Mechanical properties of carbon nanotube webs

ANAM initiative

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EPSRC
Engineering and Physical Sciences Research Council
University of Ulster
University of Cambridge

The ANAM Initiative.

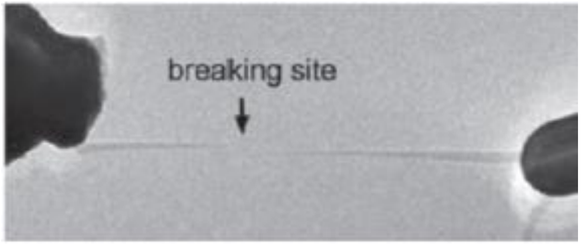
Broad collaboration between **Cambridge Engineering** and **Materials Science** Departments, and **Ulster University**, and several **industrial partners**.

Focus on **direct-spun CNT materials**, made by the ***Windle Process***

Carbon Nanotubes: Intrinsic Properties

Individual Tubes: MWNT wall structural properties

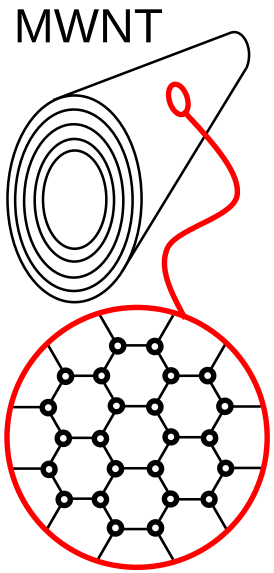
E = **1 TPa**
$\sigma_f >$ **100 GPa**
$\rho \sim$ **2200 kg/cm^3**



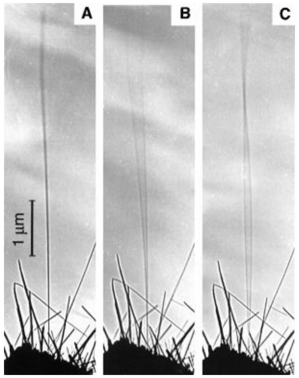
Wang *et al*, (2010)

Good **understanding** of mechanics with **strong theoretical validation**

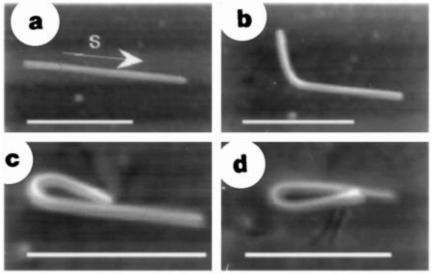
Yu *et al* (2000)
Wang *et al* (2010)
Zhang *et al* (2014)



C=C double bond
Hexagonal Lattice



(Poncharal *et al*, 1999)
Determination of modulus by electrostatic vibrations

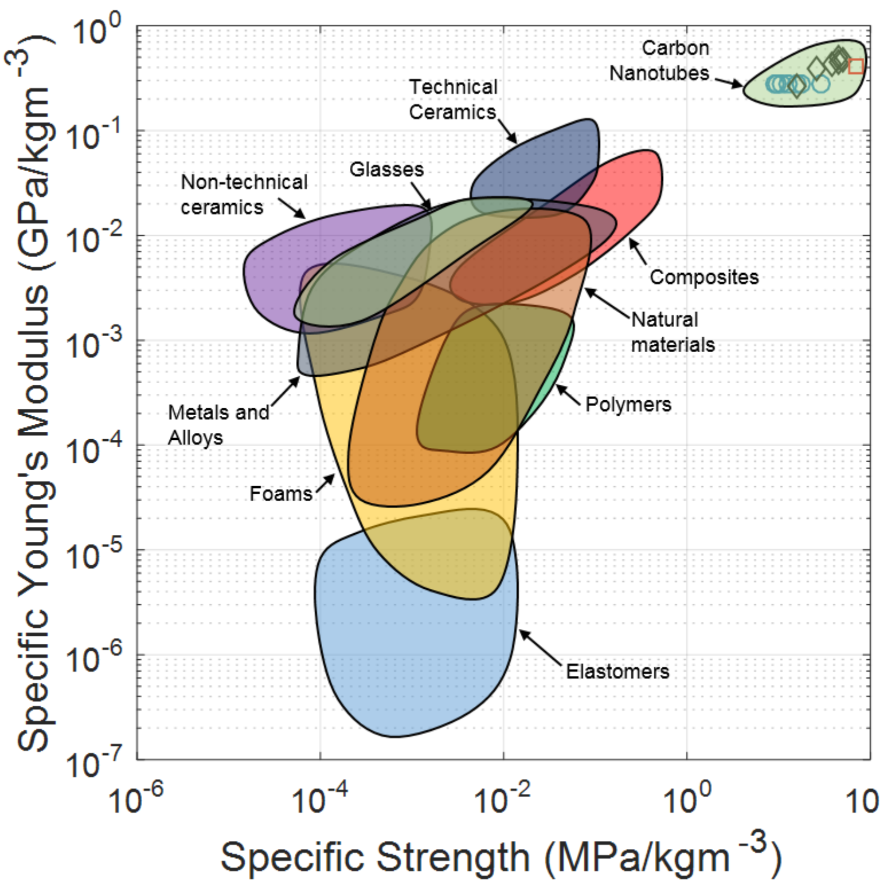


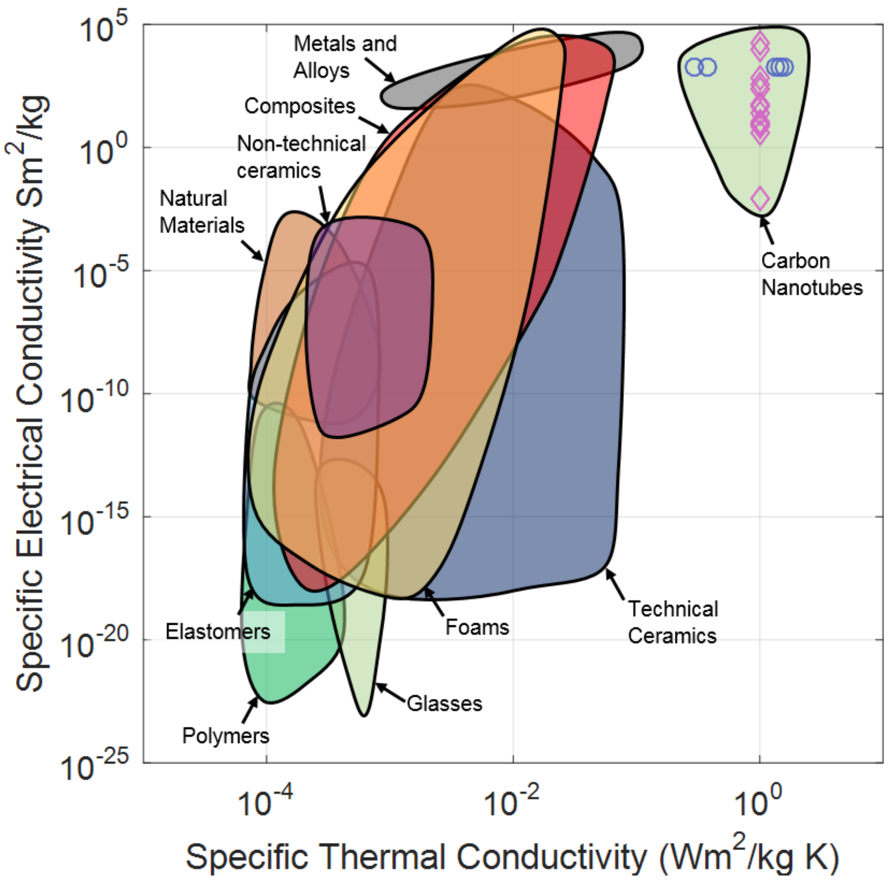
(Falvo *et al*, 1997)
Large elastic deformation

Electrical Conductivity: **2 x 10^5 s/cm**
Thermal Conductivity: **3500 W/mK**

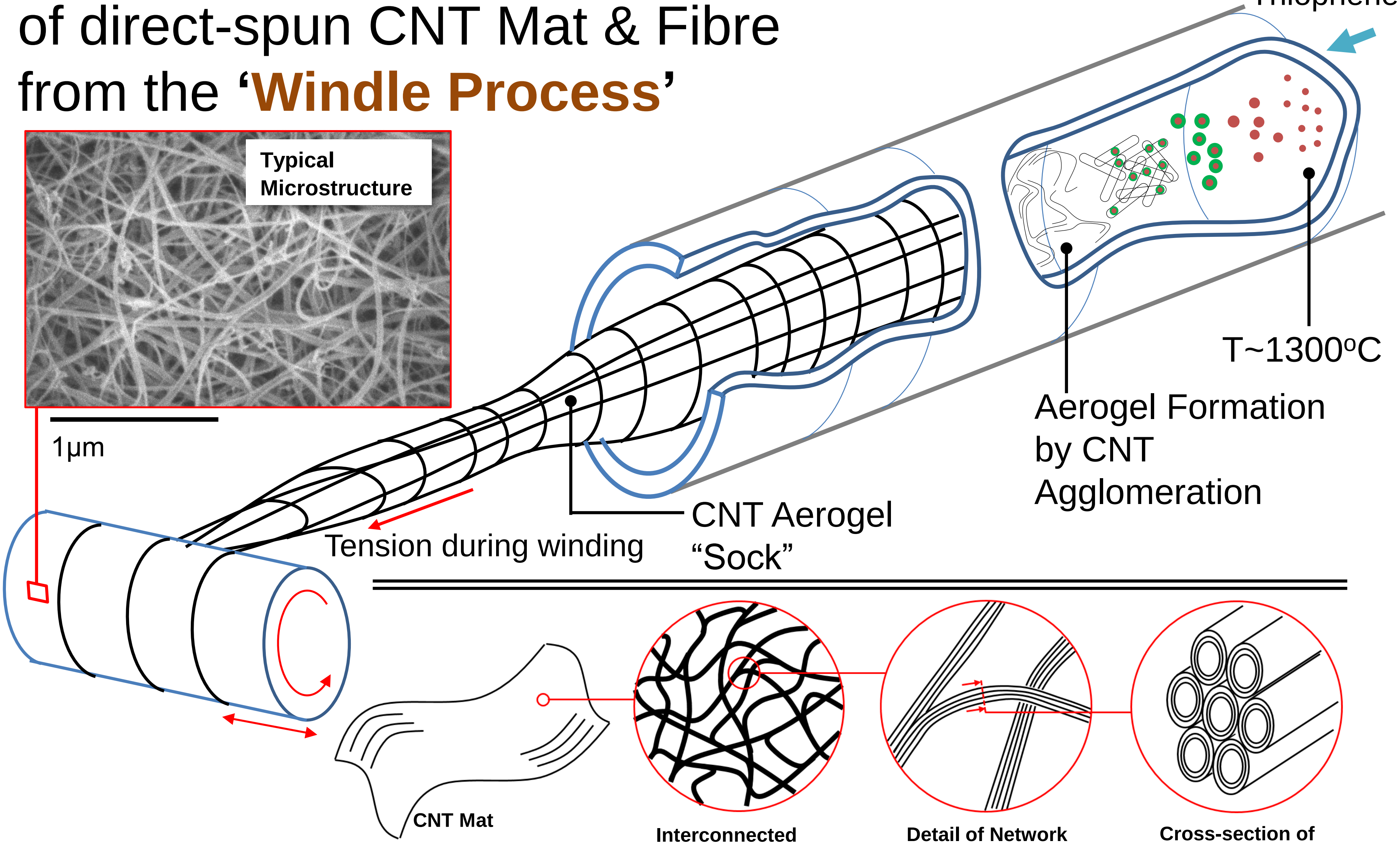
- Can we realise the **properties of CNTs** in **Direct-spun Mats** and other **Bulk CNT Materials**?
- If not, **why**?

Carbon Nanotubes: Intrinsic Properties





Production and **Microstructure** of direct-spun CNT Mat & Fibre from the ‘**Windle Process**’



Typical Microstructure

1µm

Methane, Ferrocene, Thiophene

T~1300ºC

Aerogel Formation by CNT Agglomeration

CNT Aerogel “Sock”

Tension during winding

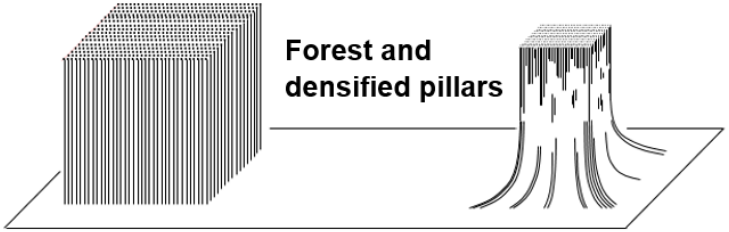
CNT Mat

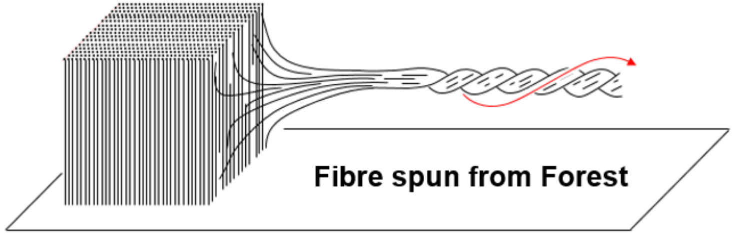
Interconnected Bundle Network

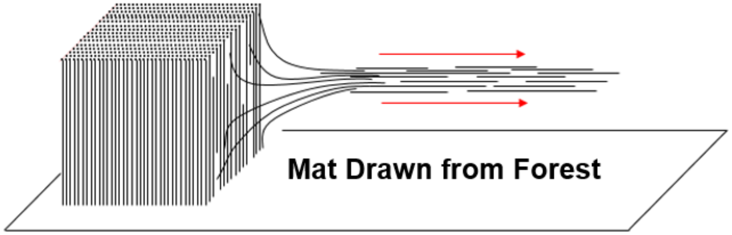
Detail of Network Junctions: Bundles branch and Cross

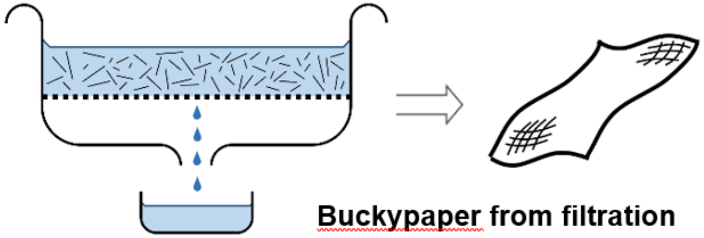
Cross-section of Bundle Microstructure

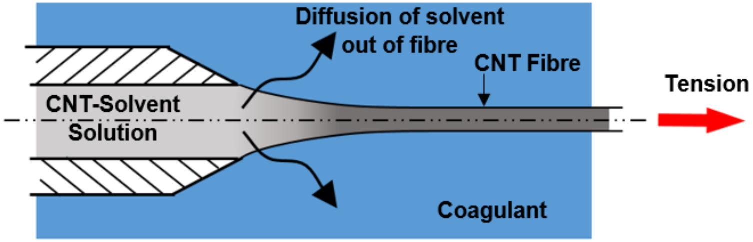
Bulk CNT Materials: *methods of manufacture*


Forest and densified pillars


Fibre spun from Forest


Mat Drawn from Forest

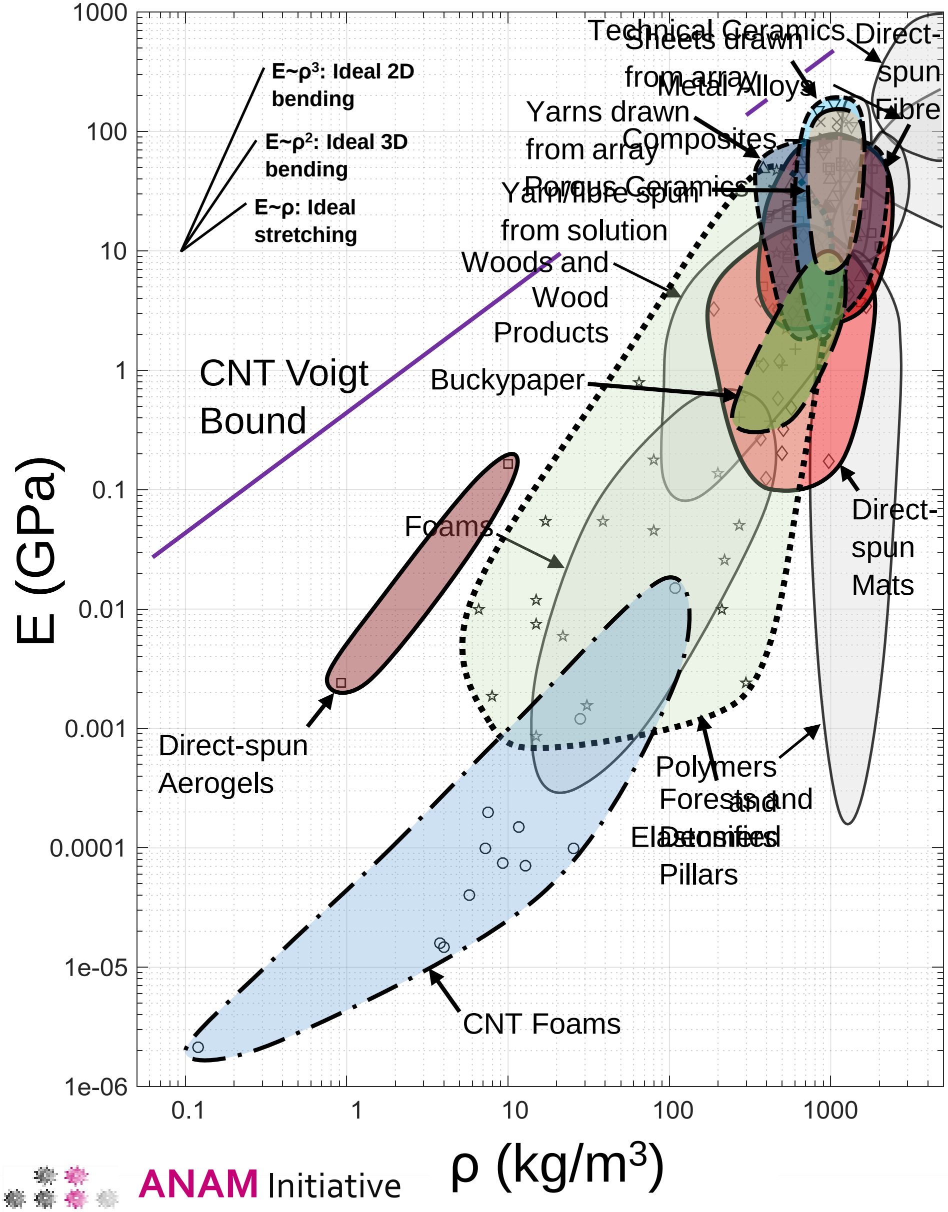

Buckypaper from filtration

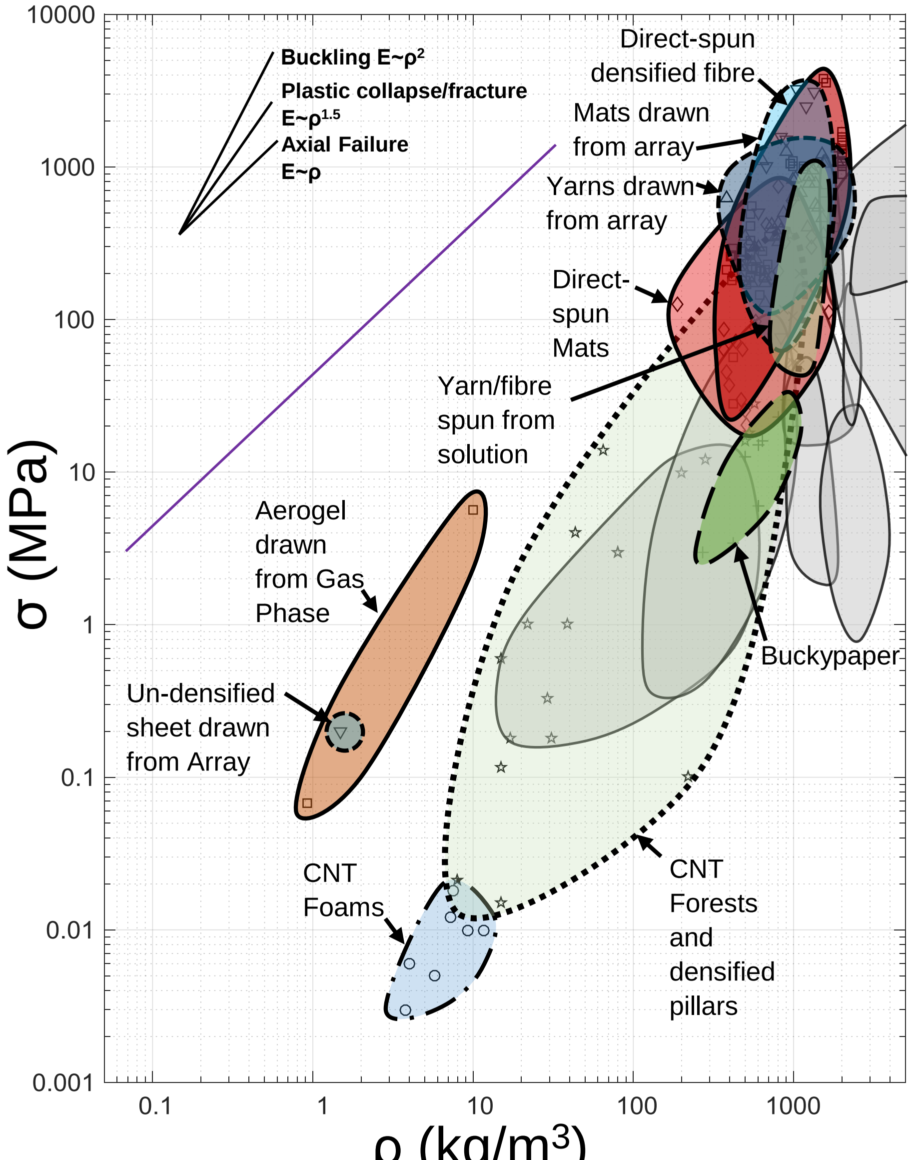


Wet spinning from solution


CNT Foam

The Properties of Bulk CNT Materials: Mechanical





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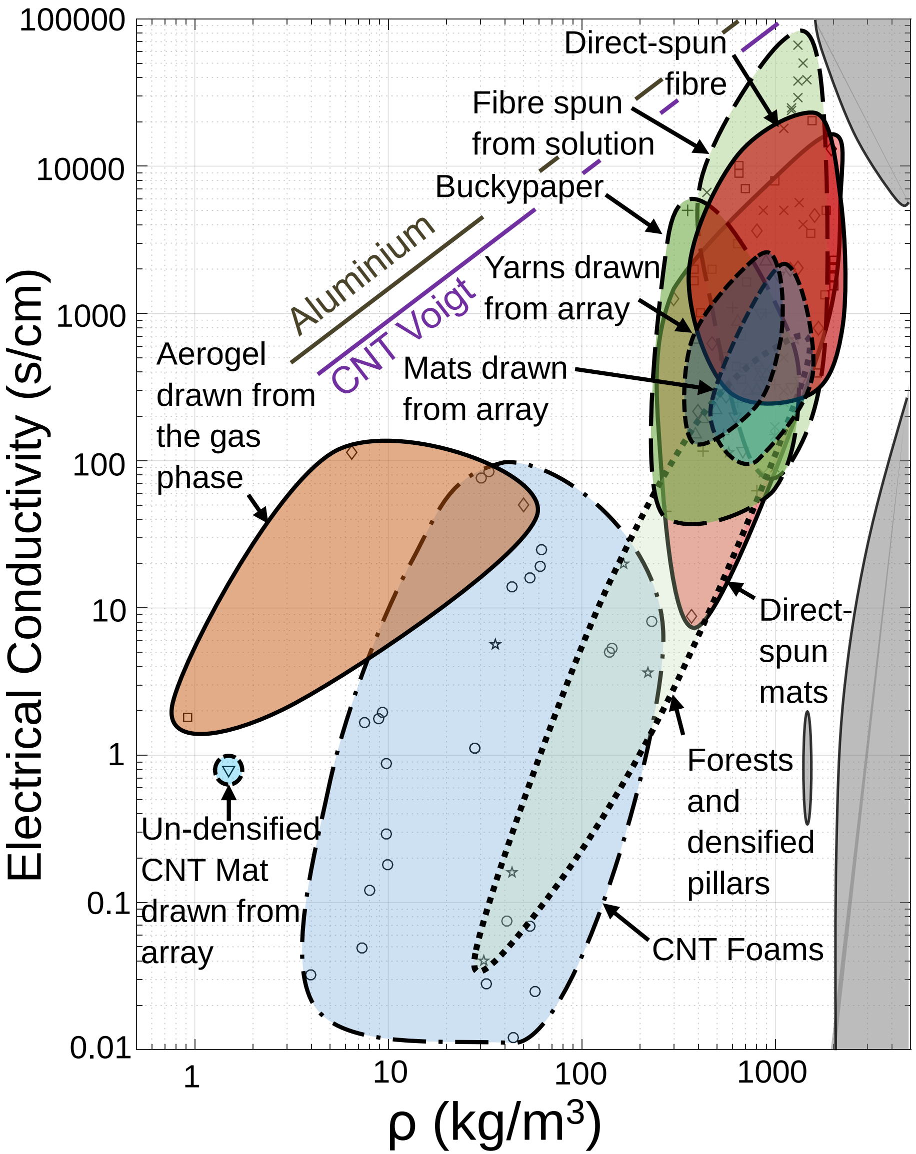
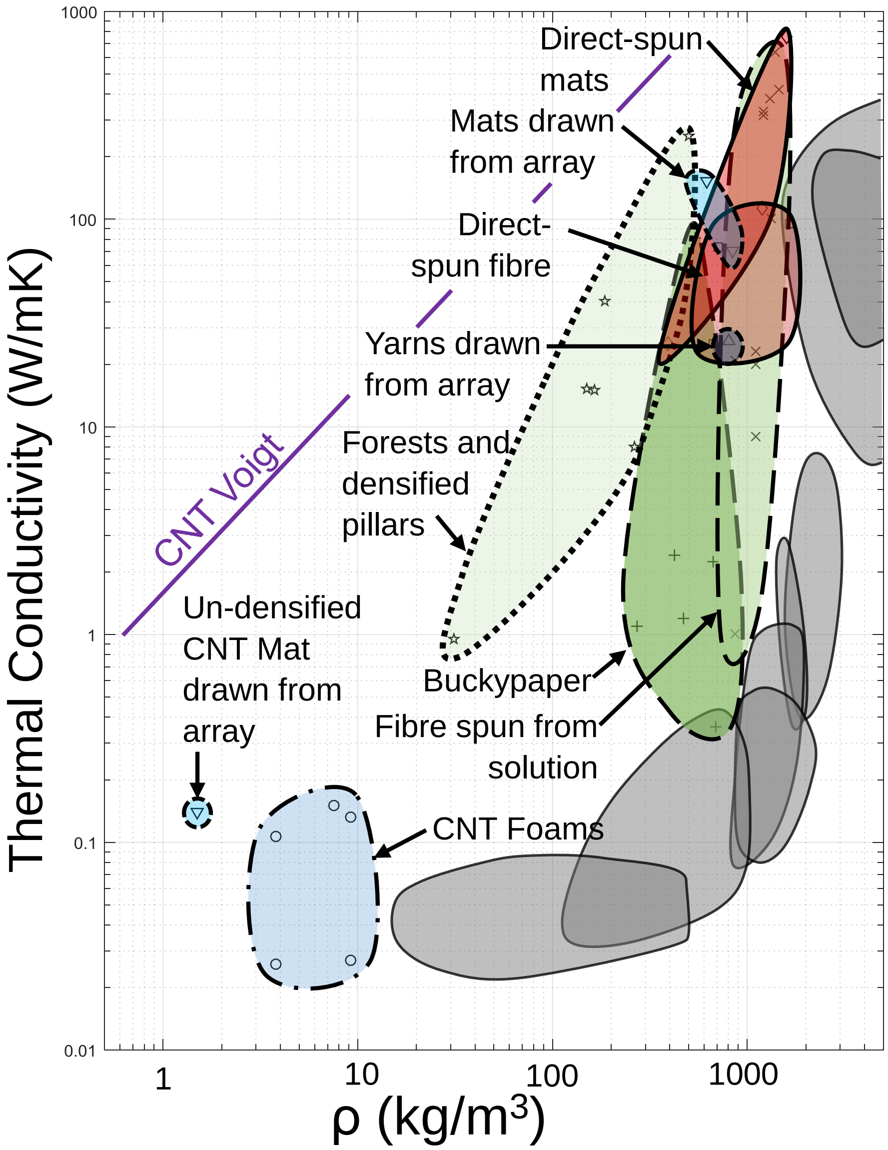
The Properties of Bulk CNT Materials: Electrical & Thermal





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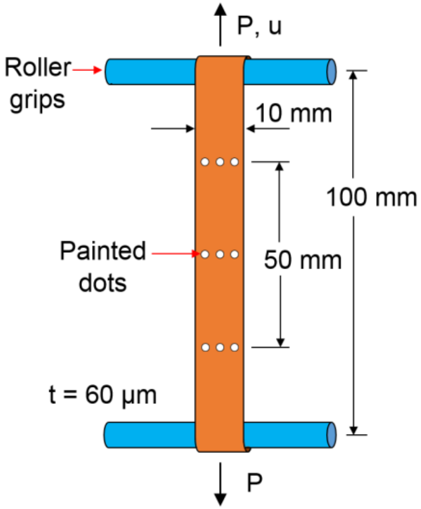
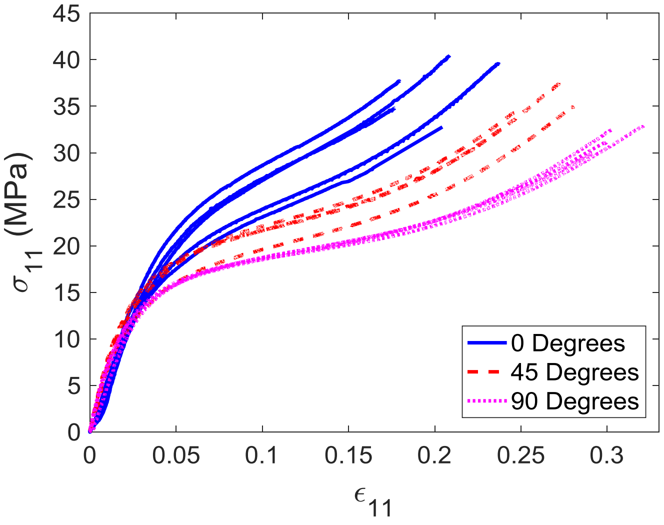
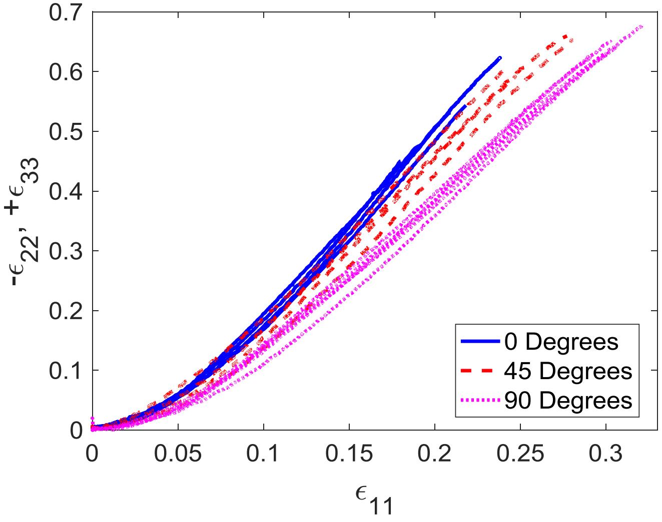
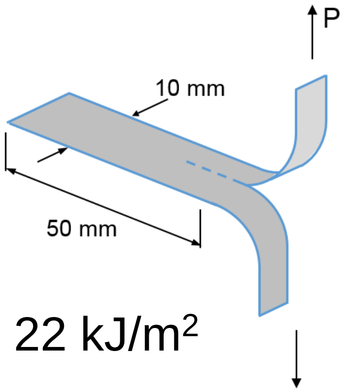
The Properties of a **Direct-spun CNT Mat**: **Uniaxial Response**, **composition**, and **electrical properties**



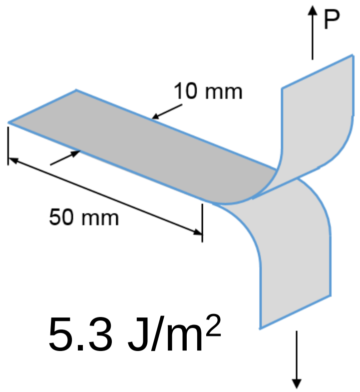




Fracture and **Delamination**

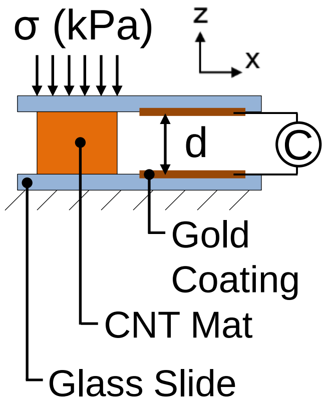


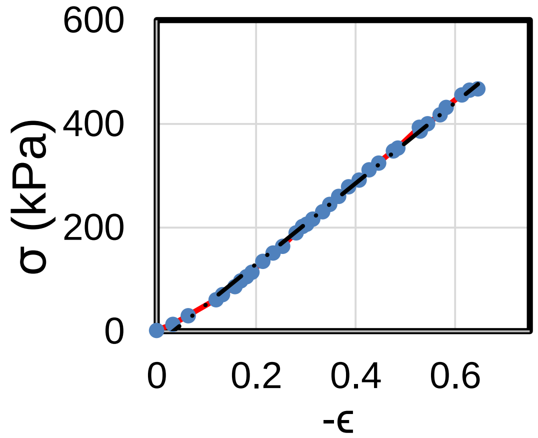
22 kJ/m^2



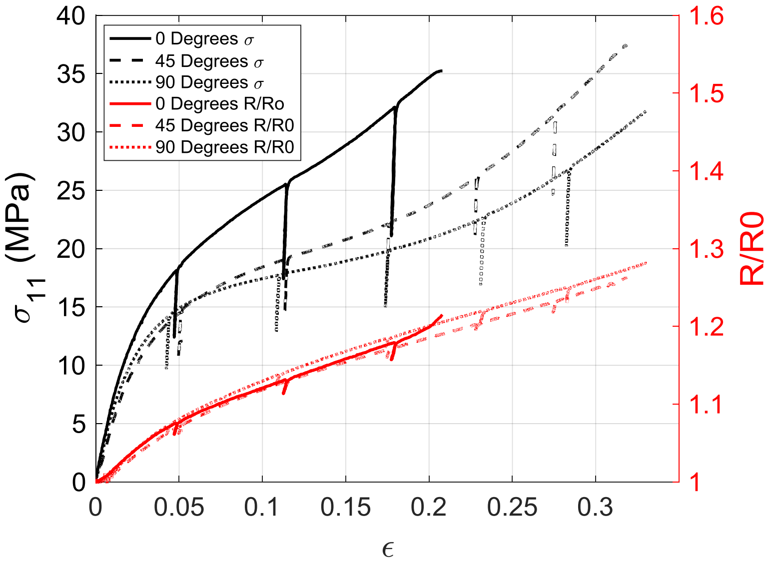
5.3 J/m^2

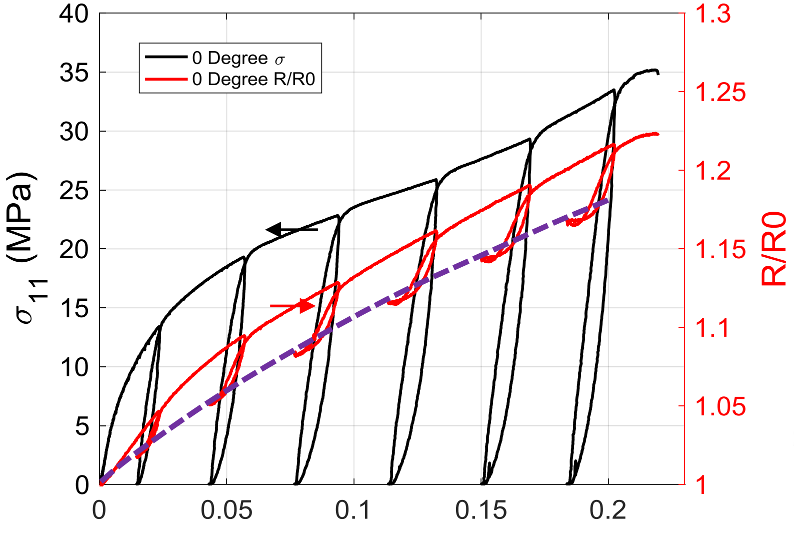
Out of Plane Response

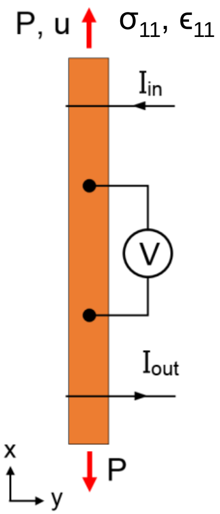


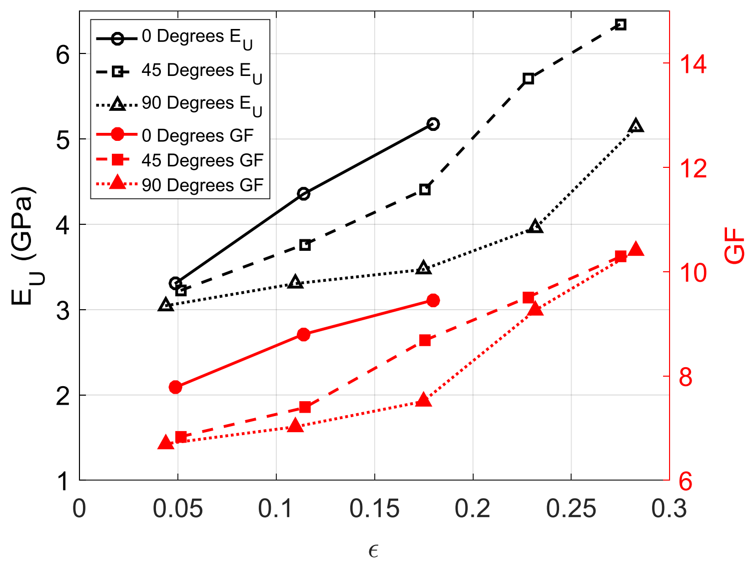


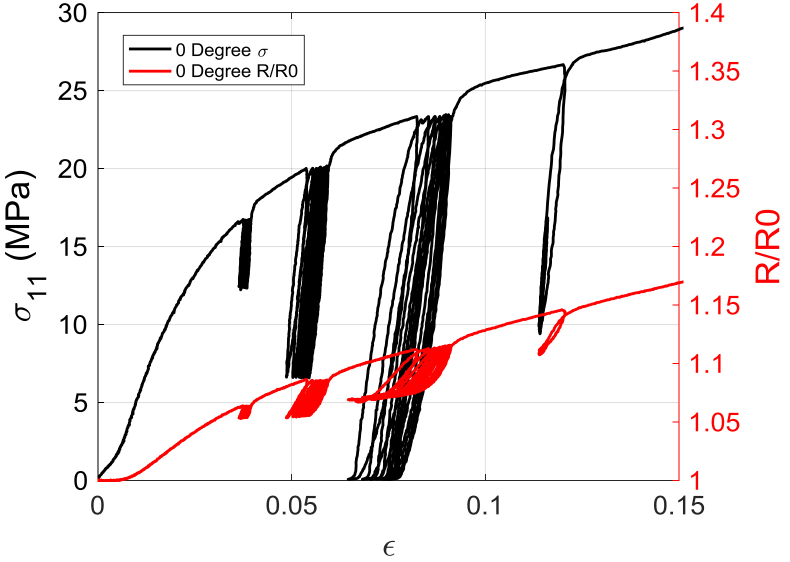
Direct-spun CNT Mat: In-Plane **Piezoresistivity,** and **Unloading**



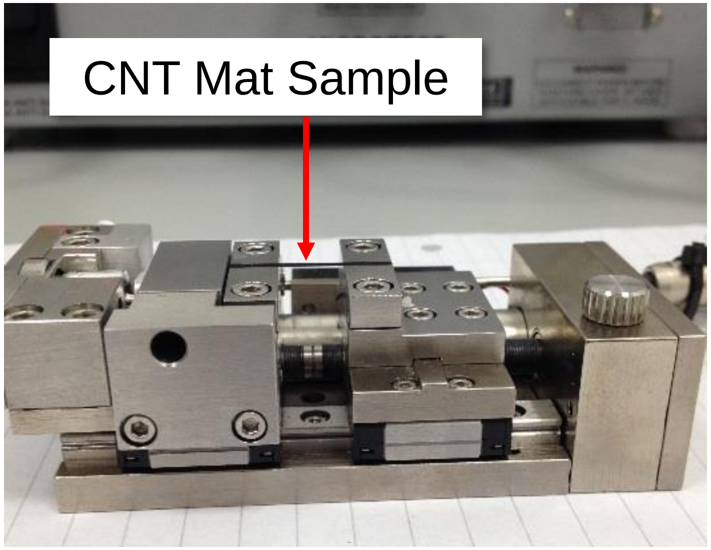


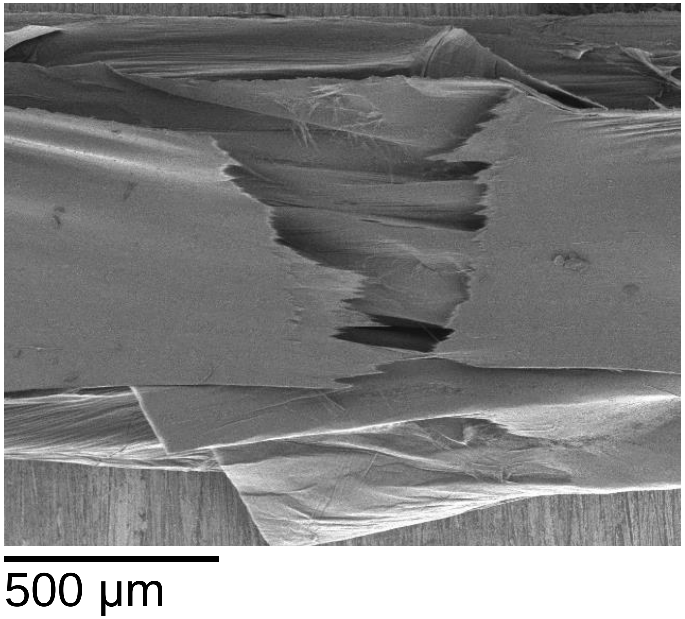


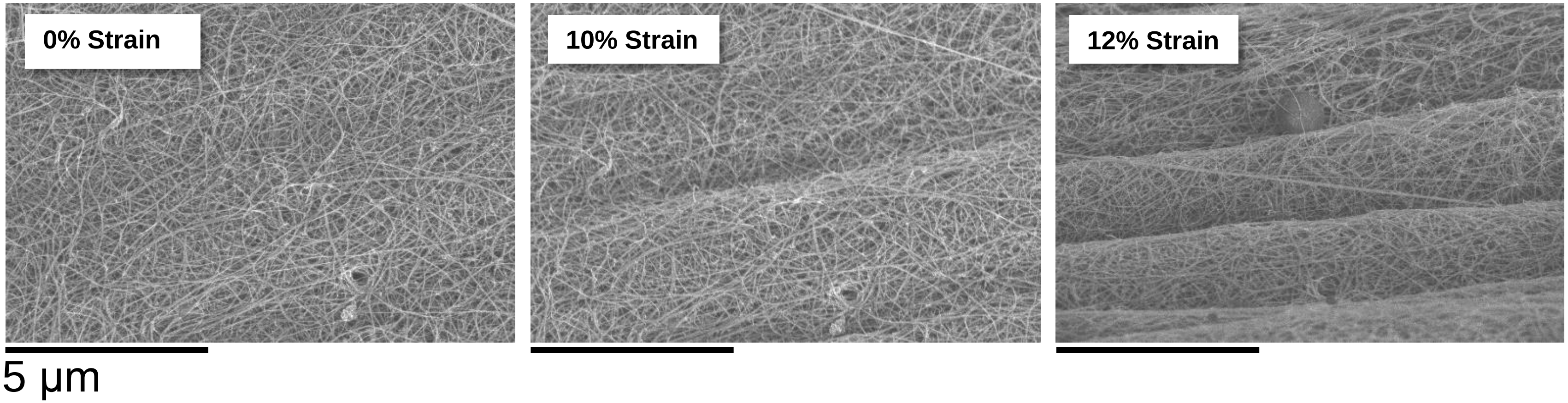




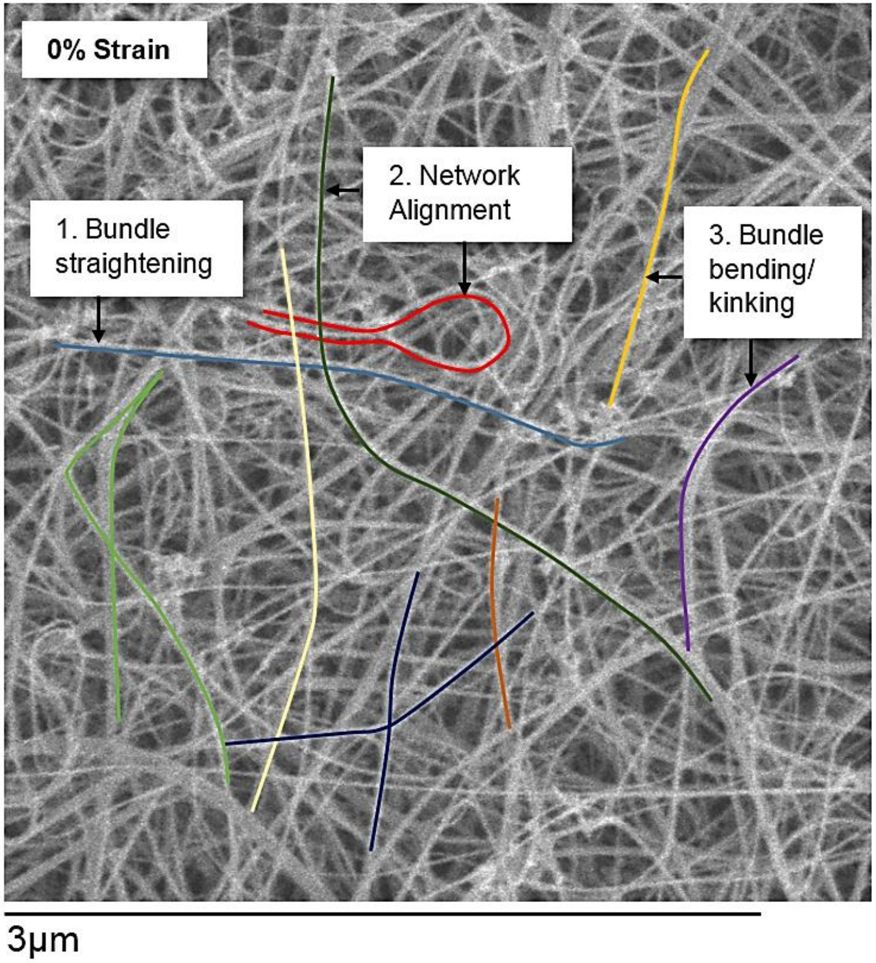
In-Situ Tensile Testing

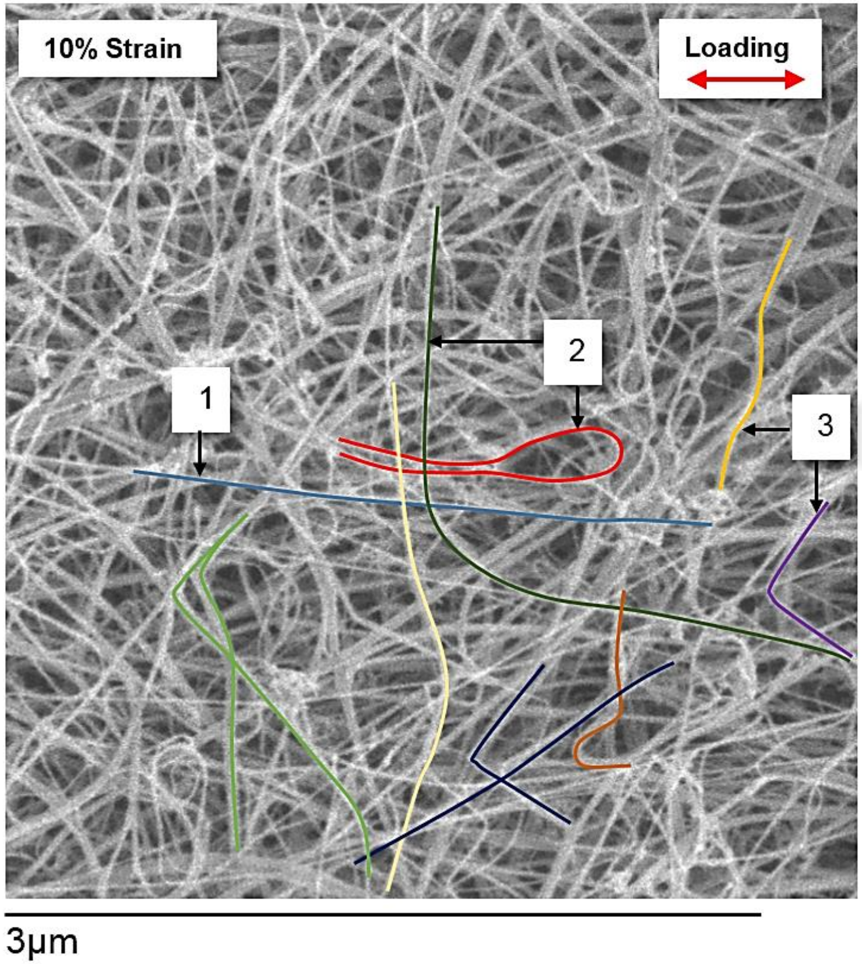






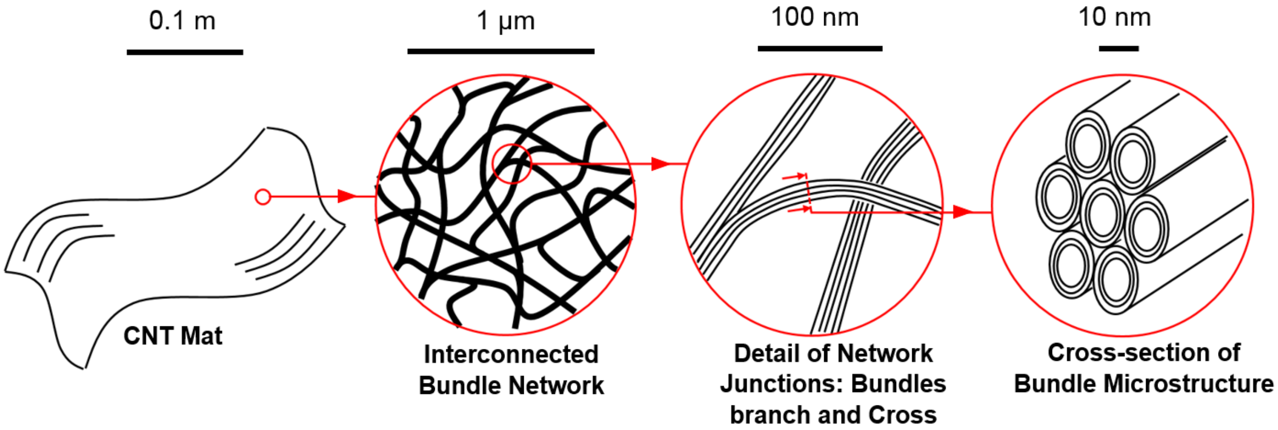
Microstructural change during the uniaxial response

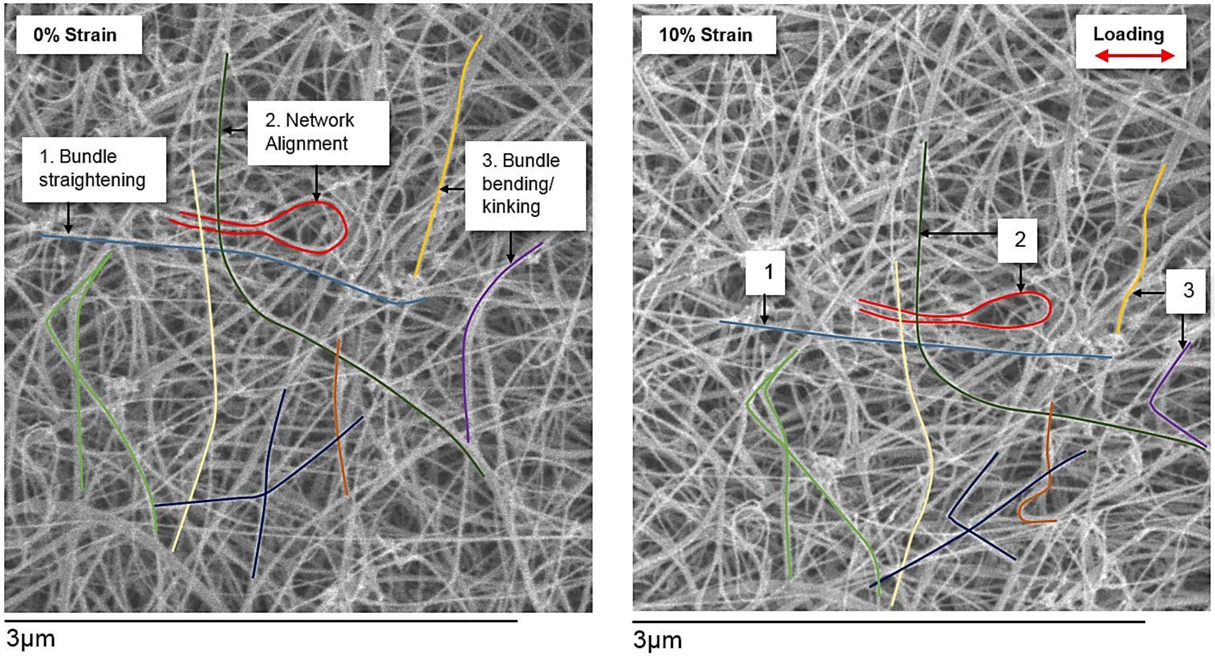


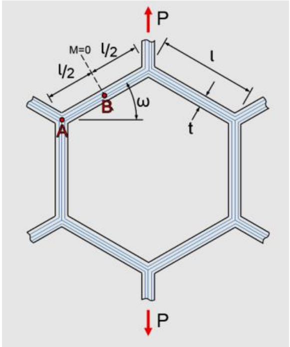


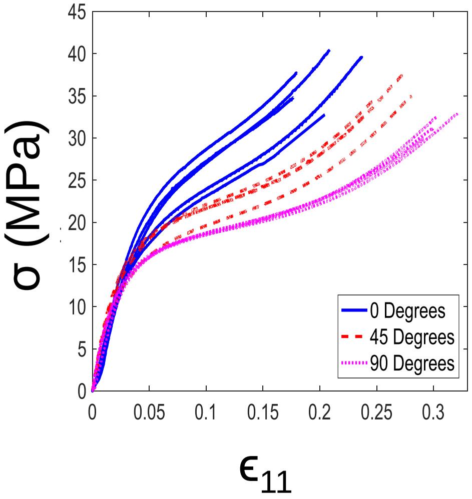
Direct-Spun Mats: the story

- Rope-like CNT bundles form random interlinked bundle network
- Network deforms like a foam, with transverse deflection of struts.

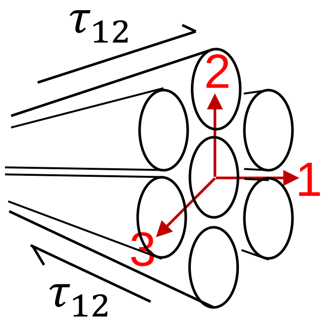




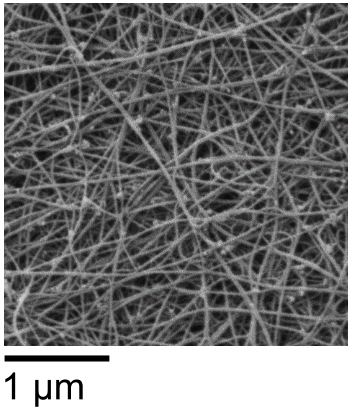


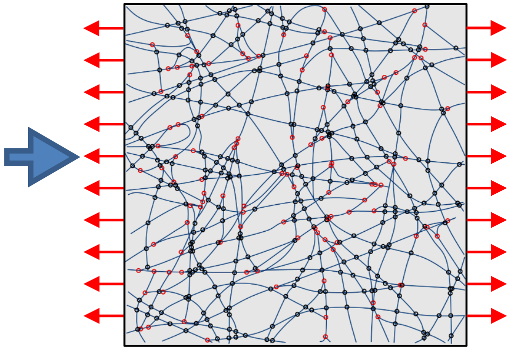


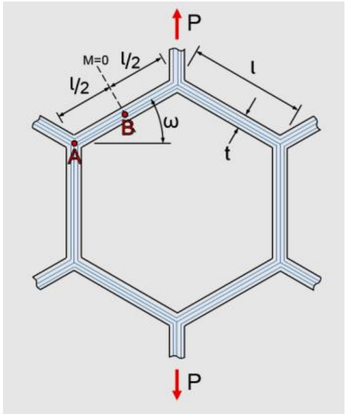
Micromechanical Model for direct-spun mat



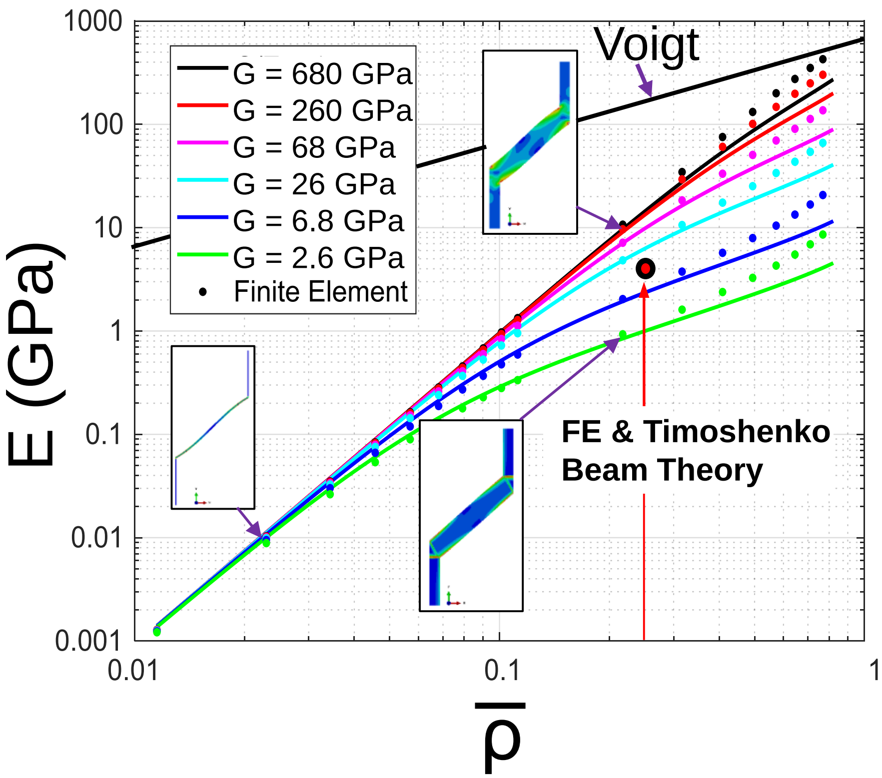
CNT Bundles are **Anisotropic**:
E_{11} = 680 GPa
G_{12}= G_{23} = 9.5 GPa
E_{22} = E_{33} = 50 GPa
v_{12} = v_{13} = v_{23} = 0.3







Approximate network with a **periodic honeycomb** unit cell

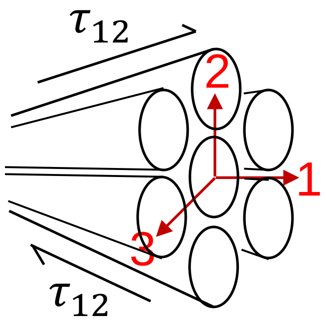


Modulus below that of CNTs because…

1 . Network structure causes foam-like network deformation.

2 . Bundles are rope-like.

Micromechanical Model for direct-spun mat



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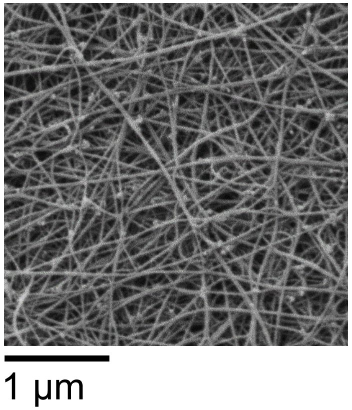

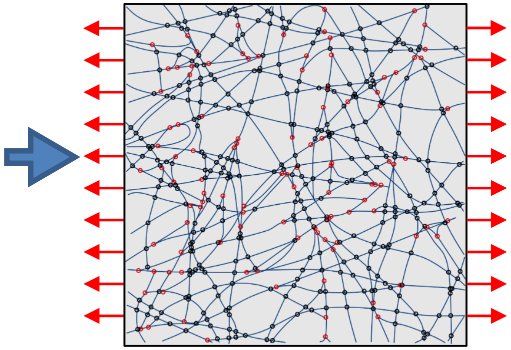

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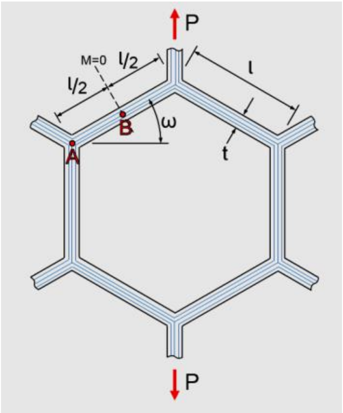
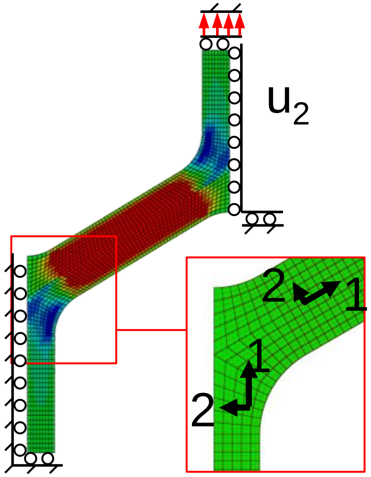
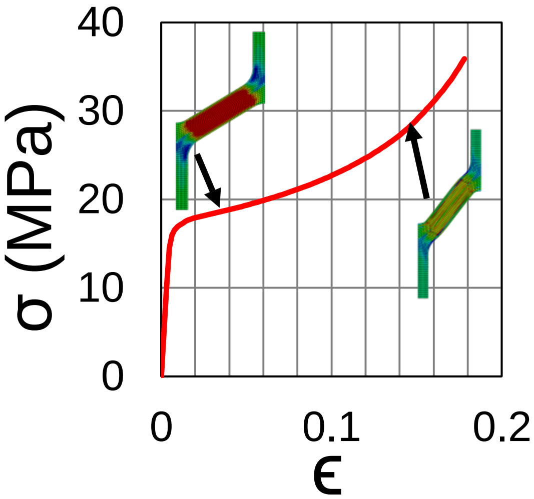


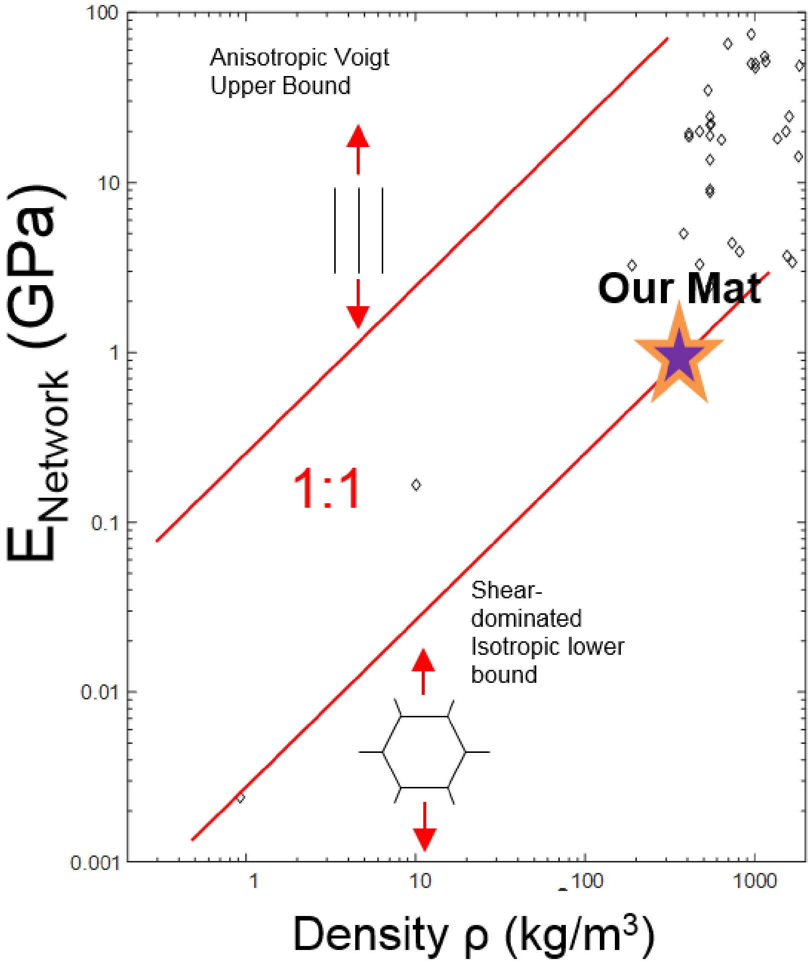


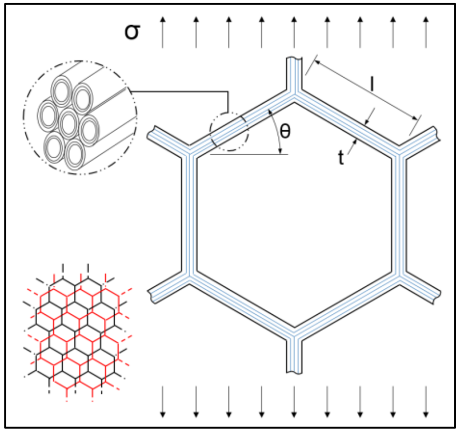
Macroscopic yield dictated by the shear strength of CNT bundles.



Network reorientation causes hardening

Routes for Improvement…



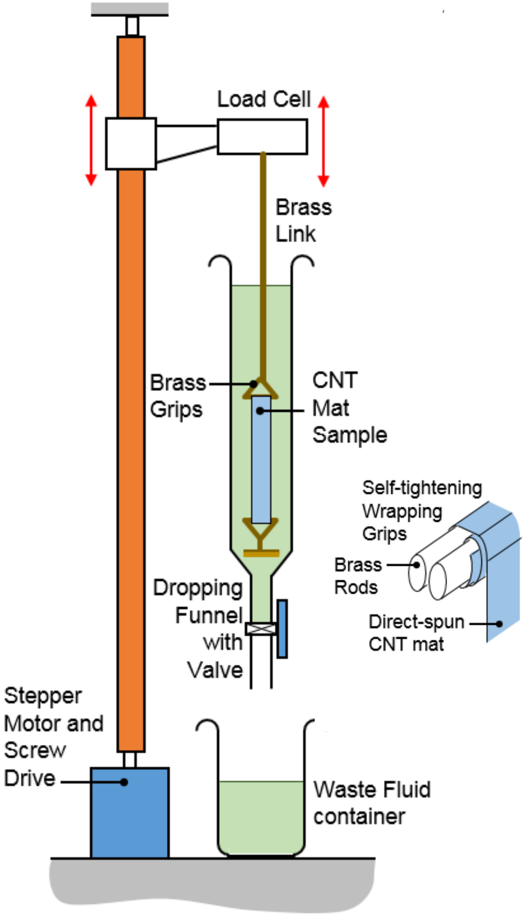


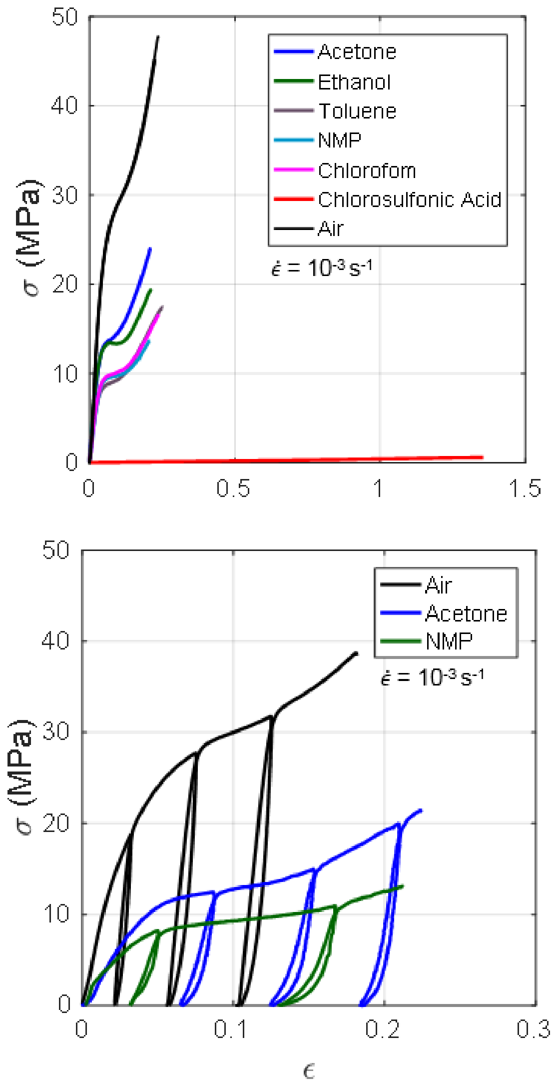
for $G_B \ll E_B$:

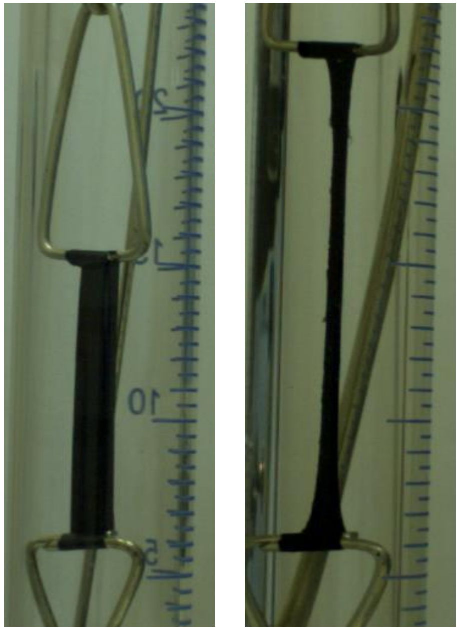
$$E_{Network} = \bar{\rho} \cdot \frac{\frac{2}{3}\kappa G(1+\sin\theta)^2}{\cos^2\theta}$$

Therefore, improvement in mechanical properties can come from **ALIGNMENT of CNT BUNDLE MICROSTRUCTURE**

Response in Fluids

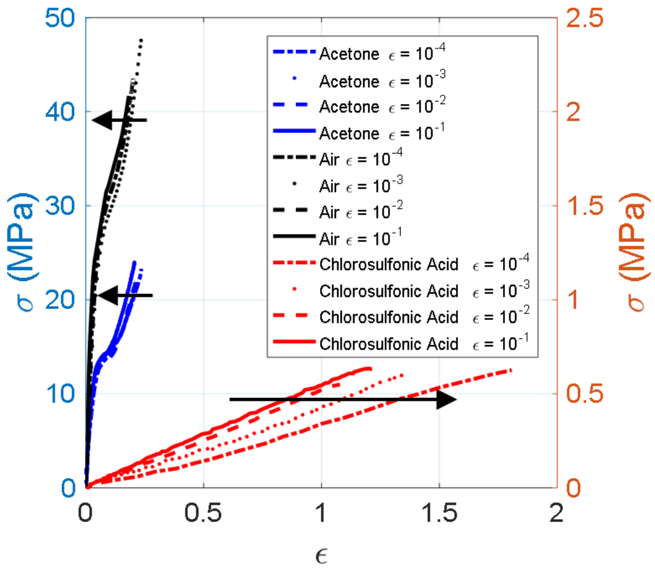


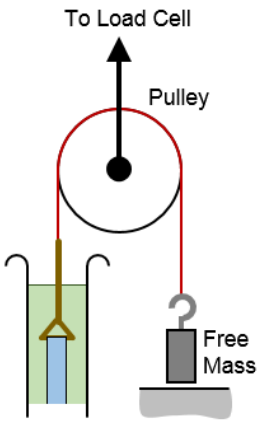


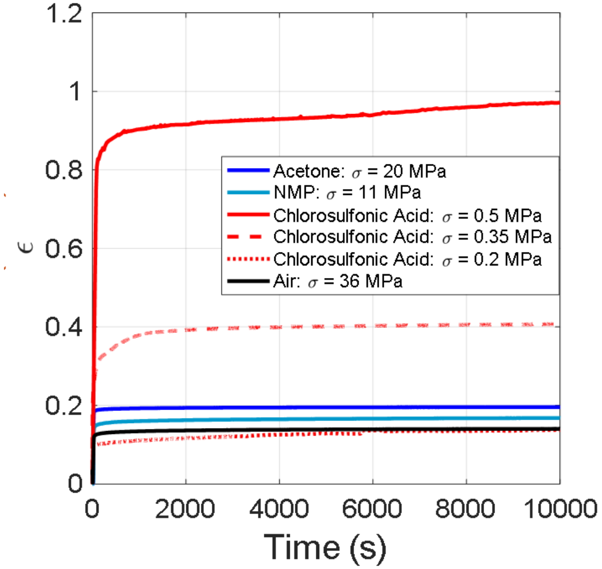


- Chlorosulfonic acid lowers σ and E by over an order of magnitude.
- ε increases to ~1.4 at same rate.

Response in Fluids

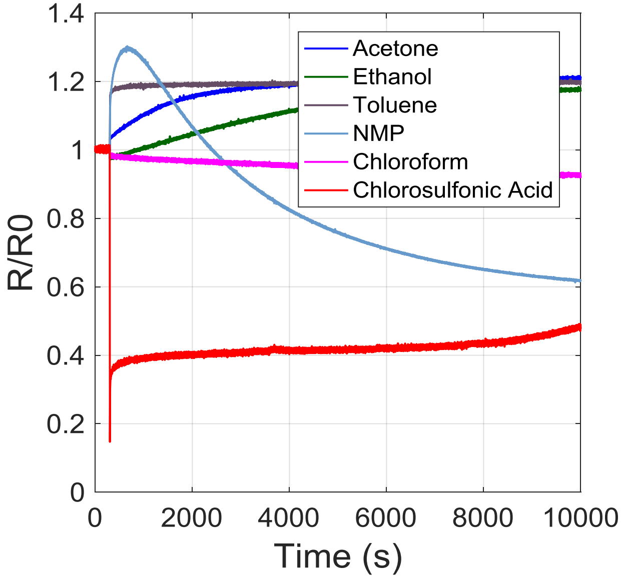




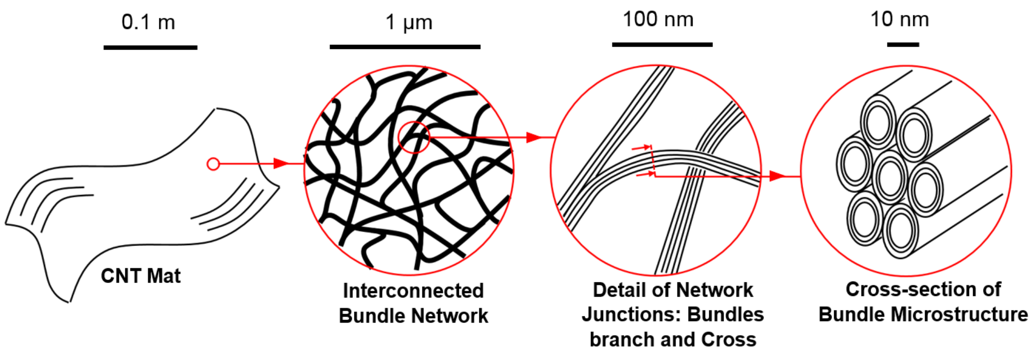


Immersion in **chlorosulfonic acid** results in **creep** at low stresses.

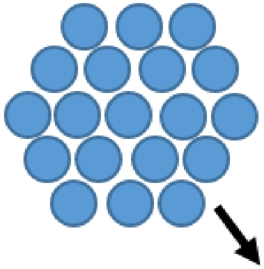
Electrical resistance also affected by fluid immersion… but **mechanical behaviour is time invariant.**



Debundling/debonding upon CSA Immersion

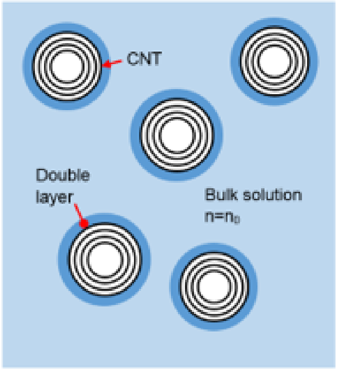


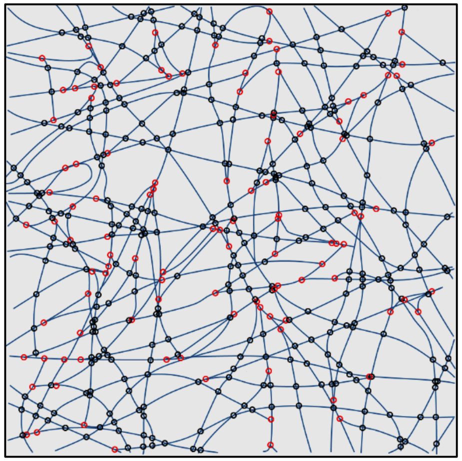
$$[\mathrm{HSO_3Cl}]_n + \mathrm{C}_x \rightleftharpoons [\mathrm{C}_x\mathrm{H}_n^+] + [\mathrm{ClSO_3^-}]_n$$



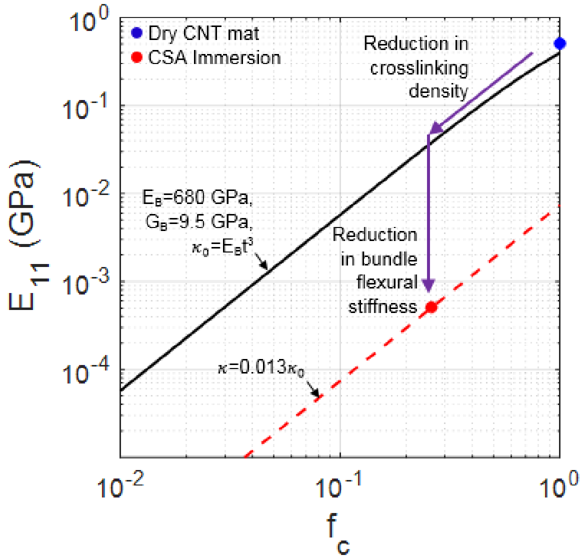
Dry state: CNTs are closely bundled due to strong van-der-Waals bonds.

After acid infiltration, protonation separates adjacent CNTs.

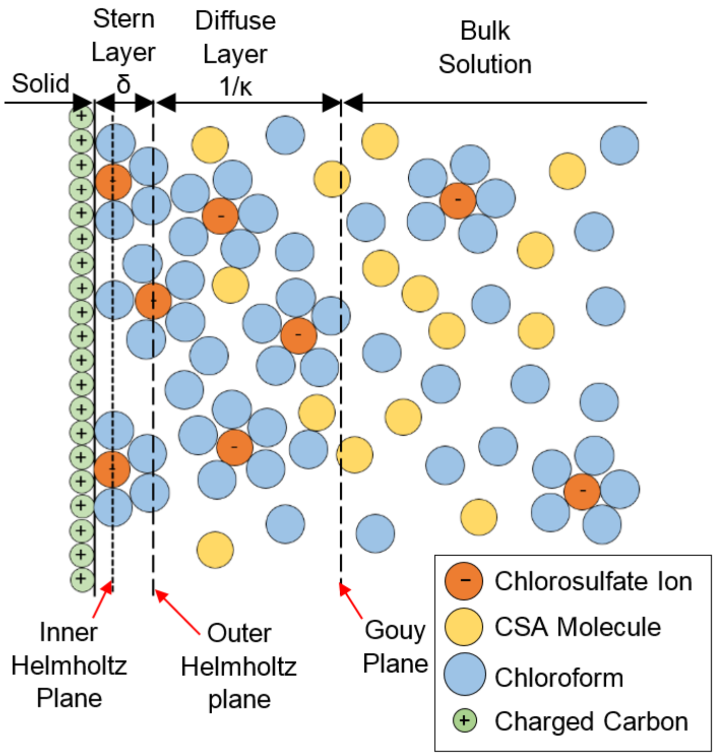


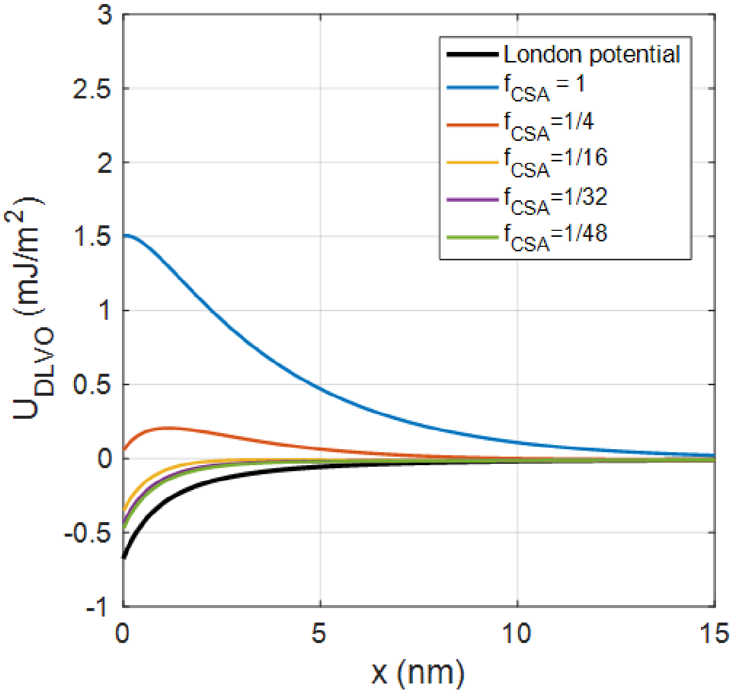


f_c~0.26



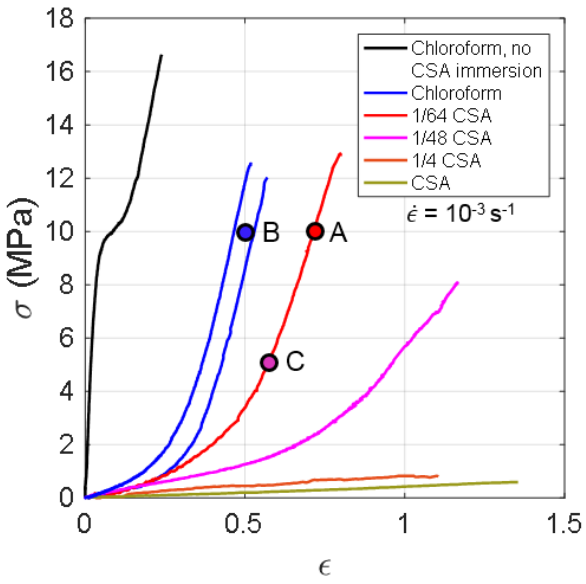
Debundling/debonding upon CSA Immersion





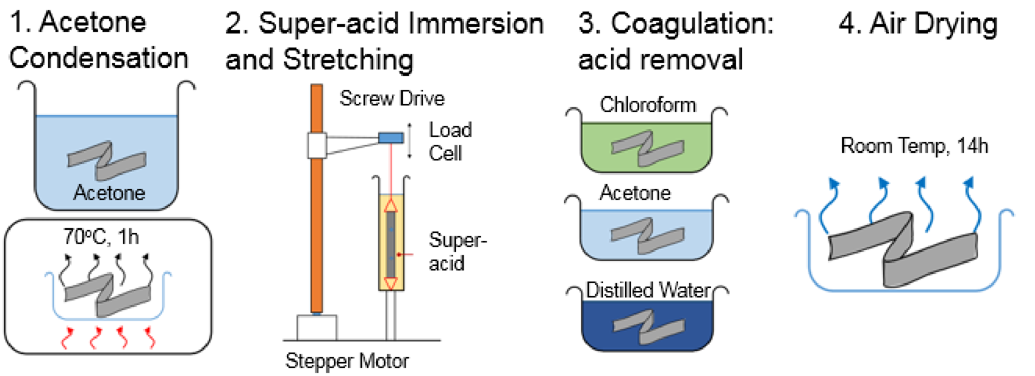
The presence of **adsorbed ions** at the CNT wall, and in the **solution** screen the positive charge upon the CNT walls, and overcome the **van-der-Waals** attraction.

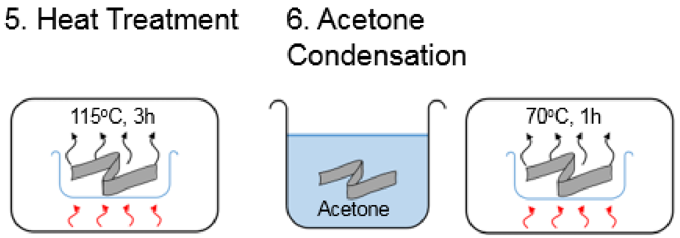
Fluid Processing in superacid solutions



Ductility and drawing stress controlled by the concentration of a superacid solution.

Drawing process to enhance **alignment**

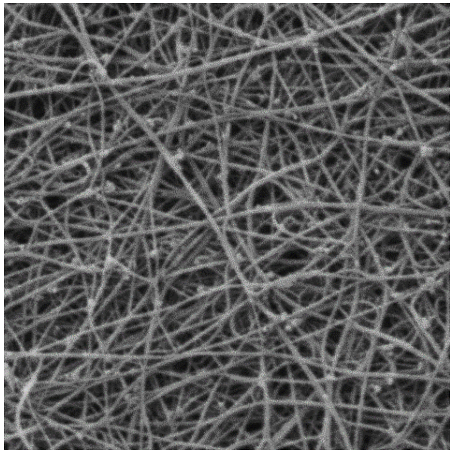


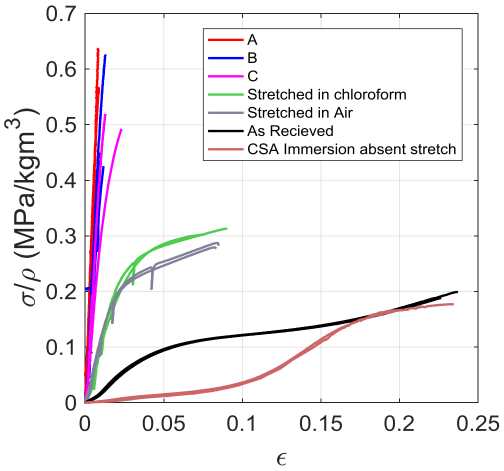


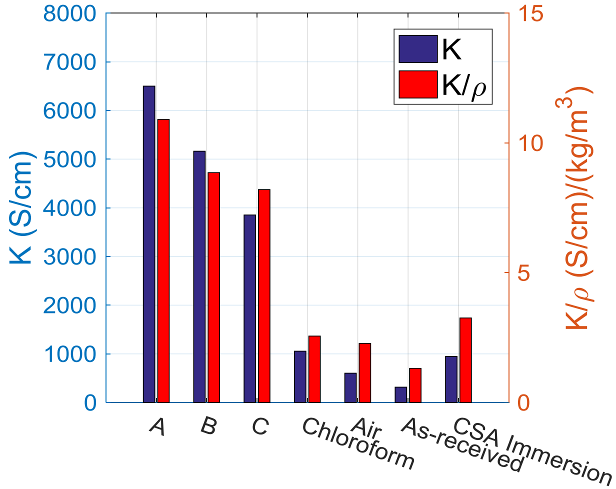
Questions:

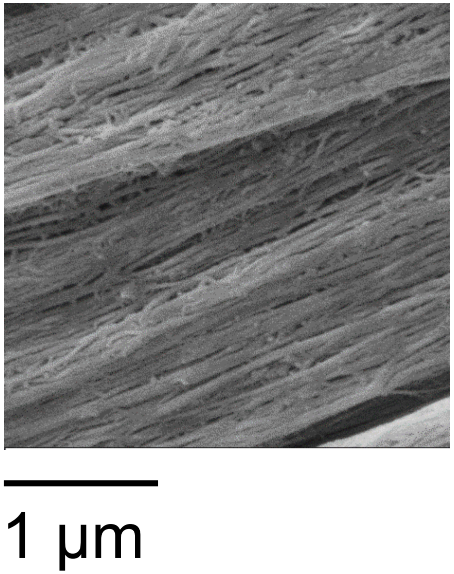
- Effect of **Acid Treatment**
- Effect of **Stretch** in Acid
- Effect of **tension** in coagulation

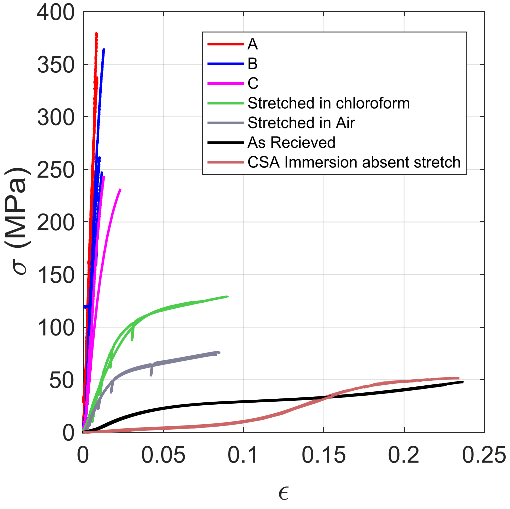
Properties of drawn fibres











- All properties improved significantly.
- Change in ultimate specific strength and conductivity a factor of 3.
- Larger change in stiffness due to switch away from bending.

Summary

- The **properties** of direct-spun carbon nanotube materials (and CNT materials in general) vary across a **wide range of density**.
- The stiffness and strength of direct-spun mats is **reduced** by the **CNT bundle network** of **low nodal connectivity**, and by the rope-like structure of the CNT bundles.
- Mechanical and electrical properties of direct-spun CNT mats are **enhanced** by tensile drawing in different fluids, particularly in **superacids**.