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13. ABSTRACT (Maximum 200 words) The goal of this program was to produce continuous strong CNT-based fibers. The production of continuous fibers was met and we have matched 2/3 of the strength of what has been previously reported with CNT-PAN fibers. We believe that with additional spinning process optimization we can increase the resultant fiber strength. All of the mechanical data shown (below) was generated from a non-optimized spinning process. This preliminary data generated from just the first fiber run shows promising results. The SWNT-PAN fibers obtained using our set up have a tensile strength of 238 MPa at 300% draw ratio. The produced fibers have very uniform diameter (see SEM images) so the mechanical properties are uniform across the length of the fiber. As a comparison to our initial data, Satish Kumar was able to produce SWNT-PAN fibers using 5wt% of SWNT with a tensile strength of 360 MPa at 460% draw ratio. We have started to optimize the spinning process and the other parameters to improve the overall mechanical properties of the fibers.				
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Multifunctional Next-Generation Carbon Nanotube Super Fibers

**Defense Advanced Research Projects Agency (DOD)
(Controlling DARPA Offices)**

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Executive Summary

The goal of this program was to produce continuous strong CNT-based fibers. The production of continuous fibers was met and we have matched 2/3 of the strength of what has been previously reported with CNT-PAN fibers. We believe that with additional spinning process optimization we can increase the resultant fiber strength. All of the mechanical data shown (below) was generated from a non-optimized spinning process. This preliminary data generated from just the first fiber run shows promising results. The SWNT-PAN fibers obtained using our set up have a tensile strength of 238 MPa at 300% draw ratio. The produced fibers have very uniform diameter (see SEM images above) so the mechanical properties are uniform across the length of the fiber. As a comparison to our initial data, Satish Kumar was able to produce SWNT-PAN fibers using 5 wt% of SWNT with a tensile strength of 360 MPa at 460% draw ratio. We have started to optimize the spinning process and the other parameters to improve the overall mechanical properties of the fibers.

Task 1: Select Materials

Task 1.1: Carbon nanotubes (SWNT) selection

Different SWNT sources were evaluated using Zyvex's qualification criteria which are:

- 1) Purity
- 2) Dispersion using Kentera technology
- 3) Properties (mechanical and electrical) in manufactured nanocomposites

After screening various SWNT sources, we used SWNTs from Swan Chemical (UK). These SWNT are very easy to disperse using our Kentera polymer, they have the highest level of purity and they provide good mechanical and electrical properties. These properties were determined in polycarbonate/SWNT composite.

Task 1.2: Host matrix selection

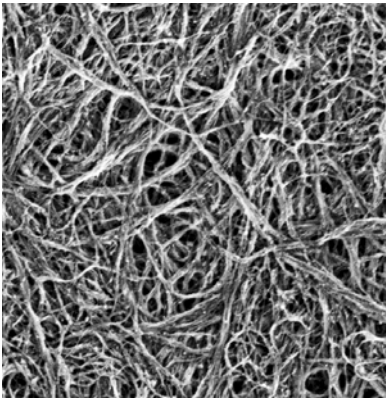
The identification of the host matrix is based on the structural properties, glass transition temperature, and chemical structure (side groups and solubilization in organic solvents). Our goal was to investigate various host polymers such as polyacrylonitrile (PAN), Parmax® and polyethylene (PE), however, due to time constraints we were forced to limit our work to one polymer. We chose to use polyacrylonitrile (PAN) as host the matrix polymer for two main reasons:

- 1) PAN is being used as the precursor for Carbon fibers. They have a larger market potential than other polymer fibers. Additionally, the strongest fiber available in the market is the carbon fibers, so by improving the PAN strength it will be further possible to enhance the strength of the carbon fibers. Carbon nanotubes possess high tensile strengths and high elastic moduli. The addition of nanotubes to the PAN fiber should further improve the overall elastic modulus and tensile strength. Importantly, the addition of the nanotubes will lead to multifunctional carbon fibers by improving the thermal and electrical properties of PAN precursor fibers as well.
- 2) PAN fibers are well studied polymer fibers, so high technical readiness levels should be achievable sooner. All the aspects in making the PAN and Carbon fibers are well established in industry and can be adapted. Choosing the PAN fibers also coincides with continuing a fiber program with DARPA through Hexcel Corporation.

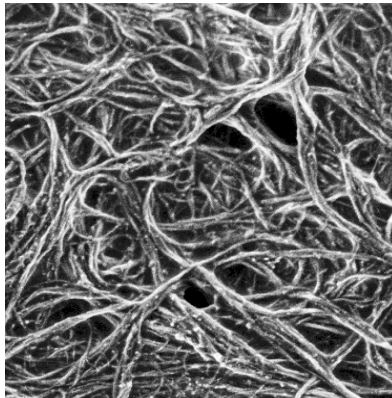
Task 2: Functionalization of SWNT

Carbon nanotubes with their graphite-like structure and high aspect ratio have great mechanical properties. They have the potential to increase the mechanical strength of a composite material when two conditions are met. The first condition is that the nanotubes are properly dispersed throughout the host matrix. The second condition is that the nanotubes interact properly with the matrix. Raw carbon nanotubes cannot meet these conditions. Zyvex's KenteraTM technology can and has been proven to overcome these obstacles. The Zyvex team has designed KenteraTM that allows good debundling/untangling/dispersion of CNTs in various host matrices. The quality of dispersion of CNTs (MWNT and SWNT) using designed Kentera for various host polymer matrices is shown in Figure 1.

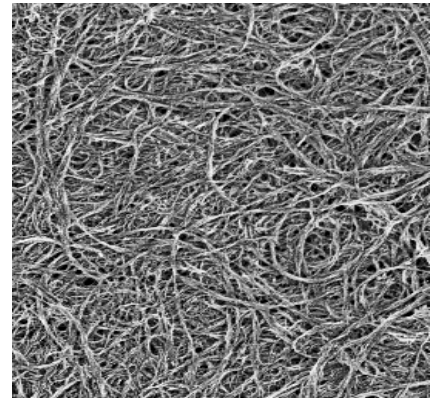
A: SWNT/Kentera/NMP



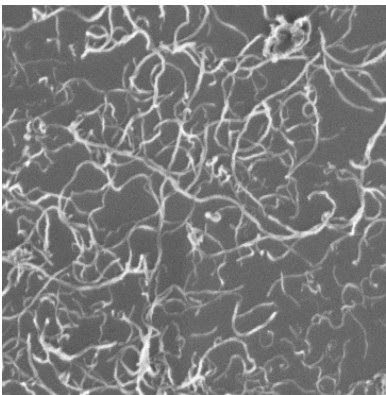
B: SWNT/Kentera/DMF



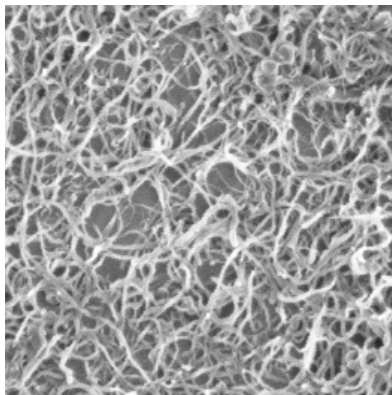
C: SWNT/Kentera/DMAc



D: MWNT/Kentera/NMP



E: MWNT/ Kentera/DMF



F: MWNT/Kentera/DMAc

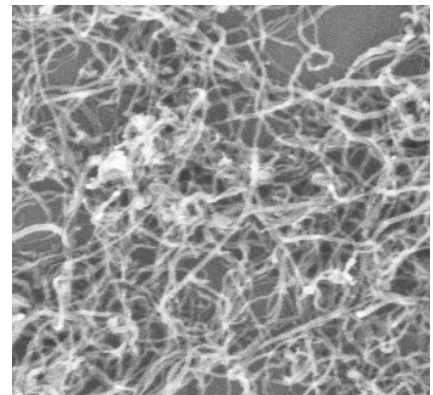


Figure 1: SEM images of SWNT/Kenteras and MWNT/Kenteras dispersion– scale bar 200 nm

We have also developed a robust and mature proprietary process to manufacture a NanoSolve powder additive (processed CNTs with Kentera technology). This powder additive is a key step in the development of next-generation carbon nanotube-based applications overcoming the

limitations of solvent-based processes and allowing introduction of greater quantities of CNTs in the host matrix. The concentration of CNTs in solvent is low, 1 wt% is the highest concentration one can achieve with good/stable dispersion whereas the powder additive can obtain concentrations up to 20%.

Our developed powder additive was introduced into various thermoplastic and thermoset resins and was also used to prepare dispersions in organic solvents and water without the use of ultra-sonication techniques. This solvent-free process allows the introduction of large quantities of Kentera™ processed (exfoliated/dispersed) carbon nanotubes in various matrices. We can introduce 20 wt% of processed MWNT in epoxy resin, 10-15 wt% in thermoplastic using melt process and more than 20 wt% in natural rubber and silicone. We were also able to establish using this process that a true multifunctional CNT-based composite can be developed. We produced interesting mechanical properties in polycarbonate (PC)-CNTs and polyurethane (PU)-CNTs and in proprietary polymer -CNTs composites. In the case of PC-CNTs, we were able to show by using only 3 wt% of MWNT about 100% improvement in tensile strength (~66MPa vs. ~32MPa), more than 200% improvement in Young's Modulus(~1.8GPa vs. 0.7GPa), and one order of magnitude improvement in Elongation to Break (105% vs. 10%). Regarding PU-CNTs, the tensile modulus and yield stress of 5%SWNT/PU are increased by 298% and 183% respectively compared to the neat PU.

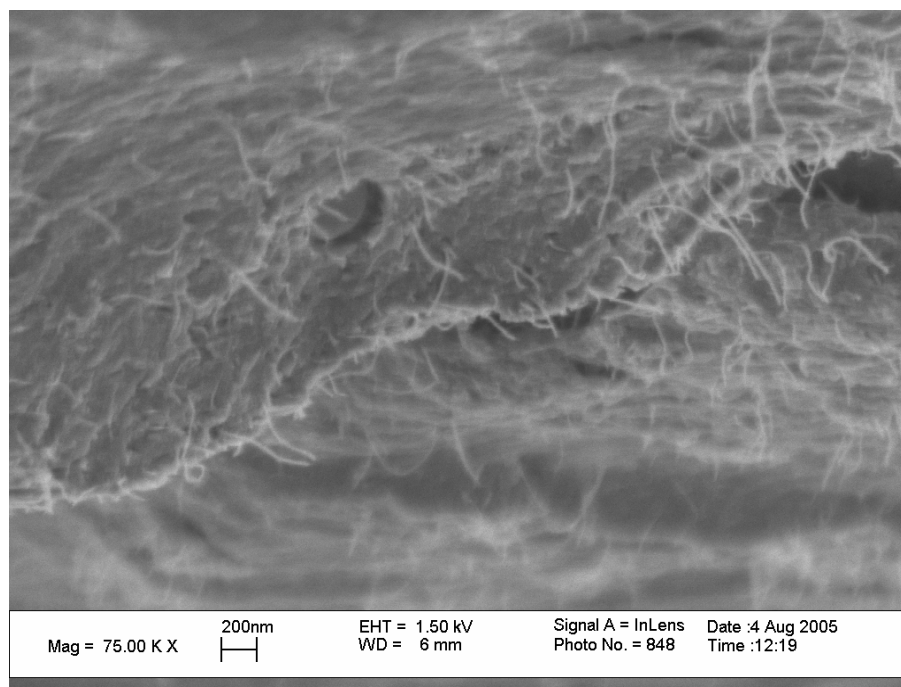


Figure 2A: SEM image of 1 wt% SWNT/Epoxy resin thin film (Scale bar: 200 nm)

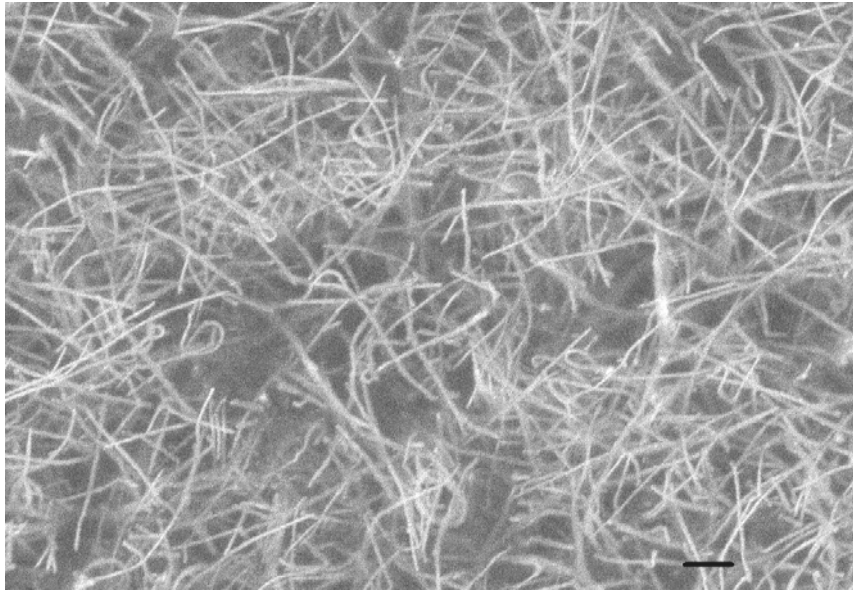


Figure 2B: SEM image of 5 wt% SWNT/Parmax® thin film (Scale bar: 400 nm)

We were also able to show significant improvement in the mechanical properties in Zen2-5 wt% SWNT composites. The tensile strength was improved from 187 MPa to 292 MPa and the Young's Modulus was improved from 3.9 GPa to 5.1 GPa. On the other hand, we were able to use this process to uniformly disperse CNTs in various epoxy resins. The quality and the uniformity of SWNT/Kentera dispersion in epoxy resin were characterized using SEM. Figure 2A and 2B show the dispersion of SWNT in epoxy resin and in Zen2 thin films.

Task 3: Develop Organic-Solvent-Based Fiber Spinning Process

PAN fibers can be spun using either solution spinning or melt spinning process. However, the solution spinning process is the best-suited technique and is more commonly used in industry. More over, a solution spinning process allows the flexibility to easily disperse the CNTs using our specific Kentera chemistries. The primary goal of this project was to prove that practically useful continuous CNT/PAN high strength fibers can be produced. The specific technical objective of this project is to improve the strength of the PAN/CNT fibers by the following methods:

1) Improve the alignment of the CNTs along the axis of the fiber

The CNTs are needed to be aligned in the fiber axis direction to transfer their useful properties to the fiber since the CNTs are stronger only in their axial directions.

2) Bonding the CNTs to the matrix polymer using the Kentera chemistries

Carbon nanotubes have the potential to increase the mechanical strength of a composite material when they are highly dispersed and when their side walls are specifically engineered to enhance their interface interaction with the host polymer. For the fibers to be strong the

matrix polymer should be able to transfer the load applied on it to the CNTs. This can be only be done by chemically bonding the CNTs to the fiber matrix. The flexibility of the chemistry in our Kentera platform allows us to modify the side chains and the backbone to enhance the interaction of CNTs to the polymer. In the case of this work, the design of Kentera should take in account the solvent used and the host polymer used in the process. For the solvent, the side chains have to be engineered to stabilize the dispersion/exfoliation of CNTs in the liquid medium (in this case dimethylacetamide, DMAc). For the host polymer, in this case PAN, which has nitrile groups, the design should either contain nitrile groups that will be used to chemically cross-link CNTs/Kentera to PAN or functional groups that might react with PAN during the coagulation/spinning process. In figure 3 we show two different structures of Kentera designed for CNTs-PAN fiber.

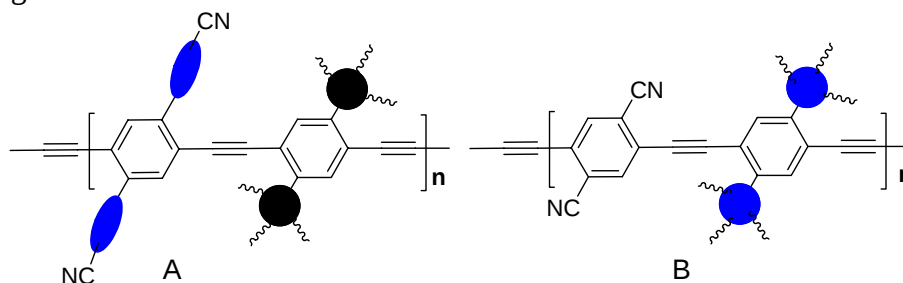


Figure 3: Two representative structures of Kentera designed for CNTs-PAN fiber

Improve the alignment of the CNTs along the axis of the fiber

Carbon nanotubes alignment can be achieved by several methods, including:

1. Electric field
2. Magnetic field
3. Flow field (Rheology – Shear and Elongational flows)

Since fiber spinning depends on the rheology of the polymer, we designed our spinning process to align the CNTs using elongational flow fields.

The experimental lab scale spinning set-up was designed based on the Auburn University's (Textile Engineering Dept.) fiber spinning set-up. The CNT alignment can be done at 3 stages using this approach:

1. *In the spinning dope during the flow through the spinneret:* Elongational flow fields will be produced in our specially designed semi-hyperbolic spinneret. The spinneret helps to create a near zero-shear flow orientation of the CNTs along the flow direction (fiber axial direction). The elongational flow field also helps in the breaking of the CNT aggregates. The elongational flow fields apply a stretching force on the CNTs along the flow direction leading to CNT alignment and improved dispersion. This elongational flow field has been achieved by special spinneret designs.
2. *In the Coagulation Baths:* The fibers will be stretched using draw rollers placed in the coagulation bath. This stretching helps to align the CNTs along the axis.

3. *At the take-up rollers:* By varying the speed of the take-up rollers the fibers can be further stretched aligning the CNTs.

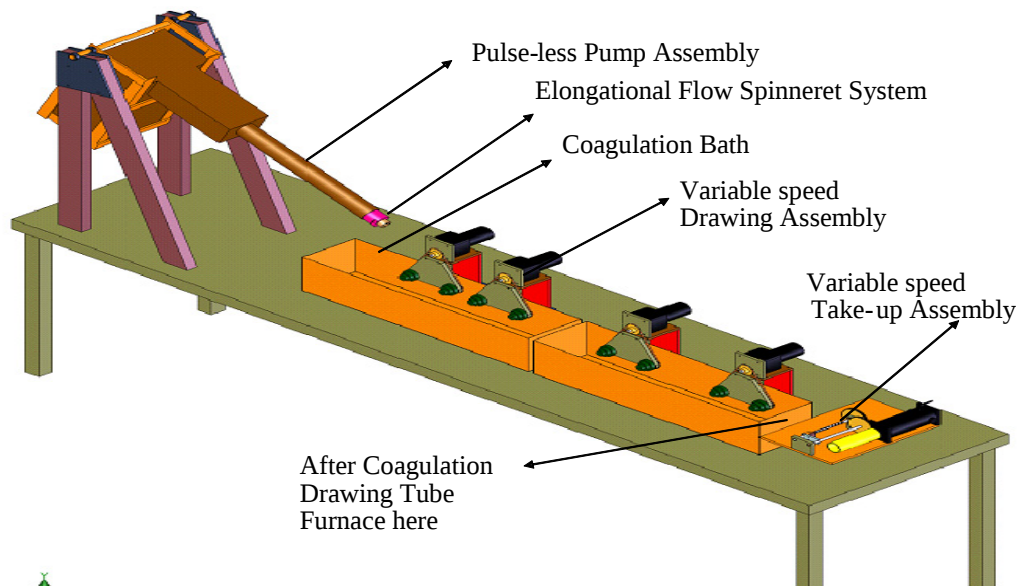


Figure 4: The Zyvex Lab-scale Solution Spinning Set-up (Based on Auburn University's design)

The spinning process:

The polymer is dissolved in a solvent and the dispersed CNTs are added to this polymer solution called the 'Spinning Dope'. The pulse-less syringe pump loaded with the spinning dope pushes the material through the elongational flow spinneret system with an exit diameter of 0.3 mm and a length of 20 mm (please refer to the spinning set-up shown above). As the dope exits the spinneret hole it enters the first coagulation bath with a non-solvent (this process can be a 'Dry-wet spinning' – the spinneret not immersed in the non-solvent placed at a distance from the bath (or) a 'Complete-wet spinning' process – the spinneret is in this case completely placed inside the non-solvent bath). The non-solvent precipitates the polymer into a thin fiber by removing the solvent from the exiting spinning dope. The first bath concentration is controlled in such a manner only to precipitate the outer skin of the fiber (this gives enough strength to the fiber to be handled in the further processes). The fiber is then collected by a set of take up rollers in the first bath and then moved to the second coagulation bath. In the second bath the remaining solvent is removed and the fiber is heated to above its glass transition temperature. Then the fibers are passed over the drawing roller assembly to further stretch them. The fibers then are wound on to a traversing take-up roller which has variable speeds to apply a stretch to the fiber coming out of the second bath.

The dynamics of solvent removal at the first bath, the process parameters (volume through-put by the pump, stretching ratios at the drawing rollers, the take-up velocity and the concentrations of the materials (polymer/CNT/solvent, non-solvent) affect the outcome of the final fiber.

Lab-Scale Fiber Spinning Set-up:

The following paragraphs explain the Zyvex flexible lab-scale set-up for spinning the CNT fibers:

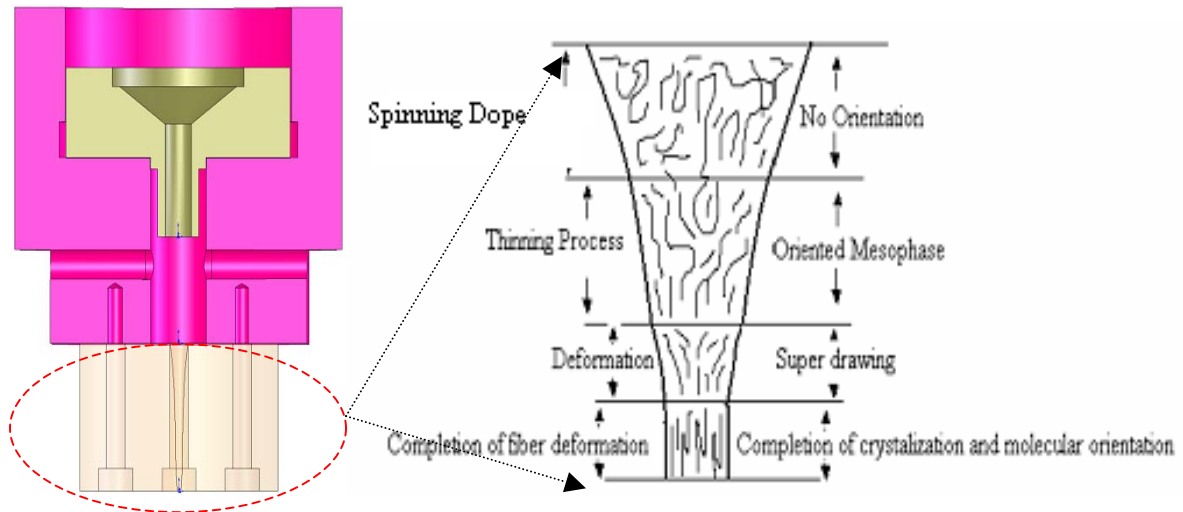
Spinneret Assembly:

Figure 5: The Spinneret Assembly

Fiber Drawing Assembly:

The drawing assembly is shown in the picture below. The assembly uses the differential circumferential speeds to stretch the fiber. The rollers diameters are 1.0 in, 1.5 in and 2.0 in. The diameter of the rollers can be easily changed to achieve even higher stretch ratios. The speed of the rollers can also be varied from 0 to 417 rpm. For the current experiment only one of these rollers will be placed in the second bath.

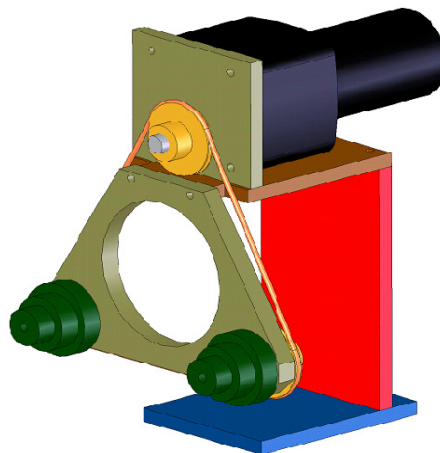


Figure 6: The Spinneret Assembly

Fiber Take-up Assembly:

The take-up assembly has been designed with a self reversing traverse screw to wind the fiber coming out the second coagulation bath very smoothly. The assembly has also a variable speed control to wind the filaments at different speeds into the take-up bobbin. The speed of the motor ranges from 0 to 1800 rpm allowing the flexibility of very high stretch ratios.

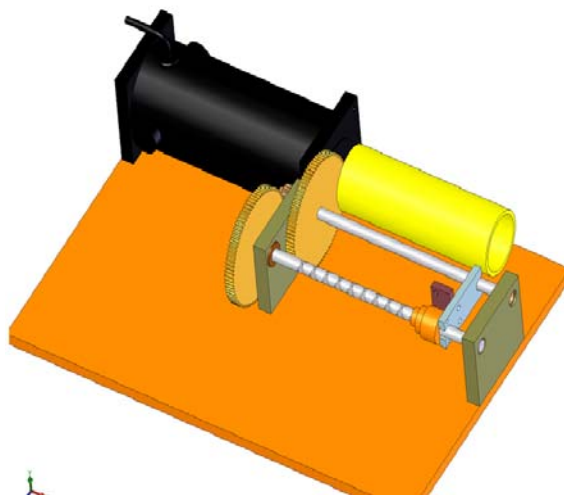


Figure 7: The Take-up Assembly

Produce Fiber Material for Characterization and Testing

Most of the PAN based carbon fibers are made from co-polymers of PAN, since PAN homopolymer is highly polar in nature (due to the Nitrile groups) preventing the orientation of the chains which gives the strength to the fibers. To overcome this problem usually PAN co-polymers are used to make the precursor fibers. We used a Poly (acrylonitrile–Co–Methacrylate) co-polymer to spin the CNT fibers. This particular polymer had a molecular weight of 100,000. Dimethylacetamide (DMAc) was used as solvent. The acrylonitrile concentration in the polymer was 94% and the remaining 6% constituted of methacrylate.

Experimental Procedure:

Dispersion: 4 wt% of SWNT were dispersed in DMAc. During the dispersion process the DMAc/CNT flask was cooled using ice bath to prevent heating of the mixture. Dispersed CNTs were then transferred to another flask and heated at 170 °C to evaporate the excess of solvent (the final wt% of DMAc/CNT mixture was 85%). To this mixture 15 wt% of P(AN/MA) was added and the solution mixed for half an hour to form a homogeneous mixture. The spinning dope was then transferred to the pump for spinning.

Spinning: The volumetric flow rate of the pump was kept at 0.25ml/minute to produce an even jet. The polymer coming out of the spinneret was coagulated in the first bath containing 55 wt% of water in DMAc at approximately 10 °C. The filament then passes into the second bath which is at approximately 90 °C. At the second bath since the temperature is higher than the glass transition temperature of the fiber, it is soft and pliable. The fiber is then wound into the

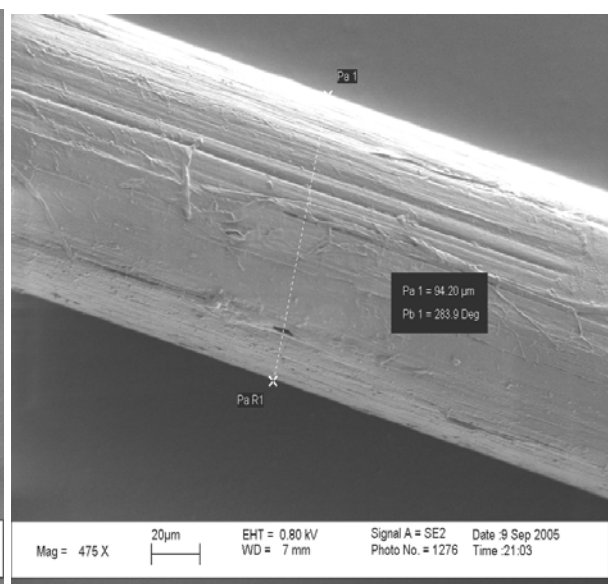
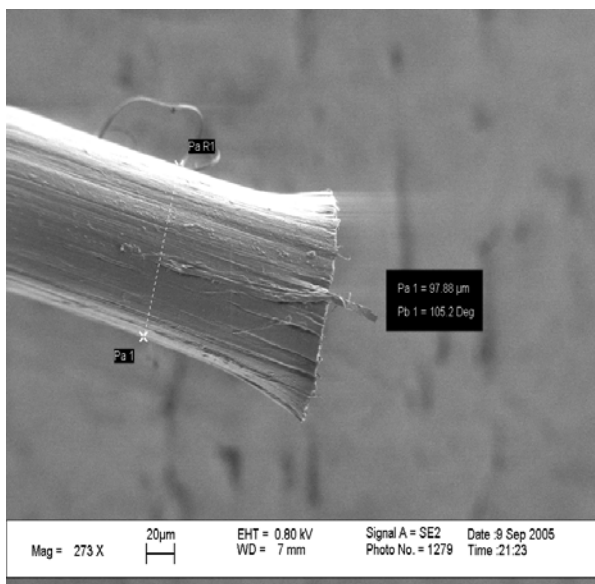
take-up roller at a constant speed; the take-up roller also helps to stretch the fibers in the second bath before exiting.

The wound filaments are then collected and immersed in a water bath over night to remove the traces of the solvent present. After this the filaments were dried under vacuum at 35 °C for 2 hrs.



Figure 8: The produced continuous CNT fibers wound on to the take-up bobbin

Due to the limitations with the spinning set-up we were not able to stretch the filaments during spinning process itself. But we were able to stretch them post spinning to start the initial characterization studies. Samples were taken out of the filaments to run the initial raw characterization studies reported below.



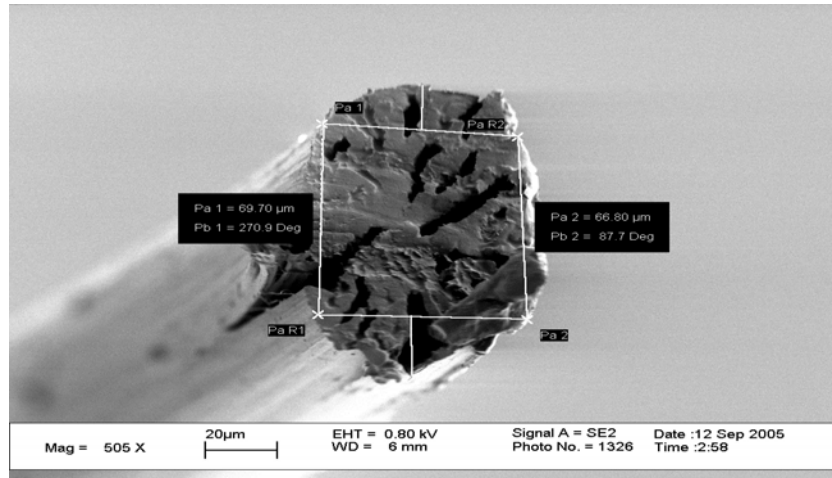


Figure 9: SEM images of the produced fibers showing the axial and cross sections

The fibers show very good skin layer characterized by very smooth fibrils, but the core of the fiber contains voids. Since these fibers were produced in initial runs, it is expected that the voids can be eliminated as the spinning process is optimized.

Mechanical Testing:

Tensile testing was performed using a 5500 series Instron Universal Tensile testing machine. The gauge length of the fiber was 25mm and the test was performed at 10 mm/minute cross head speed. To minimize the problems associated with gripping the fibers the Instron's special fiber grips were used. The load cell had a capacity of 2.5 Newton's. The cross sectional areas of the fibers were measure inside the SEM (the produced fibers were elliptical in cross section).

Stretching: The filaments were stretched to two different ratios: 0% (as produced), 100% and 300%. A 30 mm fiber was cut and stretched in an oil bath at 140 °C to reach the above mentioned stretch ratios. The oil bath was used rather than a water bath to produce an isothermal condition during stretching and to offer some resistance to the fibers while stretching which leads to better properties and higher stretch ratios.

Draw Ratio (%)	Cross-section Area of Fiber (mm ²)	Tensile Strength (Mpa)	Modulus (Mpa)	Toughness (Mpa)
0	0.02265	35.02	1477.30	1.92
100	0.00753	156.17	3708.70	22.98
300	0.00428	238.43	4937.90	24.30

Table 1: Raw Mechanical data of 4 wt% SWNT-PAN Fibers

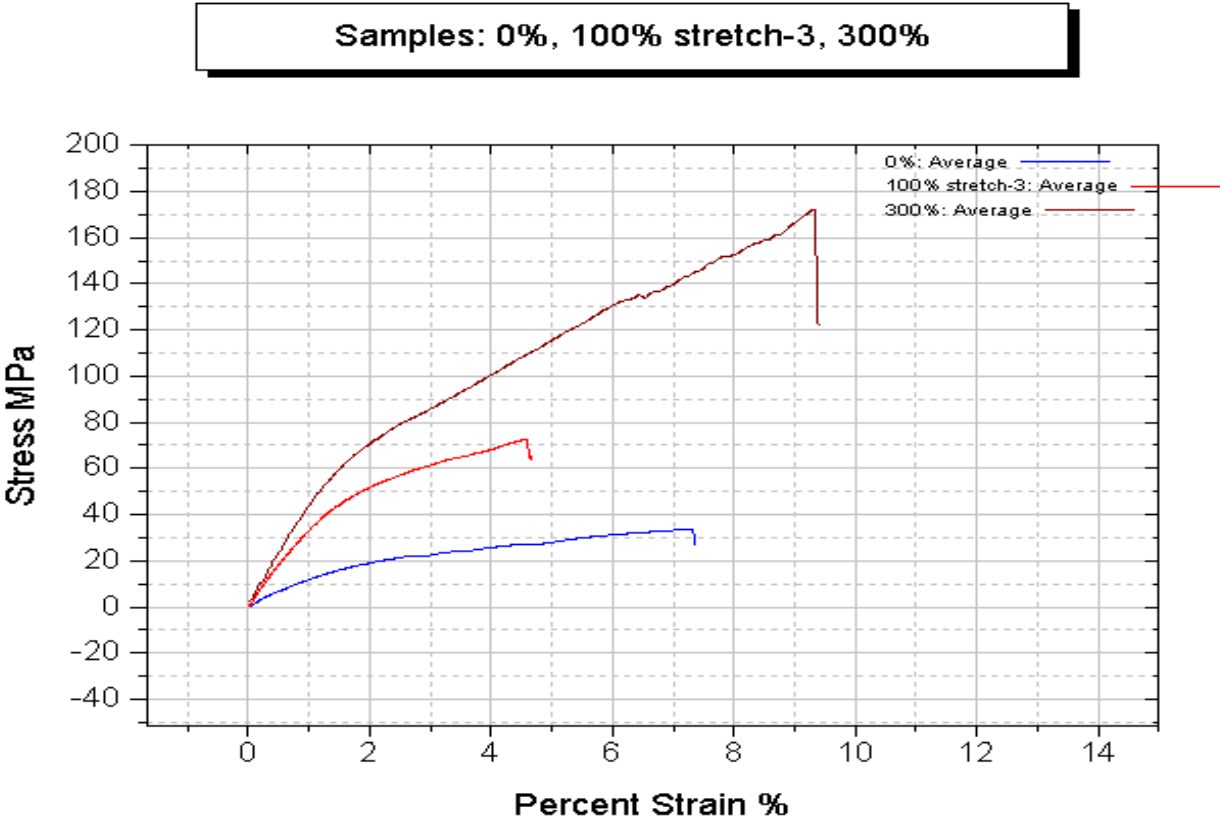


Figure 10: Initial Stress/Strain graph of raw SWNT-PAN Fibers