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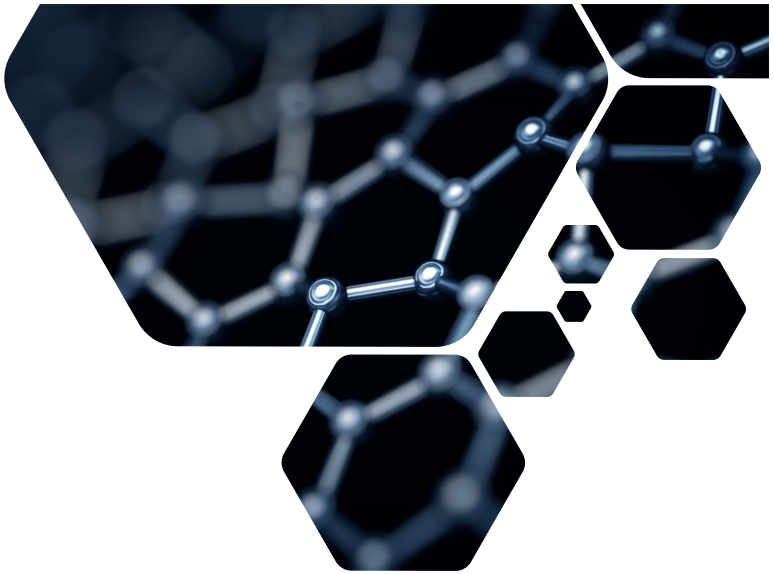

Electrical conductivity in thermoplastic nanocomposites

Kailing Lin, Yubao Deng, William Sampson, Mark Bissett, Ian Kinloch

Morgan Advanced Materials

ROYAL ACADEMY OF ENGINEERING

DPI DUTCH POLYMER INSTITUTE

GRAPHENE FLAGSHIP

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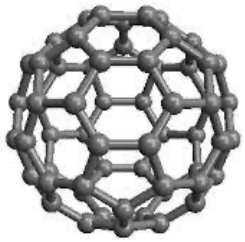
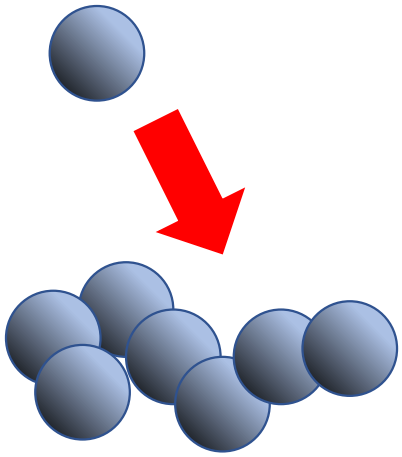
The nanocarbon family

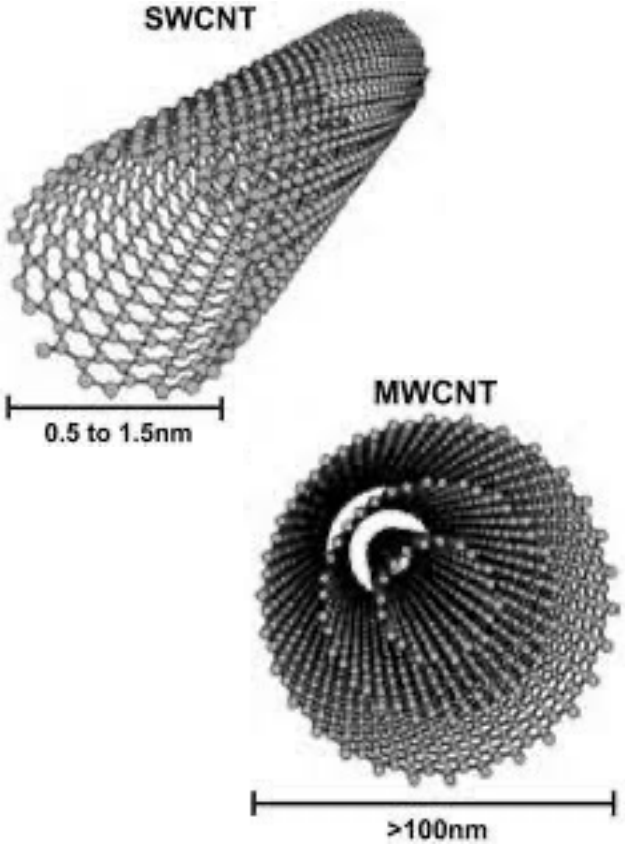
0D- Fullerenes



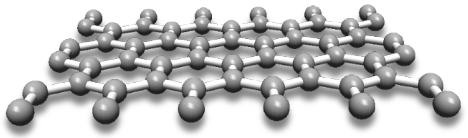
Carbon Black



1D - Carbon nanotubes

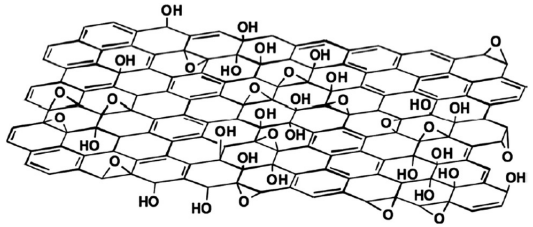


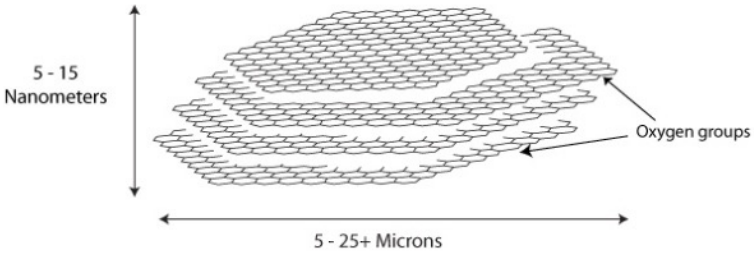
2D – Graphene *etc*



Monolayer

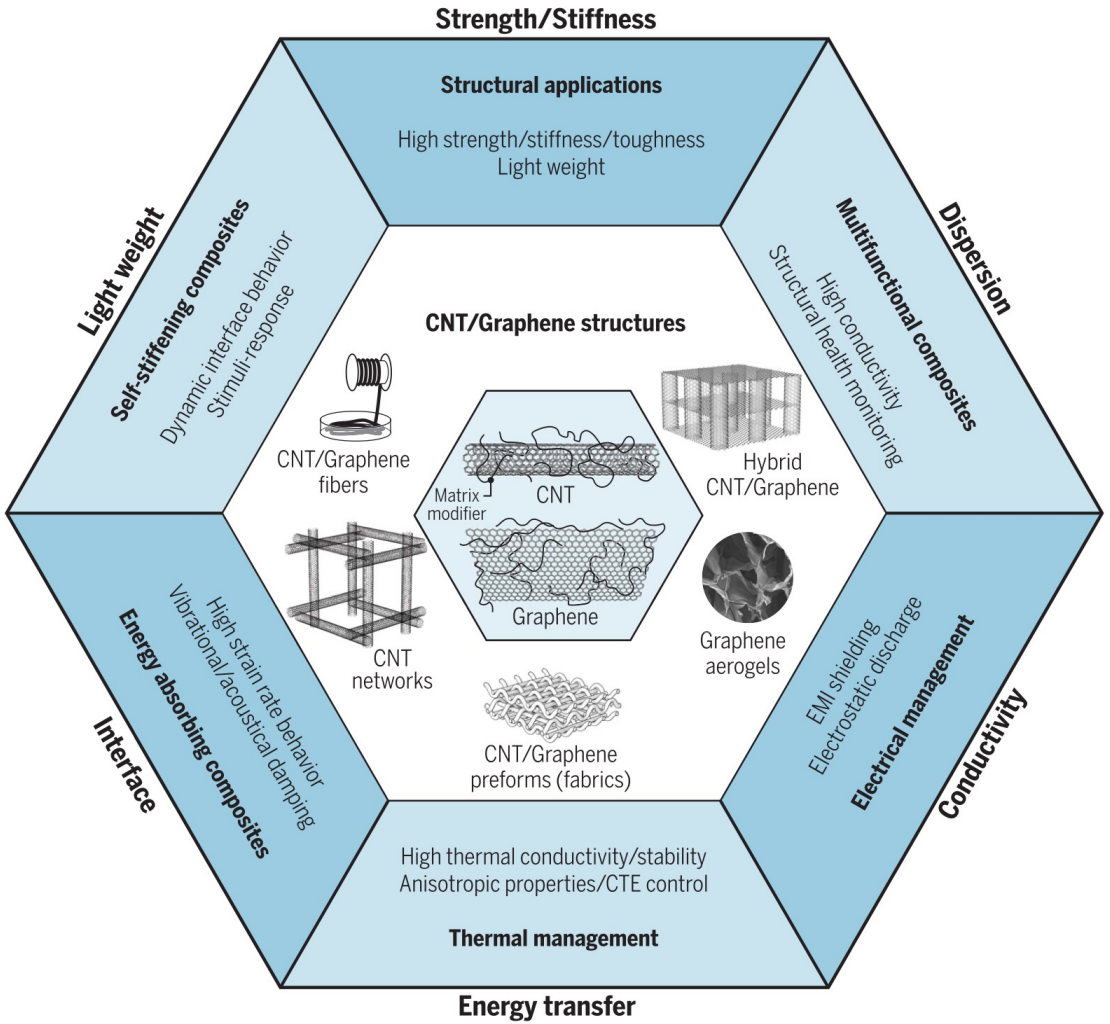
Graphene oxide (GO)
25 to 30 at% O





Graphene nanoplatelets (GNPs)

The potential of nanotube and graphene reinforced composites



Kinloch, Science 362 (6414), 547-553, 2018

Matrices in our group

- ***Thermopolymers:*** PEEK, PP, PA, Nylon
- ***Thermosets:*** Epoxies, including RTM and aerospace grades
- ***Elastomers:*** SBR, NBR, FKM, TPE, TPU
- ***Hybrid:*** Carbon-fibre, glass-fibre, Carbon black
- ***Ceramic:*** *STO*
- ***Metallic:*** *Cu, CuW, Al*

Reviews

Kinloch *et al.*, Science, 2018;
Papageorgiou *et al.*, Progress in Mat Sci 2018
Marsden *et al,* 2D, 2018
Hidalgo-Manrique *et al.*, 2019

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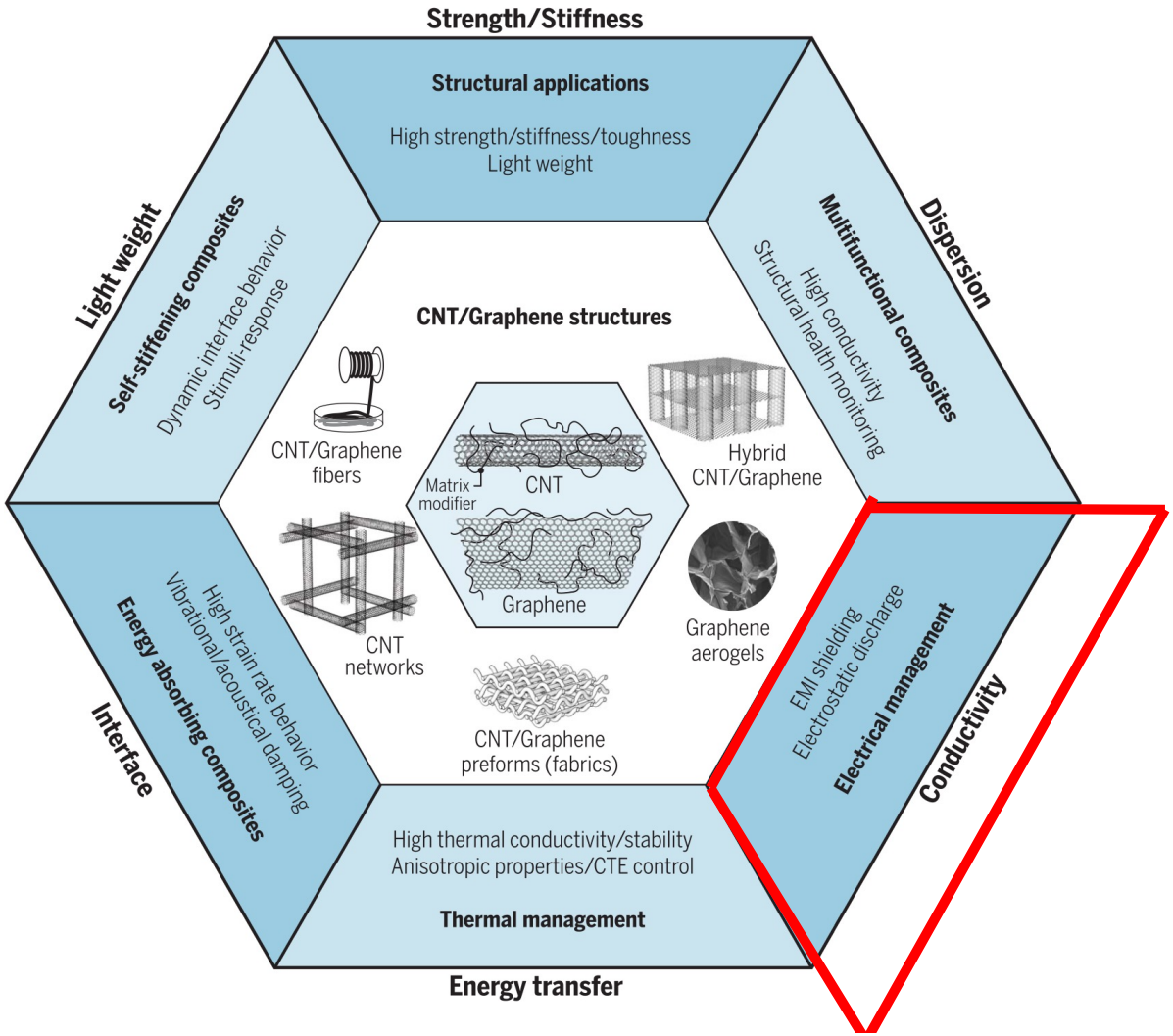
Electrical conductivity



Kinloch, Science 362 (6414), 547-553, 2018

Nanotubes as a conductive additive is the nanotube success story:

- Most masterbatch companies have a nanotube conductive grade with uses in automotive etc.
- All Li ion batteries use nanotubes as a conductive additive.

"In a bid to gain a more competitive edge in the rapidly growing global CNT market focused on electric vehicle battery materials, the largest Korean chemical company, LG Chem has revealed today that it's going to build the fourth LG Chem Carbon Nanotube Plant.

The new plant is expected to produce 3,200 tons of CNT annually, contributing to the LG Chem carbon nanotube plant's total production capacity is of 6,100 tons"

https://www.techgenyz.com/2022/08/30/lg-chem-carbon-nanotube-plant/

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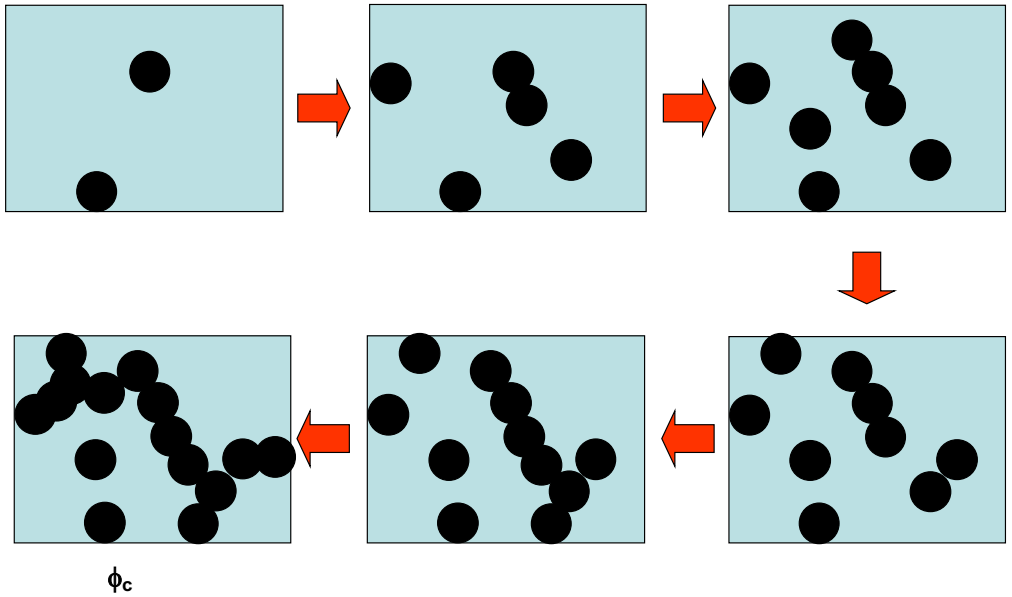
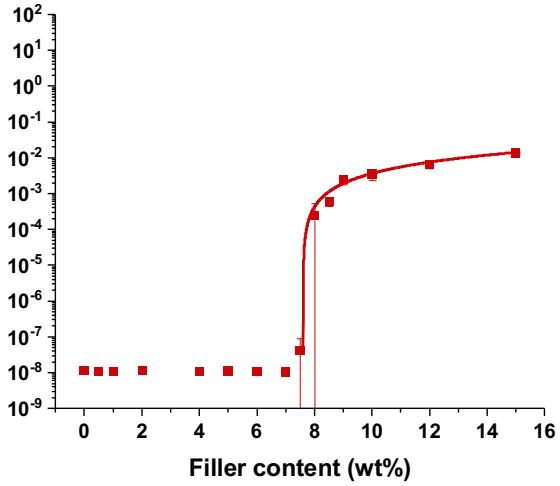
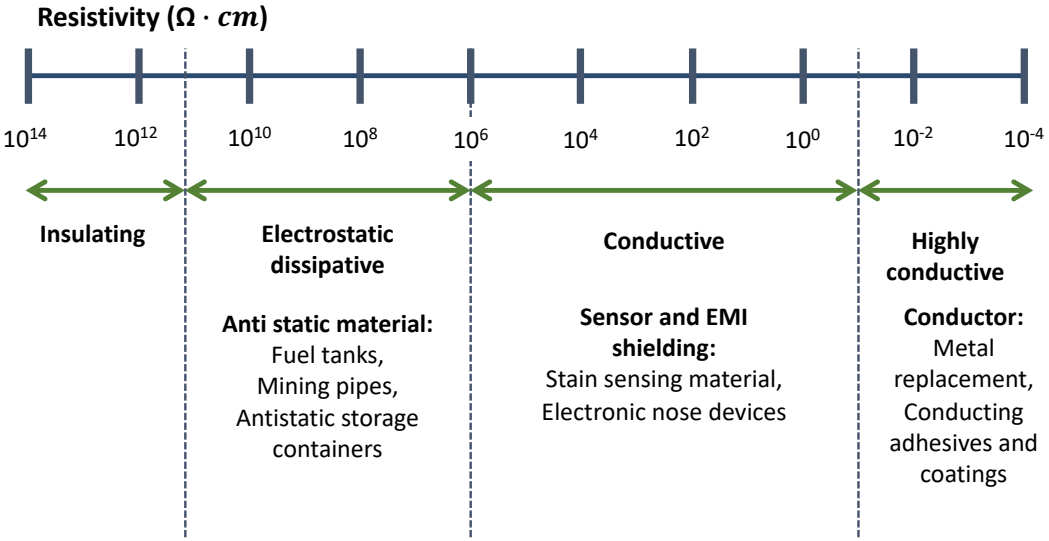
Conducting Polymer Composites



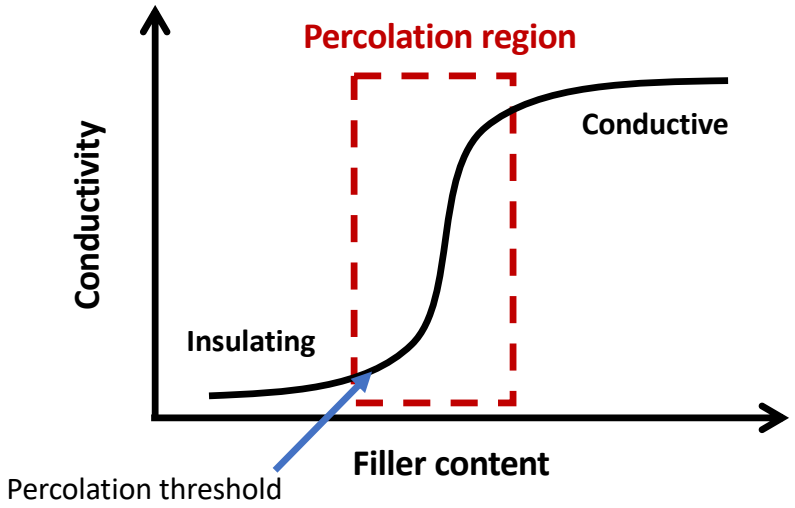
$$\text{For } p < p_c : \sigma = 0$$

$$\text{For } p \geq p_c : \sigma = \sigma_0 (p - p_c)^t$$





Controlling electrical percolation

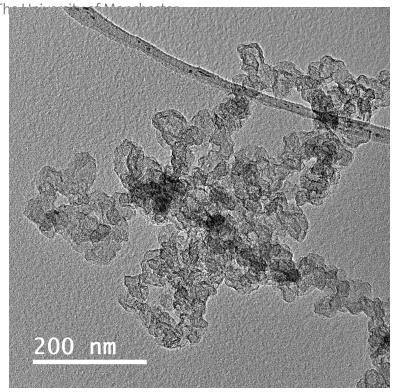


- Sharp transition between conducting and not conducting is not desirable for industry – *can we control the shape of the percolation curve?*
- *How do the standard high-end, carbon black and nanotube fillers compare to the new graphenes?*
- *Is there synergy between the fillers in a hybrid system? E.g. t*here has been theories of graphene acting to bridge nanotube network.

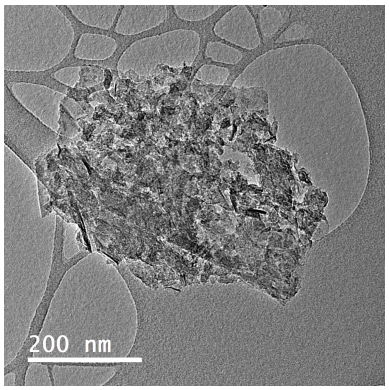
Filler morphology / Processing condition → Structure of filler network → Properties of composites

1. Marsden, A. J., et al. "Electrical percolation in graphene–polymer composites." *2D Materials* 5.3 (2018): 032003.
2. Park, Sung-Hoon, et al. "Modeling the electrical resistivity of polymer composites with segregated structures." *Nature communications* 10.1 (2019): 1-11.

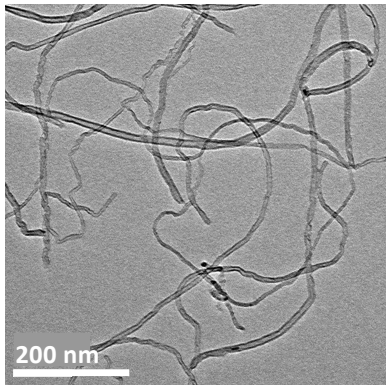
Our model system



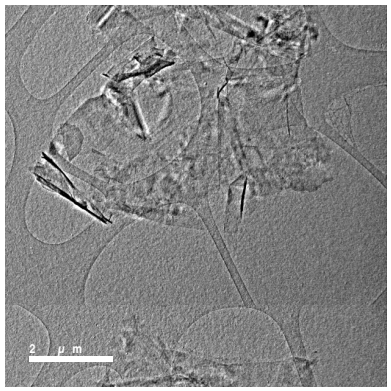
0 D
Carbon black
Ketjenblack EC600JD



2 D
Graphene nanoplatelet
XG C750 GNP

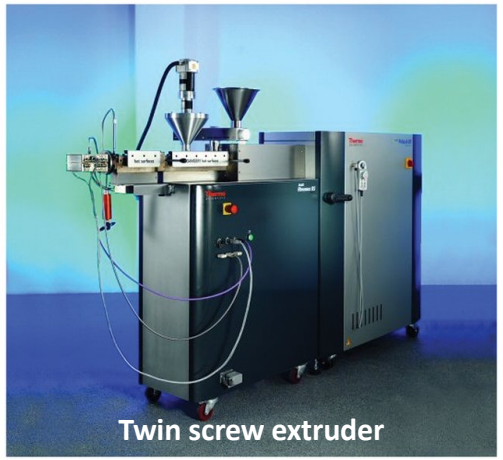


1 D
Carbon nanotube
Nanocyl®7000
s ~ 150



2 D
Graphene nanoplatelet
XG M25 GNP
s ~1000 (in theory…)

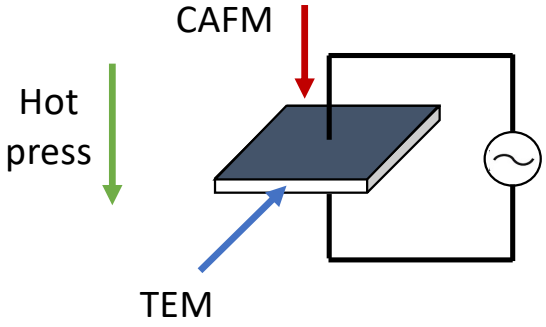
Polycarbonate LEXAN™ RESIN 172L



Hot press

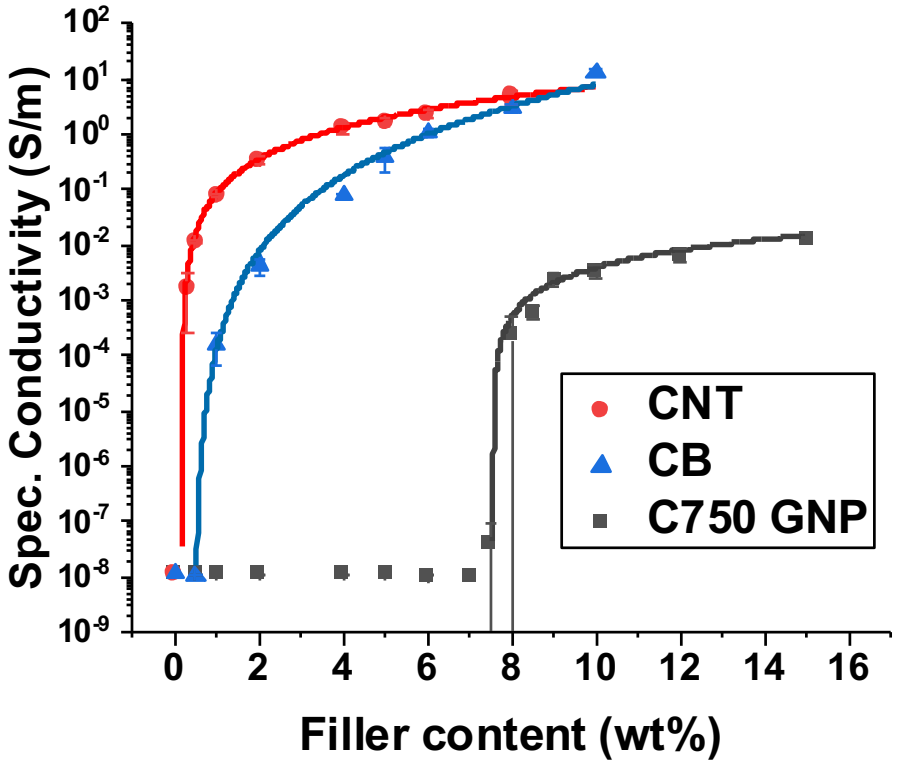
10cm*10cm*1mm

Cut for further characterization



- Electrical properties characterized in AC mode
- Through-plane direction
- Conductivity at frequency of 1Hz will be presented
- Morphology characterized by TEM and conductive AFM

Single Filler System: CB vs CNT vs C750 GNP



- **Percolation theory**

$$\sigma = \sigma_f (p - p_c)^t \qquad (p > p_c)$$

Percolation threshold (p_c):

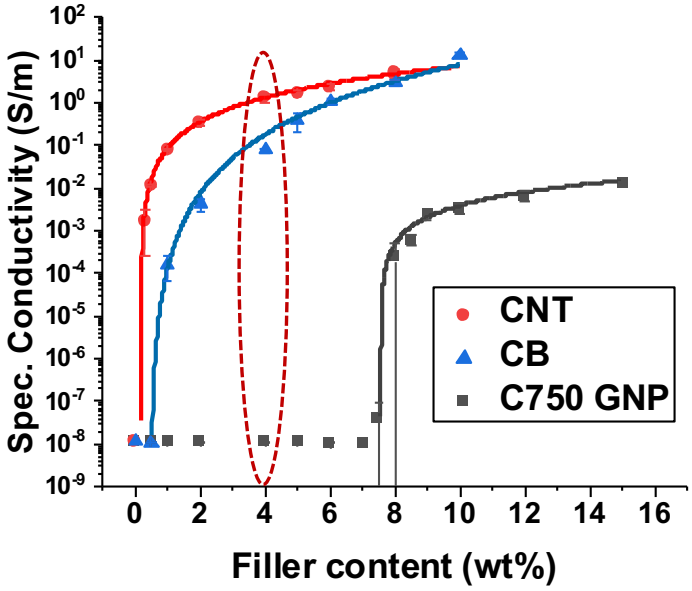
The critical concentration where conductive path forms.

Critical exponent (t)**:** Governing the percolation transition

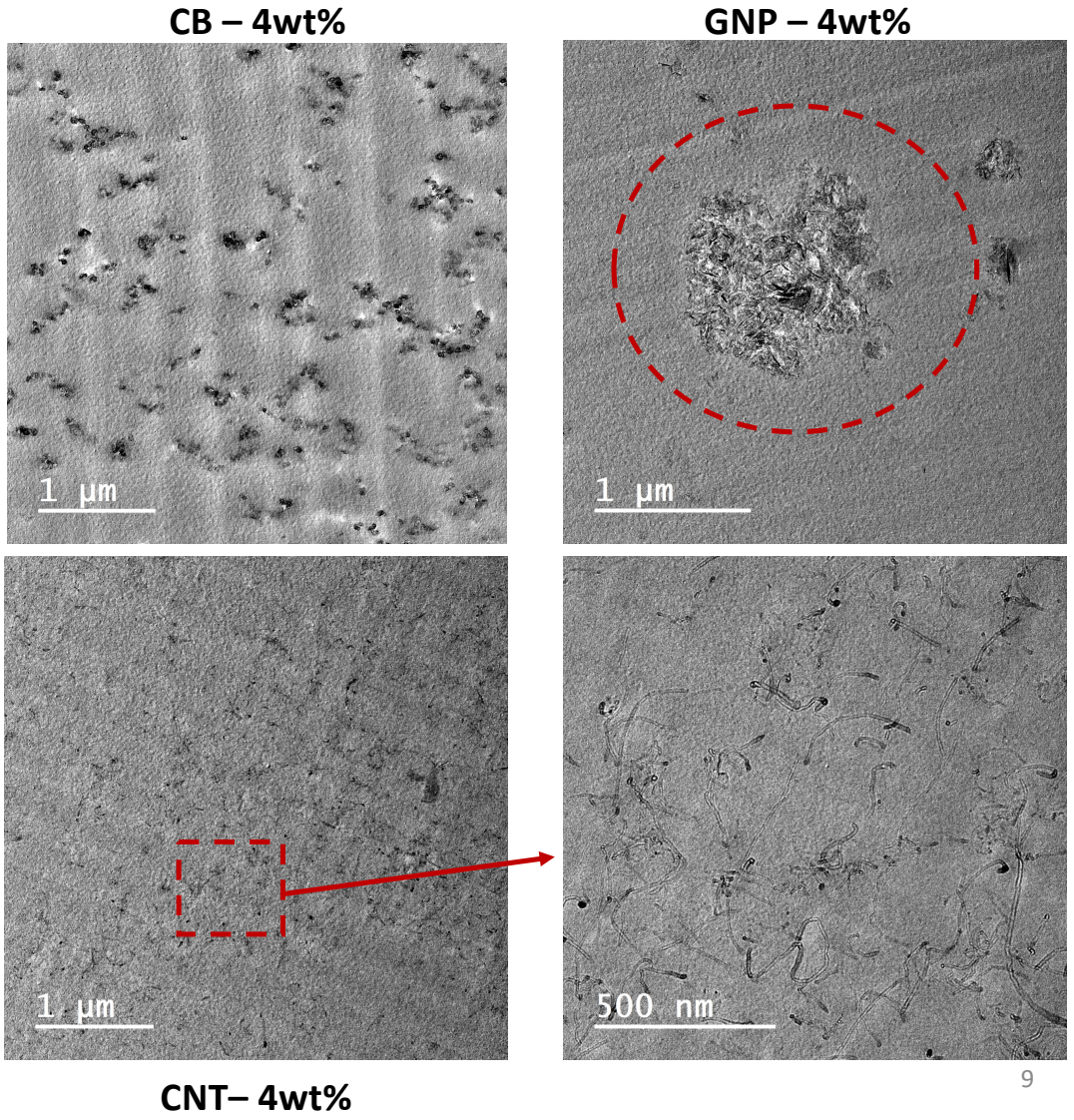
	ϕ_c (wt%)	t	R-square
CNT	0.21	1.80	0.99
CB	0.50	3.82	0.98
GNP	7.50	1.56	0.97

Essam, John W. "Percolation theory." *Reports on progress in physics* 43.7 (1980): 833.

CB vs CNT vs GNP: TEM

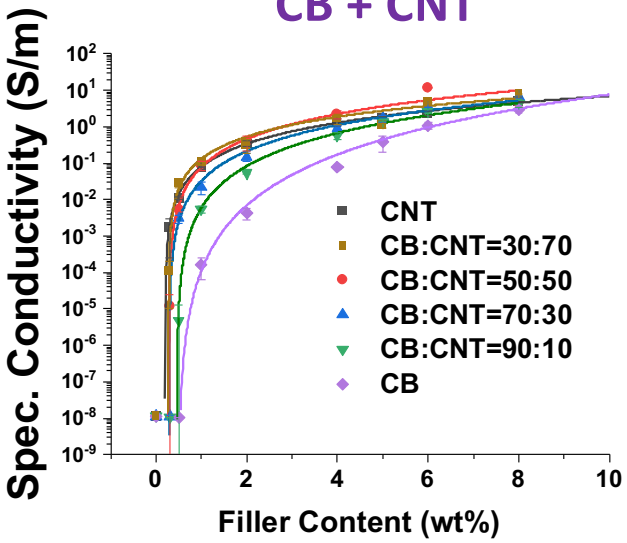


- CB: good dispersion
- CNT: good dispersion
- GNP: poor dispersion with agglomerations



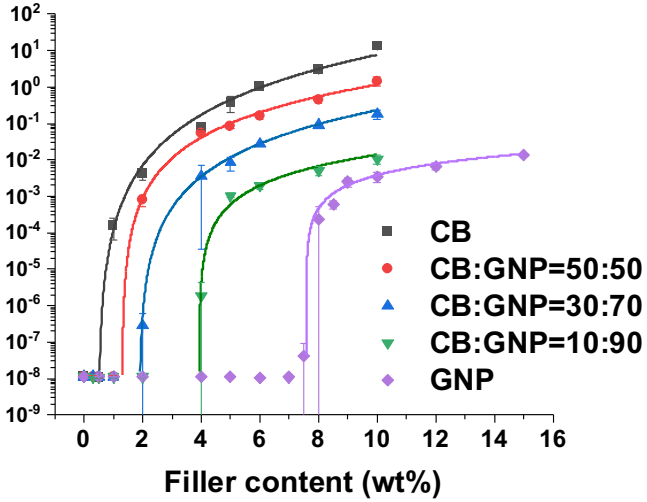
Hybrid systems: 100+ different masterbatches!

CB + CNT



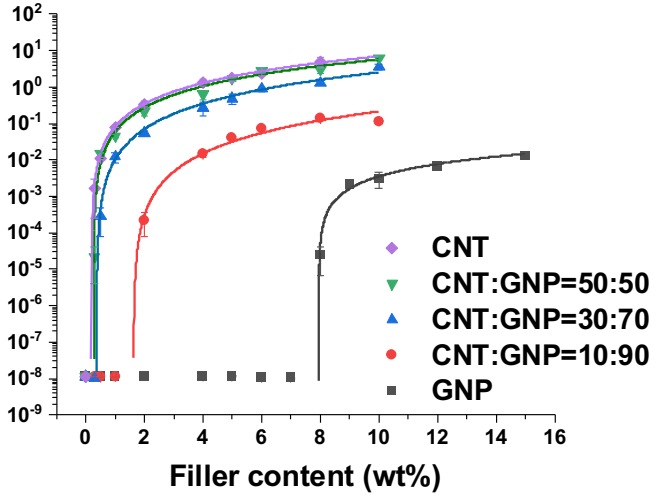
Ratio of CNT	Pc (wt%)	t
0	0.5	3.82
0.1	0.5	2.65
0.3	0.3	2.14
0.5	0.3	2.03
0.7	0.3	1.51
1	0.2	1.80

CB + GNP



Ratio of CB	Pc (wt%)	t
0	7.5	1.56
0.1	4.0	1.57
0.3	2.0	2.02
0.5	1.3	2.86
1	0.5	3.77

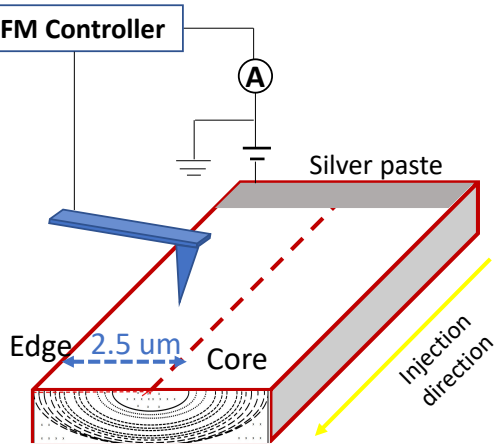
CNT + GNP

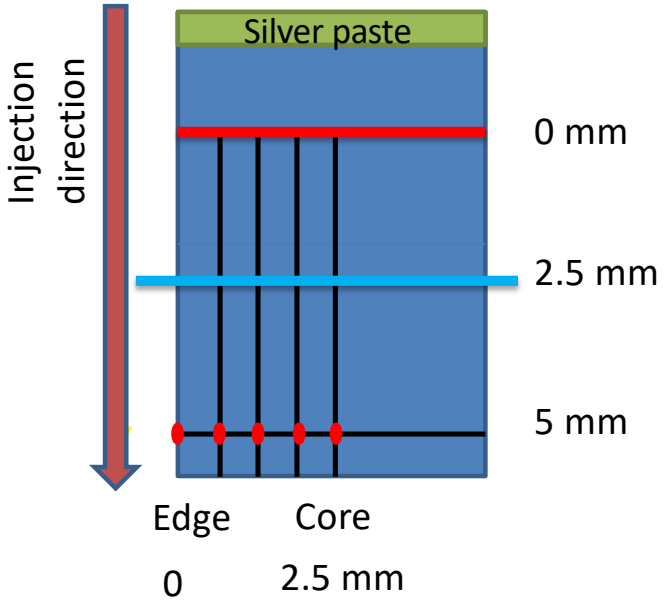


Ratio of CNT	Pc (wt%)	t
0	7.5	1.56
0.1	1.9	1.61
0.3	0.4	2.03
0.5	0.3	1.60
1	0.2	1.80

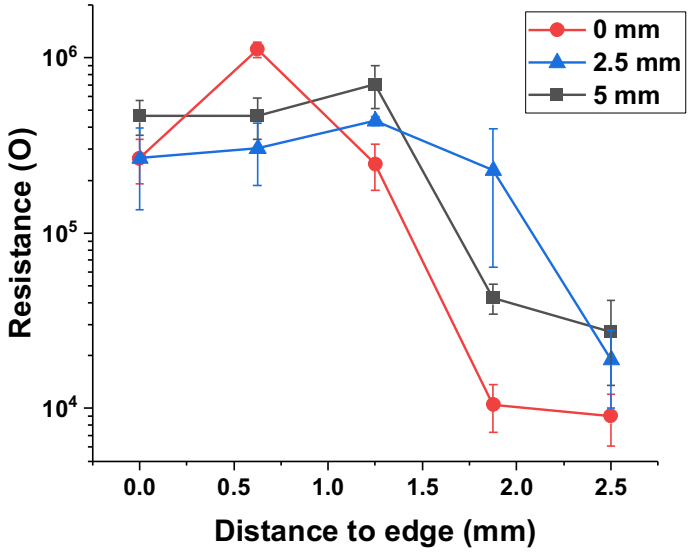
*R – Square of all fittings are higher than 0.9

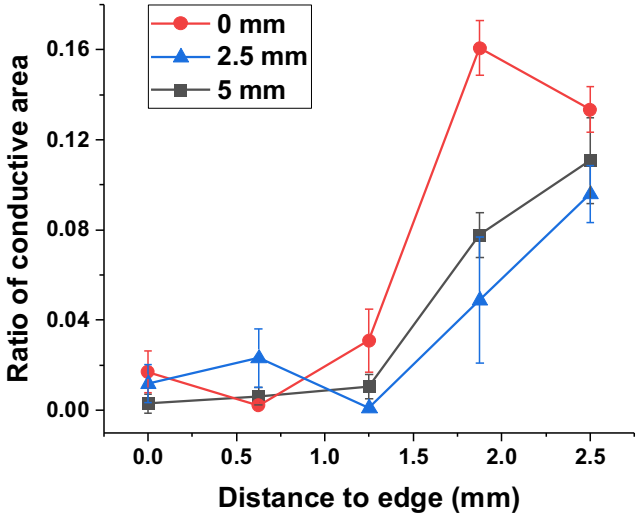
Orientation: Skin effect in the NT-PC composites





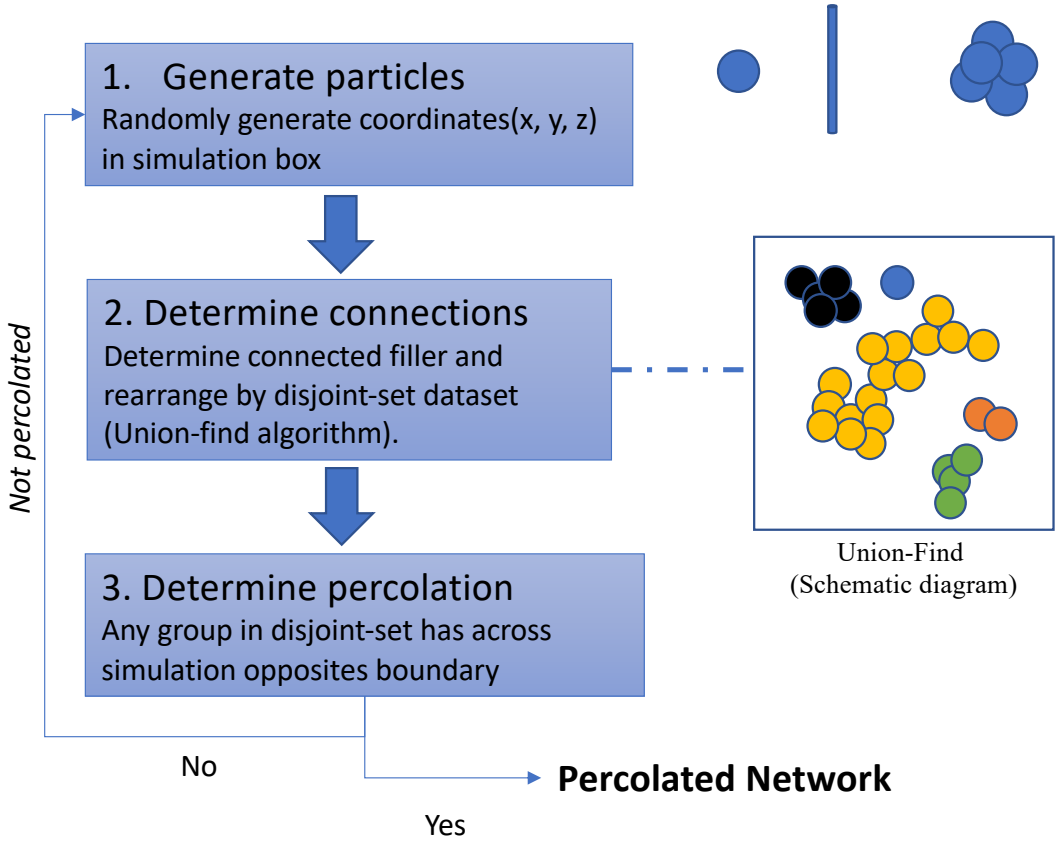
$$I = \sum_{j=1}^{J=16384} i_j \qquad R = \frac{V}{I}$$



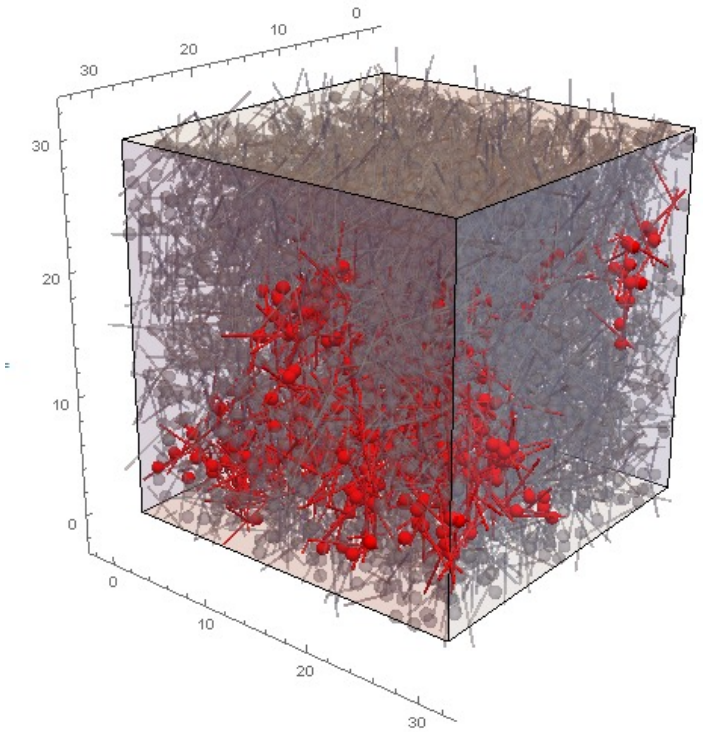


Simulation Methods

Simulations to probe percolation behaviour as a function of particle morphology and aggregation states.



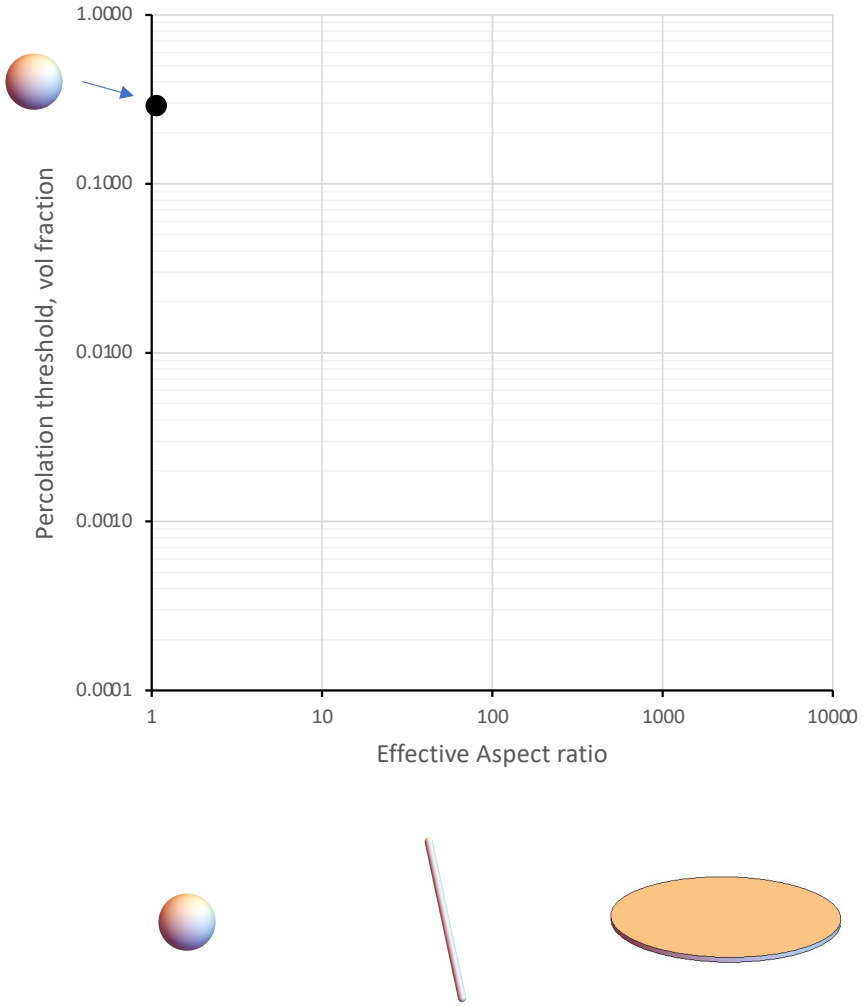
Union-Find
(Schematic diagram)

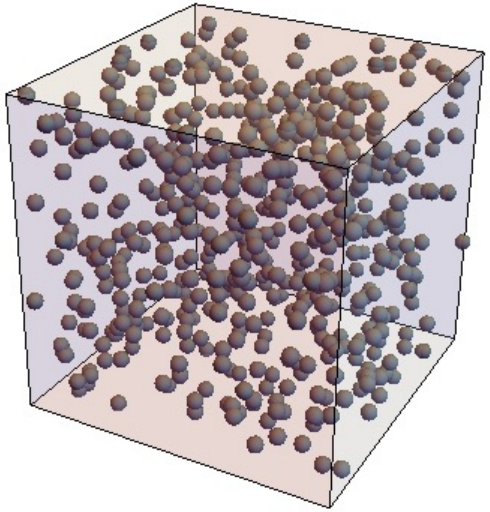


Percolation network

Percolating network(red) group that connect opposites boundary

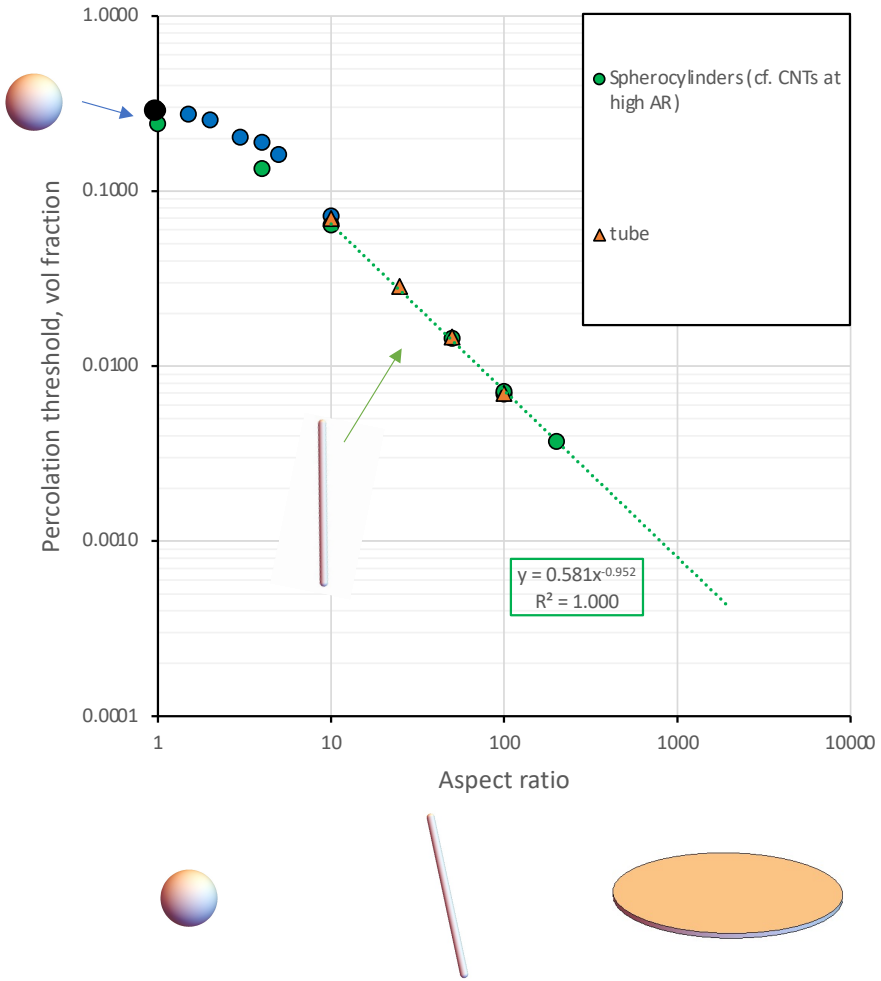
Relationship between particle morphology and percolation threshold

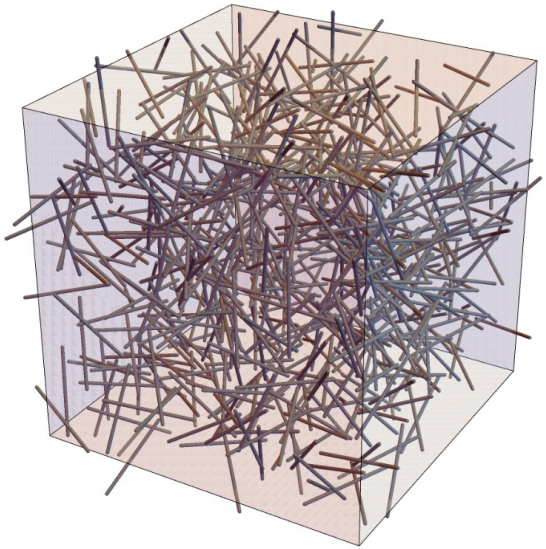




- Percolation threshold for sphere: 0.3 vol fraction
- Aspect ratio: 1

Relationship between particle morphology and percolation threshold



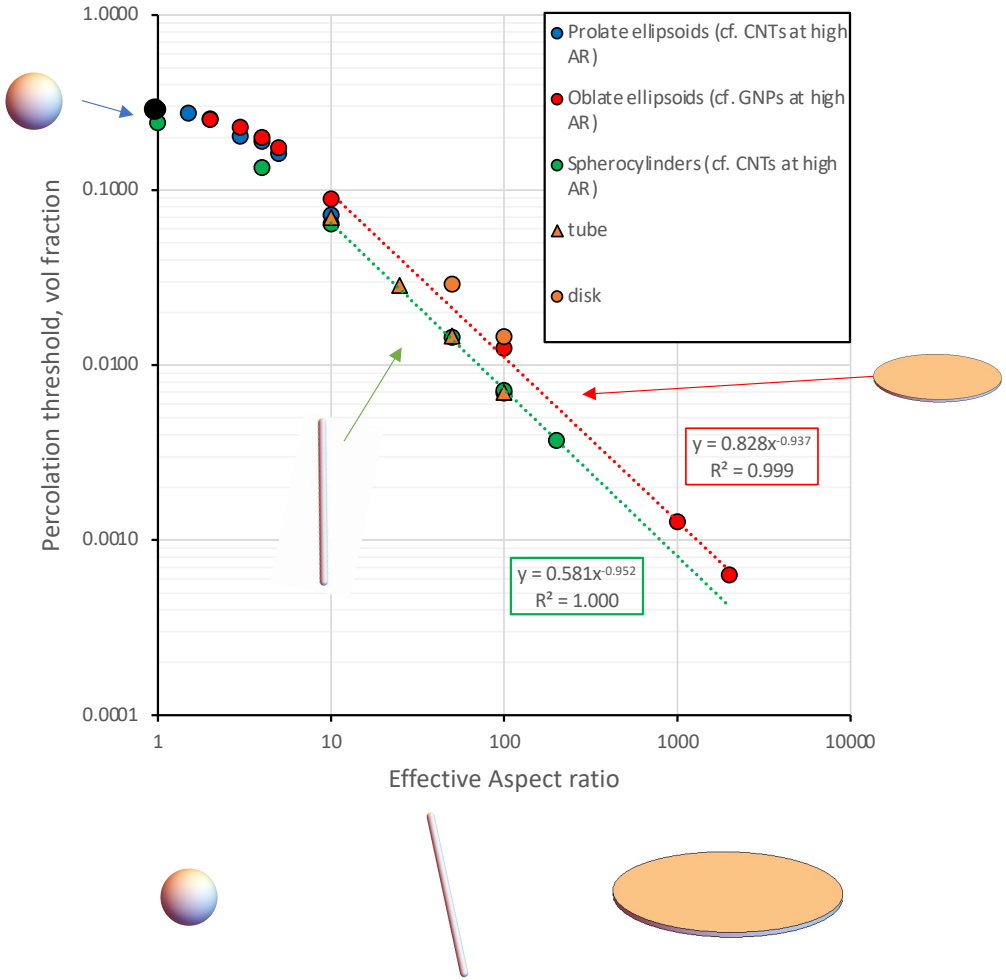


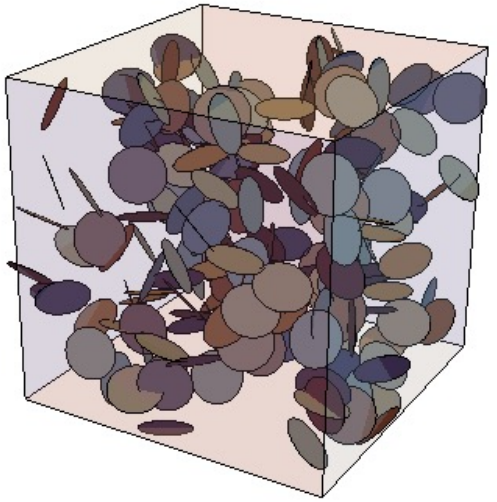
- For large aspect ratios and a statistical filler particle distribution the percolation threshold based on an **excluded volume concept** can be estimated by [1]:

$$p_c \approx 0.5 \cdot x^{-1}$$

[1] Balberg, I., Anderson, C. H., Alexander, S., & Wagner, N. (1984). Excluded volume and its relation to the onset of percolation. *Physical review B*, *30*(7), 3933.

Relationship between particle morphology and percolation threshold

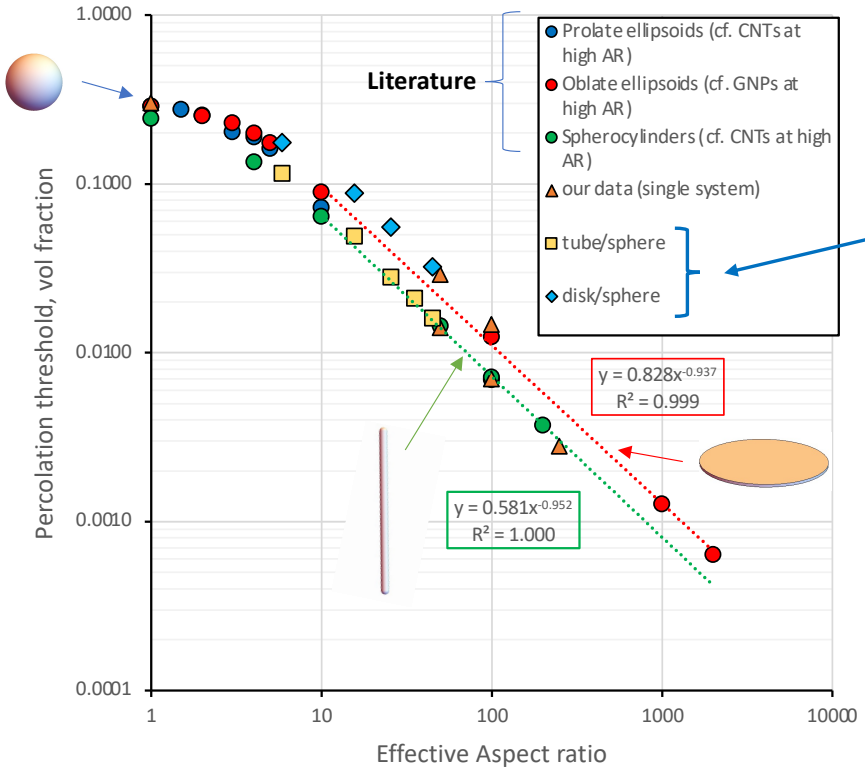




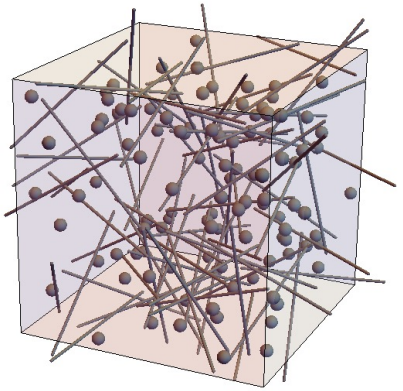
$$p_c = constants \cdot x^{-1}$$

- Percolation threshold, p_c results are collected from the literature and our data both indicate p_c dominated by filler aspect ratio.

Relationship between particle morphology and percolation threshold



$$p_c = constants \cdot x^{-1}$$



Sphere aspect ratio: 1
Tube aspect ratio: 100
Blend ratio: 1:1
Effective aspect ratio: 50

- Blends of:
  - spheres and disks (CB & GNP)
  - spheres and tubes (CB & CNTs)
  - Volume of each particle type the same
- Blend ratios: 10/90, 30/70, 50/50, 70/30 and 90/10 by volume.
- ‘effective aspect ratio’ is volume average aspect ratio.
- Data for blends fall close to lines for tubes and disks, confirming dominance of high aspect ratio.