, CNTs need to be dispersed into a liquid first, and then spun into fibers, by a process similar to that used for polymeric fibers. In solid-spinning processes, CNT fibers could be spun from vertically aligned CNT arrays [19, 20], cotton-like CNT mats [21, 22], or from an aerogel of CNTs formed by chemical vapor deposition(CVD) [23,24] or Electrophoretic spinning [25]. The Performances of CNT fibers are strongly dependent on processing methods and the detail process parameters.

METHODS OF SPINNING
CONVENTIONAL SPINNING
(SOLID SPINNING)
Spinning Fibers from Vertical-Aligned CNT Arrays.

In order to eliminate the dispersion problem existing in solution based spinning methods, spinning CNT fibers directly from as-grown CNT materials seems to be a more convenient way. A breakthrough was made by Jiang et al. [19] in 2002 by simply drawing a neat CNT yarn from a vertically super aligned CNT array. They found that CNTs could be self-assembled into yarns of up to 30 cm in length. Following that, Zhang et al. [25] produced highly orientated, free-standing CNT transparent sheets using a similar method, and further assembled CNTs into fibers by using a draw-twisting spin method [20]. The typical SEM images of fiber spinning processes are shown in the figure below.

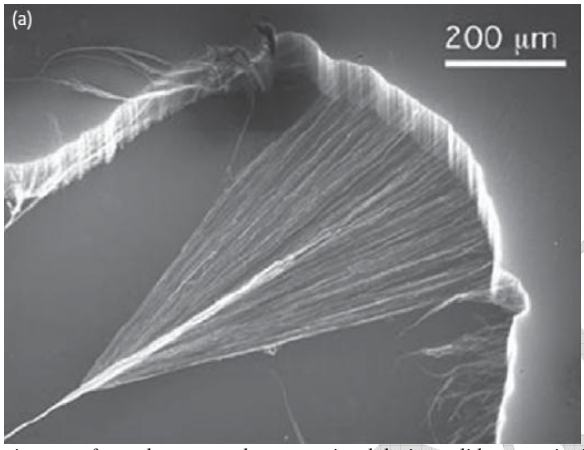

Fig. 4 Scanning electron microscopy images of a carbon nanotube yarn twisted during solid-state spinning. (Reproduced from Zhang et al[20]

Jiang et al. [19] found that the strength and conductivity of their yarns could be improved by being heated at high temperatures. By introducing twist during spinning to make multiple, torque-stabilized yarns, Zhang et al. [20] achieved yarn strength greater than 460MPa. These yarns could also retain their strength and flexibility even after being heated in air at 450°C for an hour or being immersed in liquid nitrogen. In addition to using postspinning treatment, Zhang et al. [9–11] found that mechanical properties can be significantly improved by using longer CNT arrays. The tensile strength and stiffness of their fibers spun from a 1mm long CNT array were measured in the range of 1.35– 3.3GPa and 100–263 GPa, respectively, which is many times stronger and stiffer per weight than the best existing engineering fibers and CNT fibers reported previously. Since CNTs in a yarn are nearly parallel-aligned, the CNT yarn is intrinsically an anisotropic material and has a special axis along the drawing direction, which demonstrates many fascinating properties and applications. However, some key issues need to be solved in advance to realize their practical applications. Currently the growth of CNT arrays is easy, but not all CNT arrays could be spun into yarns or fibers. Zhang et al. [26] found that strong van der Waals interactions exist between individual CNTs within super aligned arrays, and this van der Waals force makes the CNTs join end to end, thus forming a continuous yarn during pulling. Meanwhile, Zhang et al. [20] claimed that the formation of yarn was due to the disordered regions at the top and bottom of the CNT arrays, which entangled together forming a loop.

ELECTROPHORETIC SPINNING

Gommans et al. have spun fibers electrophoretically from purified laser vaporization– grown SWNTs dispersed in n, n-dimethylformamide (DMF) at concentrations of about 0.01 mg/ml [27]. A commercially available carbon fiber (8μm in diameter, about 12 mm long) was connected to a conducting wire (0.5 mm diameter, 10 mm long) with silver conducting paint. The wire was attached to a motor-driven stage via a pin vice. The carbon fiber translated along its axis into the suspension at a depth of a few millimeters. The carbon fiber was turned into a positive electrode by applying voltage, causing the SWNTs to migrate toward it and to form a cloud around the carbon fiber. SWNTs migrate because they are negatively charged in DMF and move electrophoretically toward the positively charged carbon fiber. As the carbon fiber was slowly withdrawn from the suspension, another fiber attached to its end spontaneously formed from the SWNT cloud. The fiber length was limited by the travel distance of the translation stage, the size of the SWNT cloud, and the smoothness of the withdrawal from the solution. Fibers were typically several centimeters long with diameters between 2 and

10 µm. The mass of SWNTs below the bath surface and the surface tension in the meniscus promoted the coalescence and axial alignment of bundles of SWNTs. Alignment was measured by polarized Raman spectroscopy and the axial versus perpendicular ratio was in the range of 2 to 6 [27].

SPINNING FIBER FROM AEROGEL OF CNTS.

Zhu et al. [28] have first reported the formation of a 20 cm long CNT thread after the pyrolysis of hexane, ferrocene, and thiophene. This work shows the possibility of fiber formation directly in a furnace. Based on this phenomenon, a totally different fiber spinning method was developed by Li et al. [23]. They were able to spin neat CNT fibers directly from an aerogel of CNTs formed in CVD reaction zone, as shown in Figure. The precursor materials include liquid hydrocarbon feedstock, ferrocene which forms the iron nanoparticles that act as nucleation sites for the growth of CNTs, and thiophene which is an established rate enhancer for vapor grown carbon fibers. The key requirements for continuous spinning are the formation of CNT aerogel and removal of the product from reaction zone. These were realized through the appropriate choice of reactants, control of the reaction

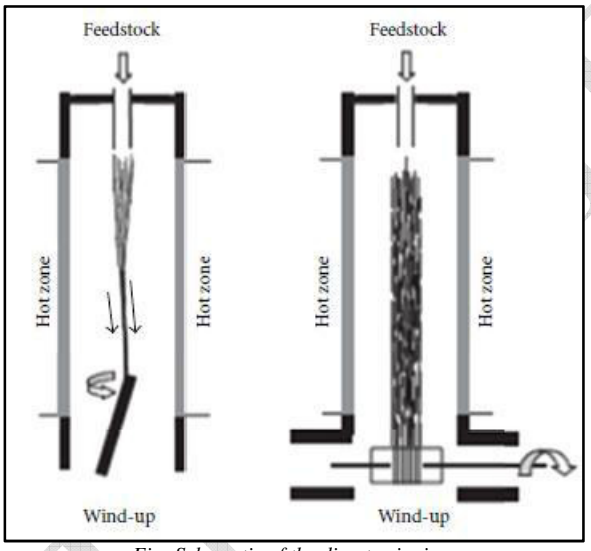

Fig: Schematic of the direct spinning process

Conditions and continuous withdrawal of the products with a rotating spindle used in various geometries. From the view of reactants and growth conditions, the continuous spinning process is possible with a range of oxygen-containing carbon sources. Aromatic hydrocarbons lead to the deposition of carbon particles and thick fibers, but cannot enable a continuous spinning process unless they are mixed with another oxygen-containing source. Thiophene is found to be a necessary additive. It was used as an established rate enhancer for vapor growth of carbon fibers [28], but its actual role played in CNT aerogel generation is still open to discussion. Regarding the processing parameters, it is found that CNT alignment, the density, and microstructures of fibers can be controlled by drawing/winding rate and post processing methods. They have also shown that the mechanical properties of the fibers directly relate to the type of CNTs, which in turn, can be controlled by the careful adjustment of process parameters. Through the optimization process, Koziol et al. [24] have found that, by drawing the aerogel at a winding rate of 20 mmin−1, the strength of the fiber, mainly containing DWNTs, can reach around 10 GPa, which is the highest value reported so far. The strength of CNT fibers peaks at around 1 GPA in the case of 20mm gauge lengths.

SOLUTION BASED SPINNING TECHNIQUES

Surfactant based spinning

CNTs are dispersed in an aqueous solution containing a surfactant such as Sodium Dodecyl Sulfate (SDS); the solution is then sonicated to break up CNT bundles and allow the surfactant micelle to encase the CNTs[28]. The surfactant concentration is critical for the formation of a good dispersion. If it is too low, stabilization is

inadequate; if it is too high, the osmotic pressure of the excess micelles causes depletion-induced aggregation. Surfactants such as Tetra-triMethylammonium Bromide (TMB) and Lithium Dodecyl Sulfate (LDS) have also been used. In this process, a surfactant-stabilized SWNT solution is coagulated in a PolyVinyl Alcohol (PVA)/water bath; PVA displaces the surfactant and induces flocculation of the SWNTs into an intermediate gel-like fiber structure, termed a ‗proto-fiber'. This protofiber simultaneously undergoes solvent loss, solidification, and stretching and nanotubes alignment to form a final solid fiber structure.

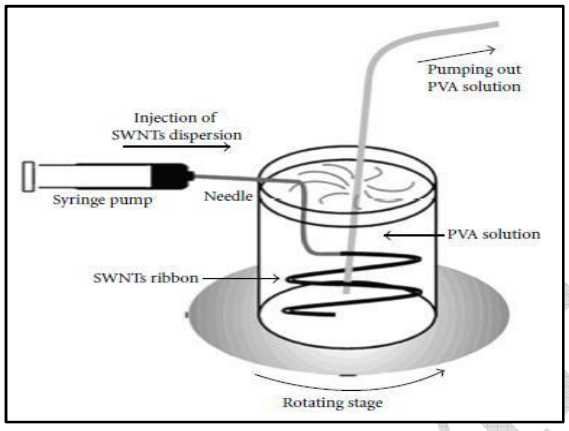

Fig: *Schematic of the rotating bath used for coagulating surfactant-dispersed SWNTs into a fiber*

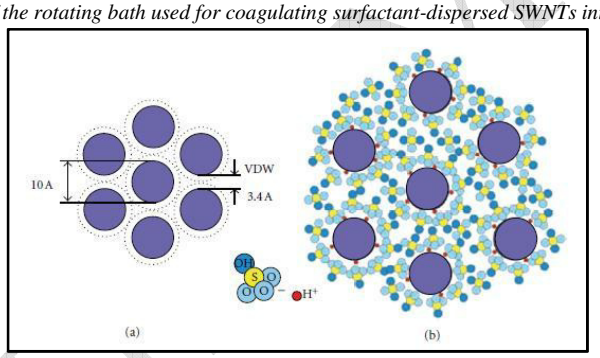

Fig: A model illustrating the swelling of SWNT ropes in sulfuric acid. (a) A cartoon of SWNTs in van der Waals contact within a neat fiber. (b) The same SWNT fiber after reexposure to sulfuric acid [16]

Liquid crystal based solution spinning

Spinning from lyotropic liquid-crystalline solution of rigid-rod molecules is another important method used for fiber production. CNTs were similar to high-aspect ratio and rigid-rod polymers and exhibit liquid crystallinity feature. Ericson et al. [16] first successfully produced well aligned macroscopic fibers composed solely of SWNTs from lyotropic solutions in super acids. Fuming sulfuric acid charges SWNTs and promotes them to order into an aligned phase with individual mobile CNTs surrounded by acid anions. This ordered dispersion was then extruded into a coagulant bath (either diethyl ether, 5% sulfuric acid, or water) to form continuous macroscopic CNT fibers. The possible mechanism, that high concentration CNTs could be dispersed in super acid (102%sulfuric acid), is the repulsive interaction between CNTs generated in super acids due to the formation of charge-transfer complexes: individual positively charged CNTs surrounded by a finite number of sulfuric acid anions. At very low concentration, such charged tube-anion complexes behave as Brownian rods. At higher concentration, the CNTs coalesce and form ordered domains, behaving similarly to nematic liquid crystalline The CNT fibers spun by such a process have interesting structural and physical properties, including high orientation, good electrical and thermal conductivities, and reasonable mechanical properties. The alignment of CNTs within these fibers is within ±15.5◦. The strength is 116 ± 10MPa, and the Young's modulus approaches to 120 ± 10 GPa. However, some protonation of the material occurs because of prolonged contact with the sulfuric acid. The CNT/acid system is very sensitive to water; the introduction of even minimal moisture causes phase separation and precipitation of discrete needle-like crystal solvates. And super acid route is also found not effective for MWNTs. To address the last problem, Zhang et al. [25] developed a new

coagulation process, by which they spun MWNTs from liquid-crystalline ethylene glycol dispersion. The MWNT fibers have a Young's modulus of 69 ± 41GPa and a yield strain of 0.3%. Fracture occurs typically at strains below 3% and stresses of 0.15 ± 0.06 GPa.

CONCLUSION

The development of CNT fibers is in its infancy, and the performance expected from the nanoscale properties of CNTs has yet to be realized in macroscopic objects. However, preliminary composite and neat fibers show promising results. It is likely that spinning processes will evolve to meet specific applications'needs. CNTs dispersed in a polymer matrix may be best suited for extending the potential applications of existing polymeric materials by enhancing thermal and electrical conductivity and compressive strength at a relatively low-cost differential. CNT/surfactant dispersions may be solution spun for applications where toughness and other mechanical properties are most critical. CNT/acid dispersions used to produce neat fibers may be best suited for applications with the most demanding thermal and electrical requirements. The development of these spinning technologies alongside with improvements in CNT production, purification, and fictionalization will undoubtedly result in a number of revolutionary fiber applications.

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