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Correlating Structural Control for Property Enhancement in Nano-Composite Fibers

Dr. Marilyn L. Minus

Professor, Department of Mechanical and Industrial Engineering, Northeastern University, Boston, MA, USA

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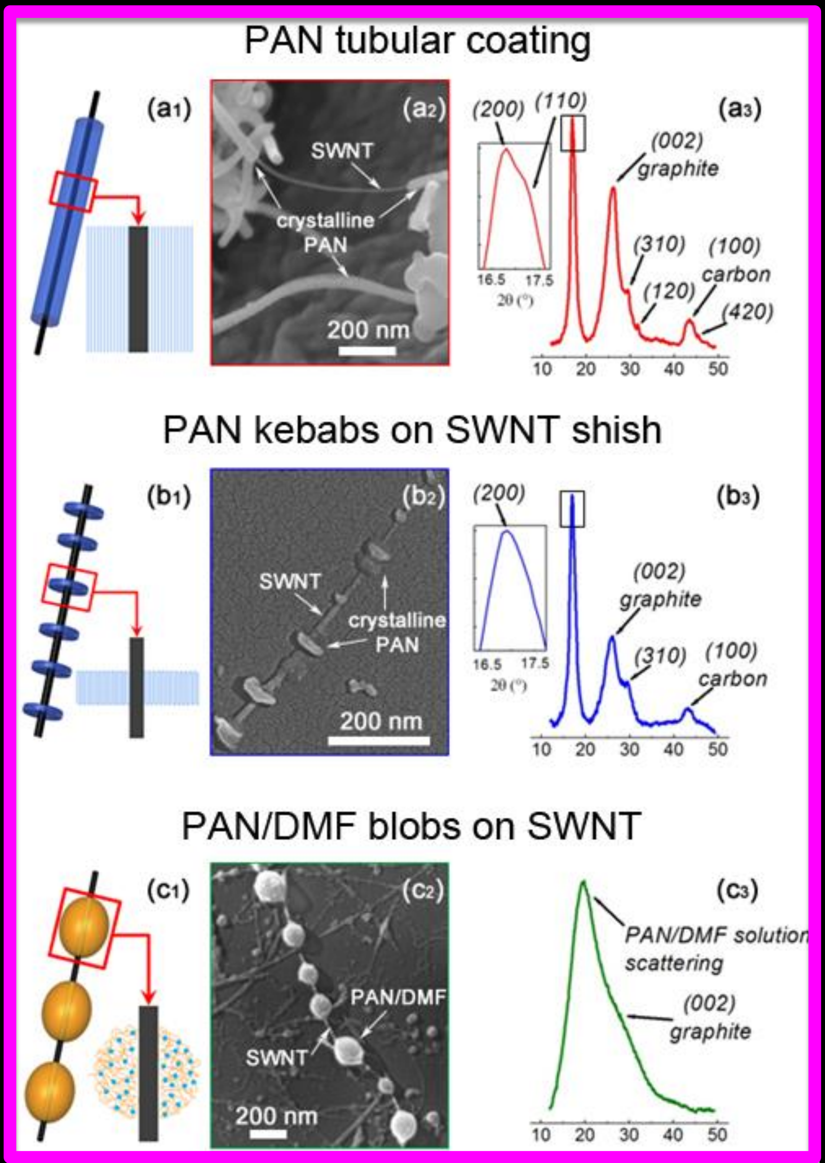
Formation of Interphase Structures

Control of Interphase Structure Formation



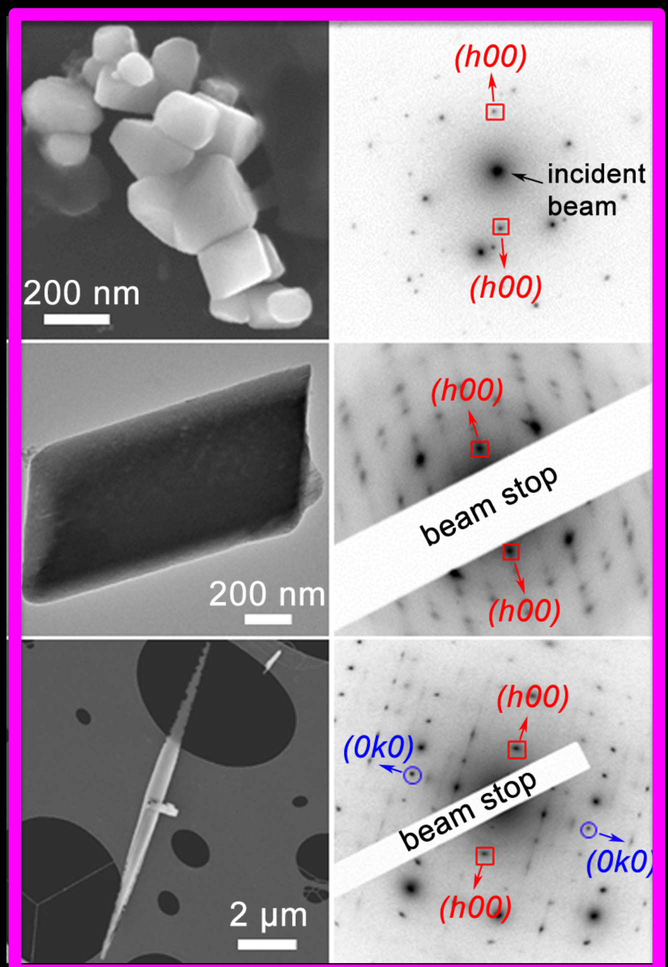
In this study polymer crystallization is combined with dispersion of the nanotubes in order to promote the formation of interfacial polymer structures. The nanotubes act as a nucleating polymer to form these interphase structures

(a) Semi-dilute PAN/SWNT solutions slow cooled under shear → ***extended-chain crystals***
* major PAN peak exhibits a distinct shoulder due to the existence of a *(200)/(110)* doublet → high crystalline perfection

(b) Slow cooled dilute PAN/SWNT solutions in quiescent state → ***hybrid PAN-SWNT shish-kebab*** (*first observation for PAN*)

(c) Quiescent dilute PAN/SWNT solutions subjected to quenching → ***PAN/DMF "blobs"*** (*due to the presence of solvent*)

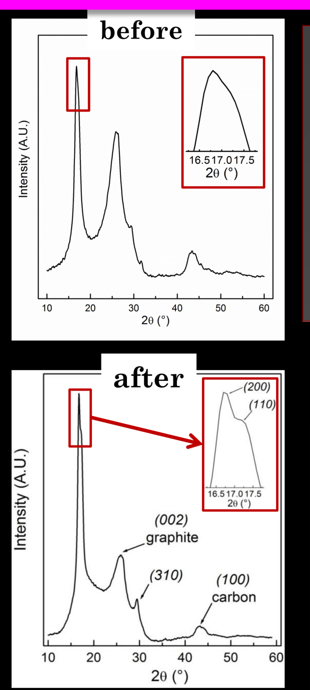
Effect of Temperature (*T*) on PAN Crystallization



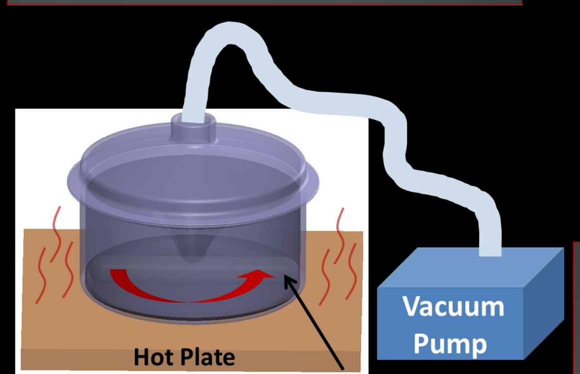
Polyhedral Single Crystals
- 90 °C → 60 °C, isothermal @ 60 °C
- Growth along multiple directions
- Small
- Not sensitive to electron beam

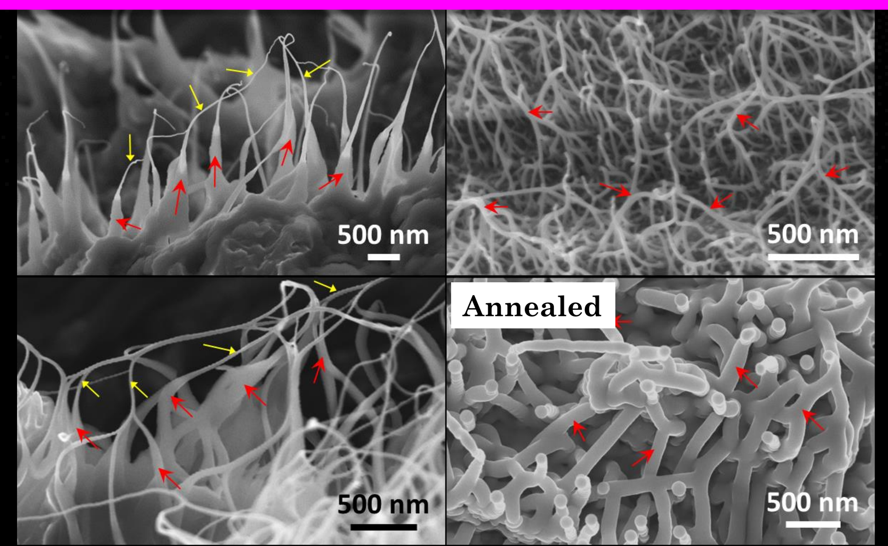
Parallelogram Single Crystals
- 100 °C → 70 °C, isothermal @ 70 °C
- Preferential growth along *a-* and *b-axes*
- Medium
- Sensitive to electron beam

Elongated Rhombus Single Crystals
- 120 °C → 90 °C, isothermal @ 90 °C
- 110 °C → 80 °C, isothermal @ 80 °C
- Extremely fast growth along *a-axis*
- Large
- Highly sensitive to electron beam



Studying the specific crystallization conditions (i.e., single crystal growth) of the polymer allows for even more precise tailoring of the conditions to be used for the formation of interphase structures



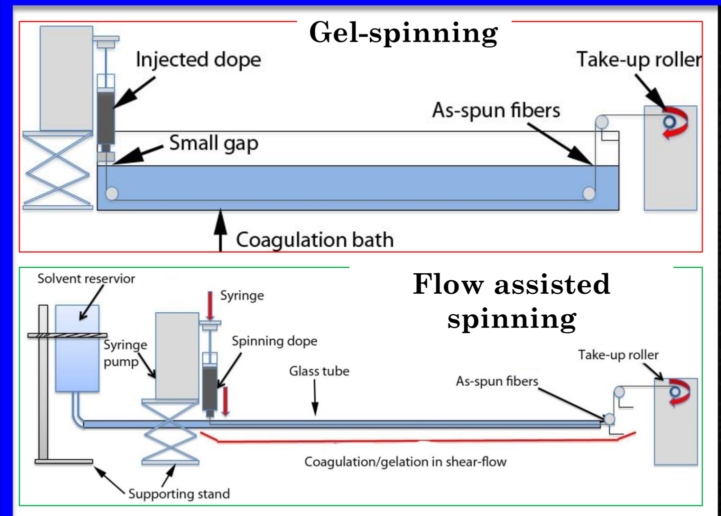


These refined conditions show that an even polymer coating can be achieved on the nanotubes. Annealing procedure help to increase the thickness of the interphase coating

Abstract

Understanding the capabilities of polymeric materials to form interfacial structures around carbon nanotube and other nano-carbon materials is instrumental toward controlling composite structure-property correlations. This work outlines developments regarding new processing routes for dispersing nano-carbons in dilute polymer solutions. This dispersion process involved steps of sonication, shearing, and crystallization. The specific combination of these processes results in the formation of polymer interfacial growth (i.e., interphase structures) on the nano-carbon surfaces. The interphase formed consists of either extended-chain or folded-chain polymer crystals depending on the processing route used. This processing approach for the dispersion of nano-carbons and subsequent formation of the polymer interphase is further implemented into fiber processing procedures. Polymer materials used in these composite fiber studies include polyacrylonitrile (PAN), polyvinyl alcohol (PVA), polyethylene (PE), as well as collagen proteins. The nano-carbons include carbon nanotubes (CNT) and carbon nano-chips (CNC) (i.e., platelet morphology). In addition, boron nitride platelets were also studied. Several process modifications were made to the fiber spinning procedure to ensure the formation of interphase structures within all the composite fibers formed. It was found that polymer crystal growth and entropy changes in the system (e.g., biological materials) should be well-controlled to form specific interphase morphology. For this reason, such studies were also performed for all the polymeric materials used in the presence of the nano-materials. In general these composite fiber studies showed that the inclusion of interphase structures in the composite fiber led to dramatic increases in the mechanical properties. Beyond mechanical enhancement, the composite fiber morphology was also examined to understand the fundamental links between the processing route use and the resultant structure-property relationship. A general overview regarding the results of these studies will be outlined and discussed in this talk.

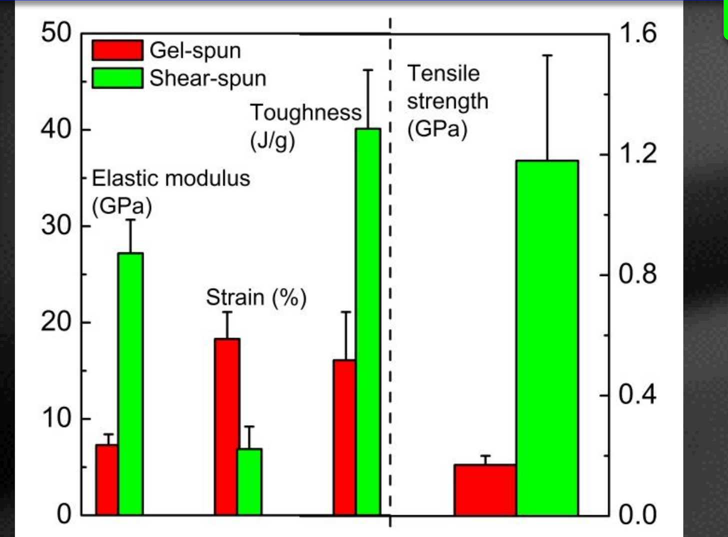
Processing Composites with Interphase Structures

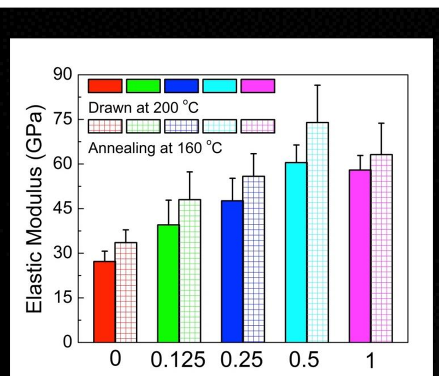


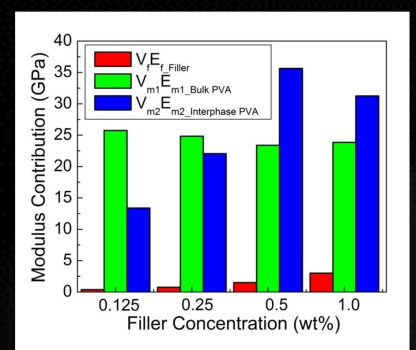
In order to ensure that the formation of polymer-nanotube interphase structure is translated to the composite fiber we investigate a modified spinning approach

Elongational flow has been added to a traditional gel-spinning approach in order to promote polymer alignment in the presence of the nanotubes. Temperature changes are introduced between the spinning dope and coagulation bath

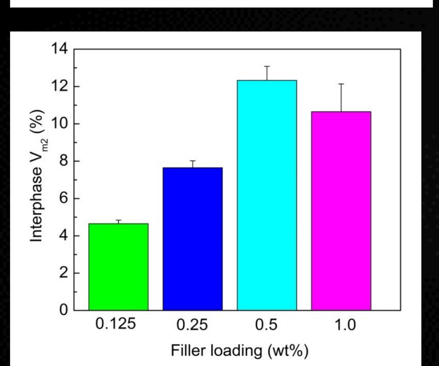
Initial characterization shows that the flow modification leads to much improved fiber performance →







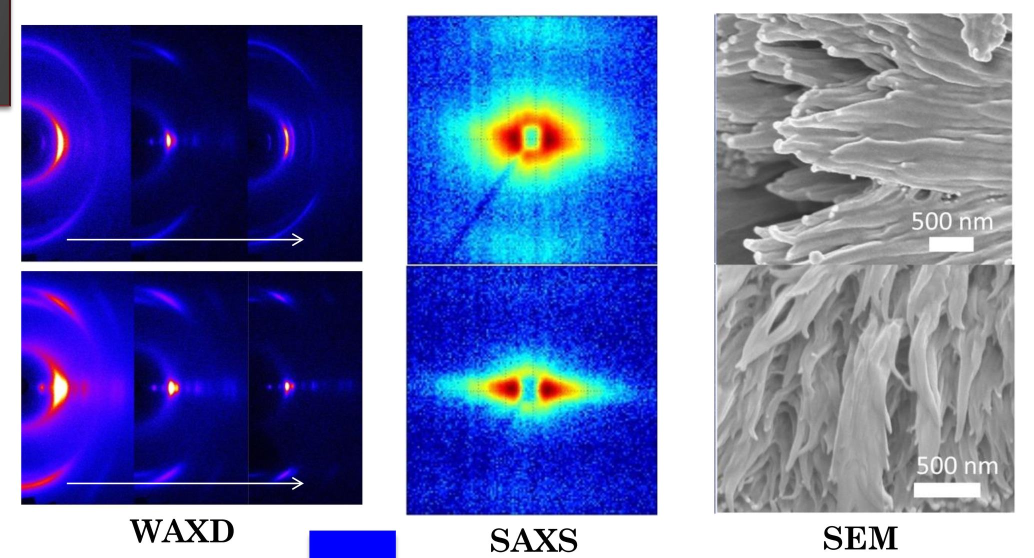
X-ray diffraction and scattering are used to analyze the structural characteristic of the composite fibers

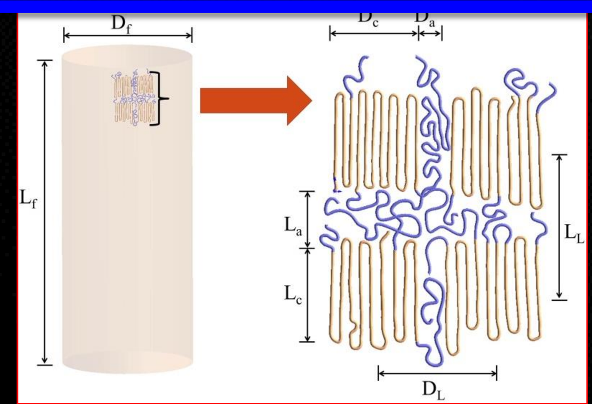


Polyvinyl alcohol (PVA)/carbon nano-chip fibers were spun using the modified spinning approach

Composite fibers show the presence of interphase structure, and this contributes greatly to the mechanical performance

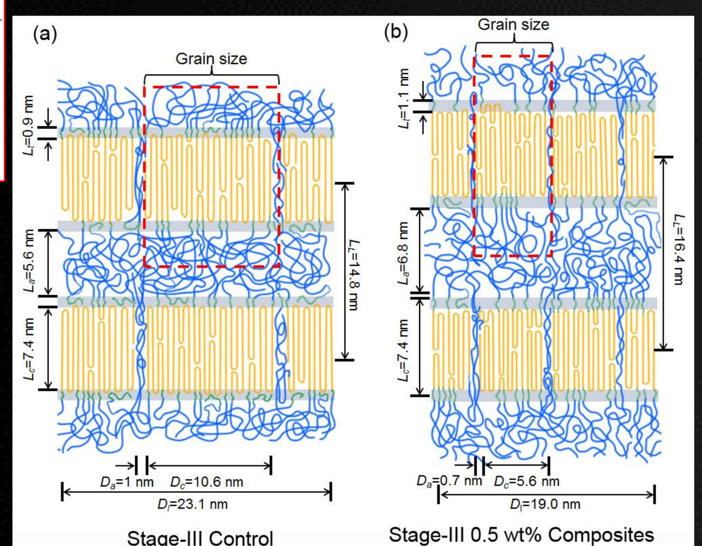
Structural and Morphological Improvement from Control PVA Fiber to PVA/CNC Composite Fiber





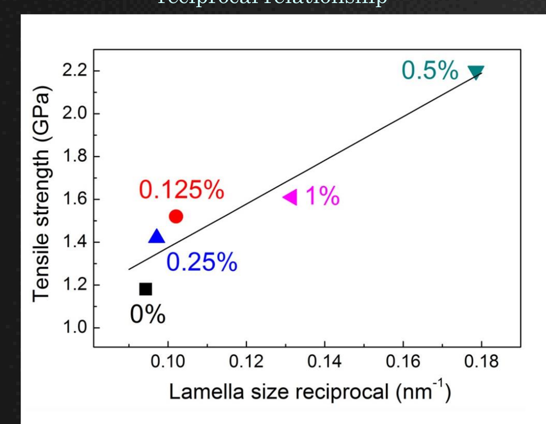
lamellae stacks showing the crystalline, and amorphous regions

a single fibril consisting of lamellae stacks



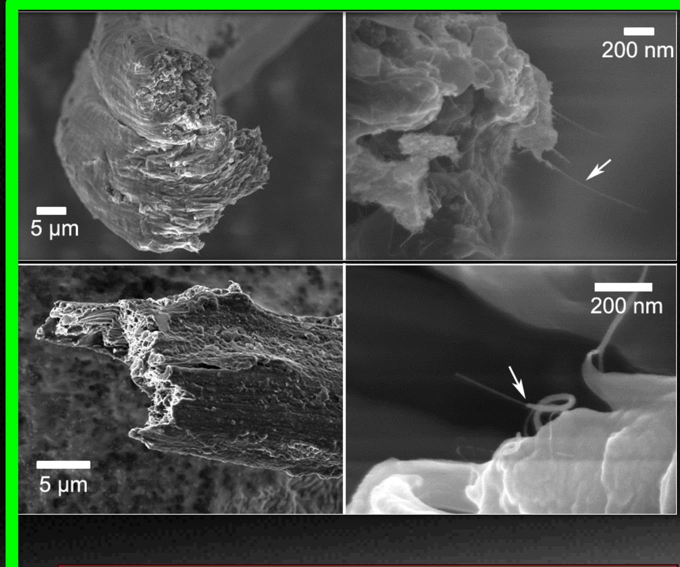
Schematic models showing the lamellae microstructure for the fully drawn (Stage-III) fibers

tensile strength *vs.* lamella size reciprocal relationship



Scattering analysis is shows that the composite exhibits a smaller (i.e., finer) grain size. Increasing strength is associated with higher grains per fibrils. This is analogous to metallic materials

Understanding Property Effects of Interphase Structures

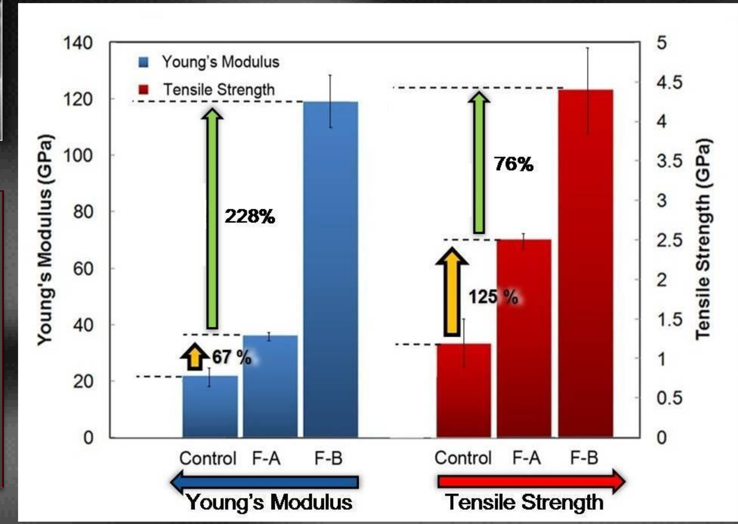


Templated interfacial crystallization of PVA in the vicinity of SWNT is controlled by tailoring the degree of undercooling (i.e., crystal growth) of PVA during dope preparation

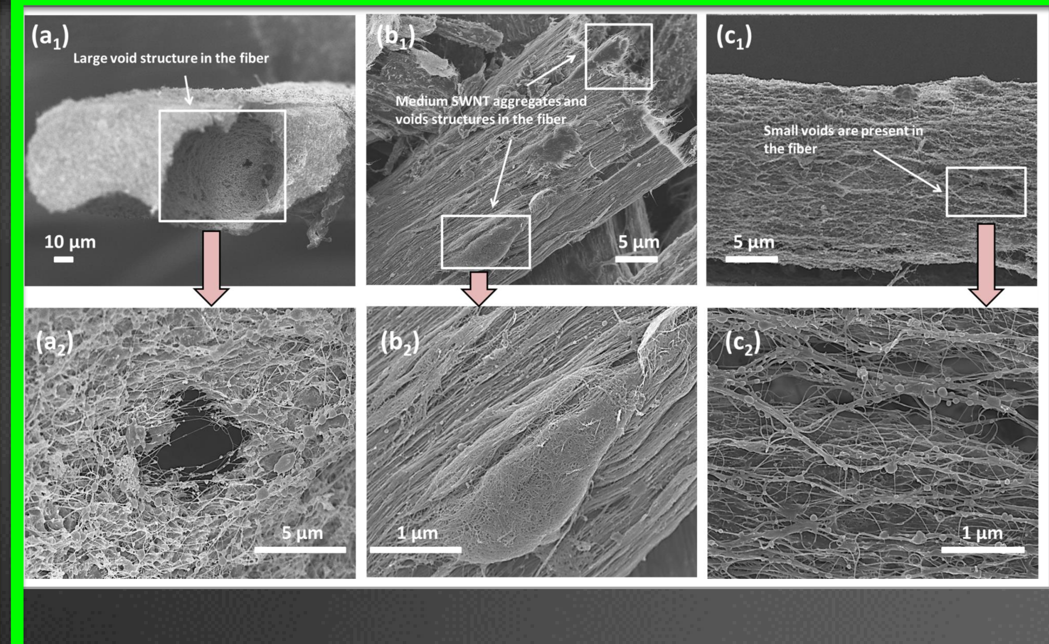
The PVA interfacial region around SWNT has denser crystalline chain-packing

The resultant composite fibers (F-A and F-B) show excellent tensile strength, modulus, and toughness properties

The fibers with interphase structure present (F-B) show the most significant increase



Nanotube Dispersion and Polymer Conformational Confinement



Fibers are spun with differing degrees of dispersion quality to study this effect of interfacial polymer-CNT interaction

(a) F-1 fibers have large voids due to phase separation between polymer and nanotubes

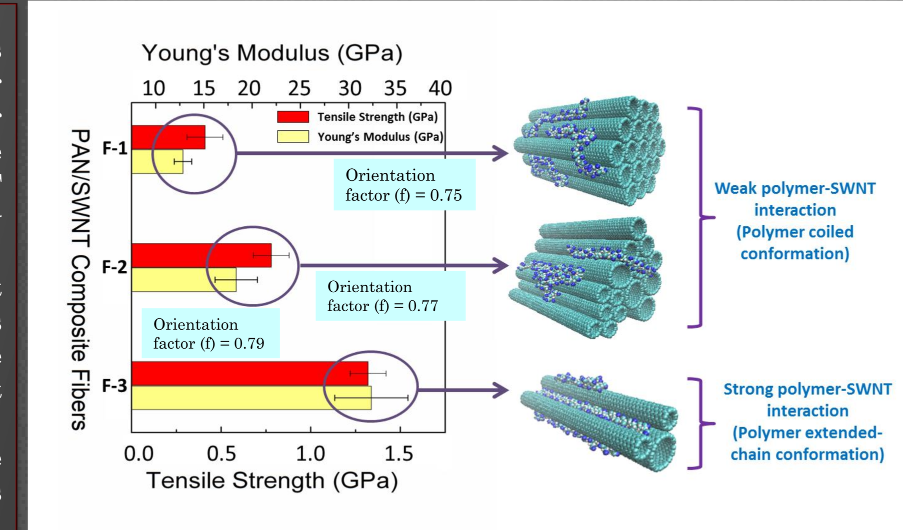
(b) F-2 fibers have large nanotube agglomerations and entanglements

(c) F-3 fiber have most even dispersion quality

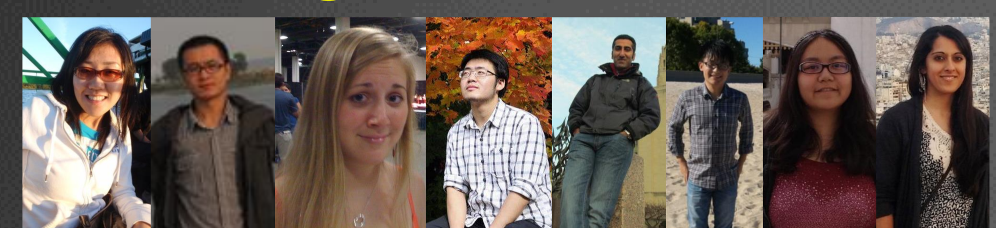
Confinement of the polymer chains between SWNT bundles or individual tubes (i.e., molecular crowding) resulted in large increases in the PAN–SWNT interaction energy

Computational studies show that the polymer chain alignment is most influenced when the dispersion quality is highest

Interfacial structures also influence the mechanical properties



Acknowledgements



MINUS Lab Graduate Students

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