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Preparation of CNTs rope by electrostatic and airflow field carding with high speed rotor spinning

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Abstract. The large-scale preparation of disorderly CNTs with a length larger than 3 mm using CVD method were aligned in polymer monomer airflow fields in a quartz tube with an internal diameter of 200 μm and a length of 1.5 m. The airflow aligned CNTs at the output end of the pipe connects to a copper nozzle with an electrostatic field of applied voltage 5×10^5 V/m and space length of 0.03 m, which were further realigned using via electrostatic spinning. End to end spray into the high speed rotor twisted single-stranded carbon nanotubes threads via rotor spinning technology. The essential component of this technique was the use of carbon nanotubes at a high rotory speed (200000 r/min) combined with the double twisting of filaments that were twisted together to increase the radial friction of the entire section. SEM micrography showed that carbon nanotube thread has a uniform diameter of approximately 200 μm. Its tensile strength was tested up to 2.7 Gpa, with a length of several meters.

1. Introduction

Single carbon nanotubes demonstrate high strength and excellent mechanical properties [1-3] but cannot form a macro-scale structural material. Due to its small specific density, high intensity, acid corrosion resistance and good low temperature and high performance, thermoset carbon nanotubes were twisted into an axially-aligned structure with excellent mechanical properties, forming a uniform diameter carbon nanotube fiber rope. It has promising applications as an excellent fiber material and could replace high-performance carbon fibers or military “armored Guardian” Kevlar (aramid) [4] The CNT thread has vital application prospects in the fields of advanced structural materials and functional materials; the application value is incalculable and widespread.

Researchers have made significant advancements in carbon nanotube fibers and composite materials [5, 6]. Currently, there are two primary methods to prepare CNT thread. CNTs prepared by A Lin H were achieved via a one-step floating CVD method [7], prepared by floating CVD spinning. The advantage of this method is that it began with entangled, disordered CNT powder as a raw material for processing of the fibrous material. However, with the addition of a catalyst, the impurity content of the CNTs increased, forming tiny amorphous carbon particles and other defects that may weaken its strength and contribute to the inhomogeneity of the CNT thread and decrease the tensile strength of the thread. Another method is preparing a directional growth of the CNT array, reported by

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Fan S S [8] Initially, this approach was modified so that CNT thread was pulled from the array and post-spin twisting was initiated by an ultra-fine probe to make a CNT thread with a high tensile strength of 1076 MPa [9]; this technique offers controllability of the spinning process, fewer impurities and stable mechanical properties of the resultant thread. The disadvantage of the method is that directional growth efficiency of CNT arrays becomes low. Prepared fiber length is affected by array size. Furthermore, low-speed twisting or small twists result in uneven diameter and low mechanical properties that limits the industrial applications. Solving uninterrupted and directional alignment problems are necessary for the preparation of long CNT threads. This paper presents a new method for preparation of CNT thread on a macro-scale with uniform diameter and excellent mechanical properties, in which carbon nanotubes are aligned along the velocity gradient field in the polymer monomer airflow and electric fields before the high speed rotor spinning and double twisting process.

2. Experiment

2.1. Preparation carbon nanotubes thread

Carbon nanotubes were prepared by enhanced chemical vapor deposition which inputs a three-channel entrance (nitrogen, hydrogen, hydrocarbon gas) at the bottom of the device. The reactor was evacuated with a vacuum pump and flushed with pure nitrogen. When the temperature of the reactor was raised to 750ºC under a flowing nitrogen atmosphere, a hydrogen gas stream 150ºC for heat preservation was continuously injected for 10 minutes ($Fe(C_5H_5)_2$) into the quartz tube with diameter of 50 mm and a length of 1.5 m by a precision metering pump at a rate of 0.1 mm/min. Meanwhile, thiophene was added to the catalyst precursor as a growth promoter. By operating the controller at a flow of 800 ml/min, a hydrogen: acetylene ration of 3:1 were mixed and reacted for 5 hours. Next, the system was cooled to room temperature in a nitrogen atmosphere to acquire CNTs with lengths exceeding 3 mm, as shown in figure 1. If the reaction time is too short, it will result in CNTs too short to match the rotor speed and form a thread. However, long reaction times will lead to serious problems such as wall thickness increases or the reunion phenomenon.

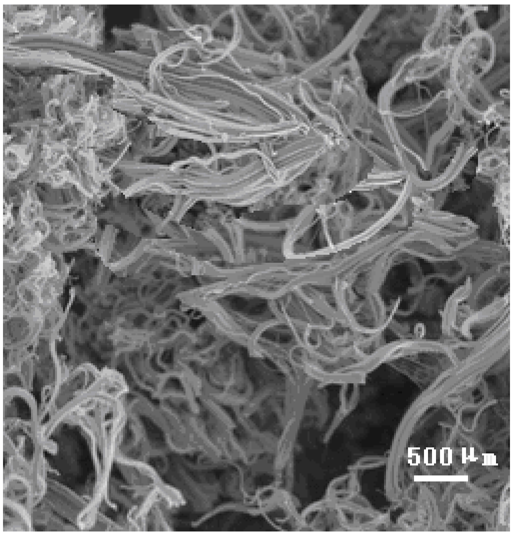

Figure 1. SEM image of CNTs prepared by CVD.

The traditional composite fabrication strict with layer and impurities of CNTs. To achieve a lot of carboxyl and carbonyl active group on the surface of CNTs and easily interface bonding with other material, CNTs was required further purified using acid mixture with V (96%H_2SO_4): V (65% HNO_3) 3:1 [10]. However, it was found that strong oxidizer will truncate CNTs and has a negative effect during the preparation of CNTs thread. It's very gratifying that there was residual chemical bond and dangling bond surface states itself during the synthesis of CNTs by CVD method. Due to the polymer monomer molecules together with the abundant surface chemical bond of it, the CNTs will obtain infrangible interface bonding bringing the CNT in closer contact to each other. Heated polymer monomer formed continuously and steadily airflow field in the quartz tube, then CNTs continuous through the quartz tube with diameter of 200 µm and a length of 1.5 m by automatic vacuum feeder in flow of 350 ml/min. Polymer flow field teased out disorderly arrangement of CNTs along the axial directional movement in capillary quartz tube, which improved the mechanical strength of CNTs. At the output quartz tube's end connects copper nozzle(150 µm of nozzle diameter) applied voltage electrostatic field of 5×10^5 V/m and space length of 3 cm. CNTs are further realigned end to end spray into the high speed rotor and twisted single stranded thread. This process solved the low mechanical strength and fiber interrupted caused by CNT arranged clutter. In comparison with the normally monofilaments, the mechanical properties of the thread were obviously improved that tensile strength increased to 150% and process equipment as shown in figure 2.

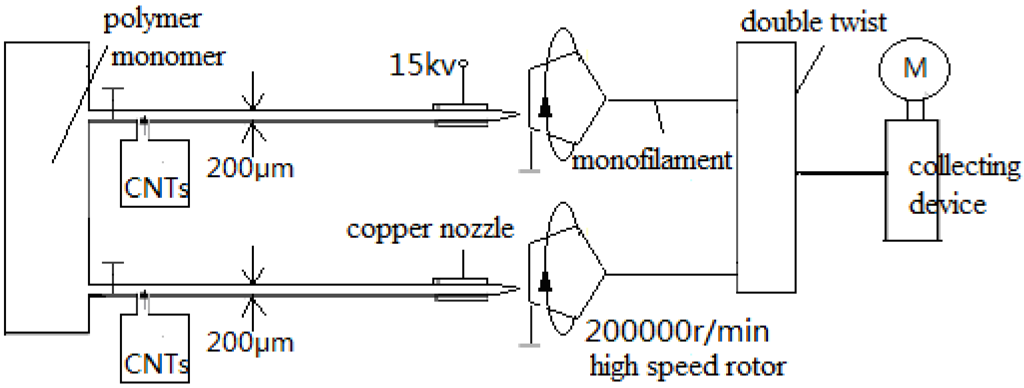

Figure 2. The flow chart of CNT thread prepared by airflow and electrostatic field combing high speed rotor spinning.

2.2. Electrostatic and airflow field carding CNTs
The monomer 4, 4 '- dichloro diphenyl ketone of Poly ether ketone (PEEK) replaces acetone and ethanol adopted by other research group [11]. Heating steam was made through high heat, the addition of polymer monomer improves the connectivity of CNTs and plays an auto-action for the preparation of super long nanotubes. Using high pressure blower (the pressure of jet cylinder piston is 0.5×10^6 Pa), the pipe were filled with high polymer airflow. Injecting CNTs into capillary quartz tube. Steam flow not only makes the directional arrangement of CNT (2 mm in length , less than 100 nm in diameter) , but also affects with carboxyl groups of ionization of CNT after being processed, which form stable chemical bonds in order to improve the cohesiveness. Then, applying high voltage (15 kv) of positive power on quartz capillary outlet, rotor grounding. Direction controlled single nanowire is obtained by high voltage electric field. The appropriate diameter ratio guarantees accelerated motion of airflow in quartz tube and reduce the fiber bending in the capillary. To further make the orientational alignment of CNT, the top of the nozzle is tangent to condensation of rotor slot. Injecting spinning into an improved German Autocoro360 suction type rotor at a speed of 5 m/s, rotor speed is 200000 r/min, the diameter of rotor is 18 mm as shown in figure 3. The increase of rotor speed makes short fiber higher tension and arranged tightly in a row. Along with the negative pressure air flow increases of the high speed forming, the continuous filament is strengthened. Since high negative pressure (7.5 kpa) can make the air draft, enhance coagulation closely, improve the quality of the silk and guarantee the stability of spinning.

2.3. The preparation of CNT thread with the double twisting
The thread is made up of fiber bundle along the whole length of the fiber or filament direction. Friction will make not loose or slippage between monofilament and monofilament after holding

closely each other. The group adopted the Oerlikon Alma TCS - ML experimental machine. Spindle number is 4, spindle pitch is 600 mm. With drawing speed (8 cm/min), the two CNT fiber bundles were twisted into a diameter of less than 200 um by air electrostatic method, length up to several meters of CNT thread. The single yarn strength of traditional cotton fiber airflow spinning is 8.4 CN/tex. Under suitable twist modulus and rotor speed, twisting strength is up to 130% [12].

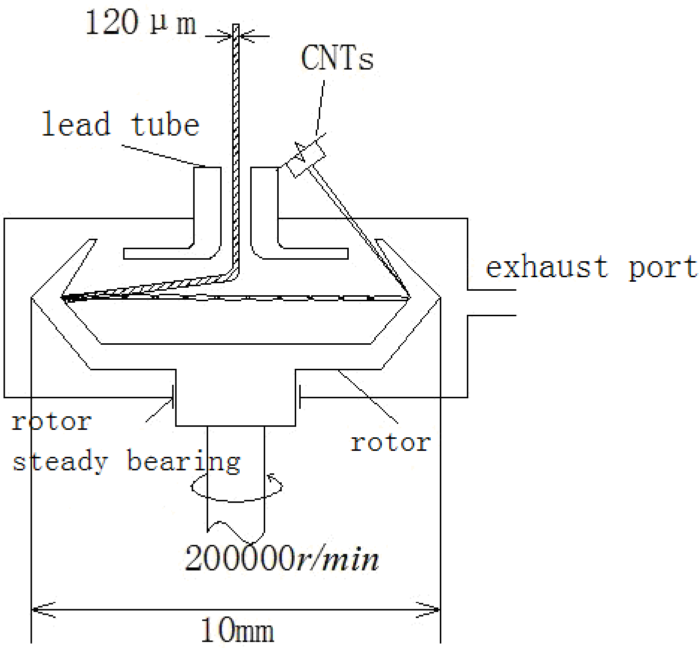

Figure 3. The schematic diagram of high speed rotor.

3. Results and discussion

3.1. The microstructure and mechanical strength

Scanning electron microscopy (SEM) analysis adopted the field emission of JSM-6700-F, which is produced by the Japanese electronics company. The preparation samples were detected by SEM, as it is shown in figure 4. It indicated that the CNT thread monofilament in diameter is about 120 μm and has good continuity, and quality line density is 30 g/km. It differs by selecting different process parameters. The mechanical properties of CNT thread are measured by INSTRON 1122 universal material testing machine, the results show that a tensile strength is up to 2.7 Gpa.

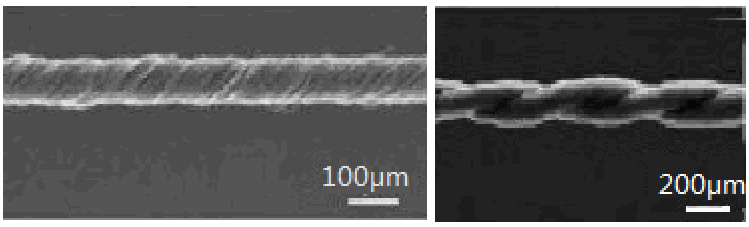

Figure 4. SEM photos of CNTs thread & double twisted CNTs rope.

3.2. CNTs orientation function of the airflow field

Based on the mass conservation law, the fluid flow steadily in the tube, liquid of per unit time flowing through a pipe of arbitrary across section are equal in quality. The continuum equation for fluid, V_1A_1 and V_2A_2 is constant. Thus the fluid flow steadily in the same pipeline, the flow rate is a constant. The smaller the cross pipe section is, the larger the flow velocity is. The author designed a new type of air ventilation with polymer monomer capillary quartz tube, the air does not only have directional effect of CNTs in the quartz tube, but also form the steady chemical bond, which improve the cohesiveness between monofilament. In conclusion, CNT has arranged the trend along the flow direction. The longer the process is, the more obvious directional trend has [13].

3.3. CNTs orientation function of the electric field

The orientation degree of CNT is in high demand of high speed rotor spinning. Single flow has a significant orientation function in carding CNTs process, what is more, adopting the electrostatic field will promote further directional of CNTs. Because the CNTs is polarized in the static electric field, bound charge is formed at both ends, single root CNT become a dipole electric in a static electric field. Electric dipole suffered the electric field force generated dipole moment M ($M = Fl\sin\alpha$), as shown in figure 5. Dipole moment makes CNTs rotated into the direction of the electric field and it also suppress that directional CNTs deviates from the direction of the electric field in the process of spinning. Experimental results show that electric field with intensity of 5×10^5 V/m can make combing CNTs oriented arrangement higher degree in the electric field. If the field voltage is too high, it can easily breakdown CNTs. If the electric field voltage is too low, then the dipole moment is not sufficient to overcome the resistance moment.

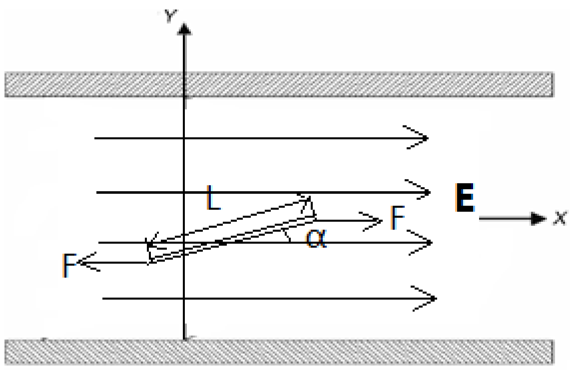

Figure 5. Illustration of CNTs in electrostatic field.

4. Conclusion

Airflow field and electric field play a crucial role in carding CNTs, along with high speed rotor spinning. The orientation, orderly and high mechanical properties of the long CNTs thread has been prepared. The technology of polymer monomer assisted that using the air induction principle make CNT oriented in the direction of the airflow in the pipe and increased the property of the bonding. Preparation of monofilament is about 120 μm, the quality density of line is 30 g/km, Two share twisting diameter of monofilament is 200 μm in diameter. Compared with monofilamentits, the mechanical strength is increased by 150% at 2.7 Gpa. A continuous supply of CNTs avoided the situation that the preparation of continuous thread cannot reel off in array due to a small array. Double twisting function as outer layers of the fiber turned into the inner layer formed inner pressure, which make the thread obtained friction along fiber radial obtain the friction and accumulate micromechanics strength of filaments, and further improve the mechanical strength of CNTs.

Acknowledgments

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