The Tony Davies High
Voltage Laboratory

UNIVERSITY OF
Southampton

Nano-Silica Filled Polystyrene:

Correlating Breakdown Strength and Particle Agglomeration.

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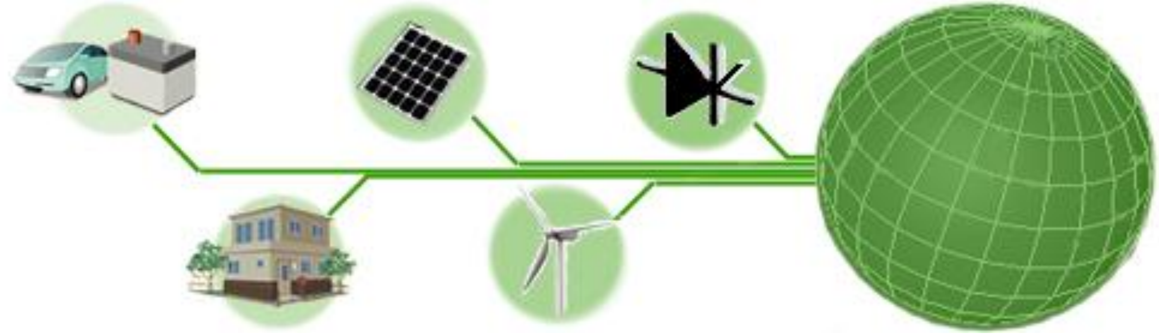
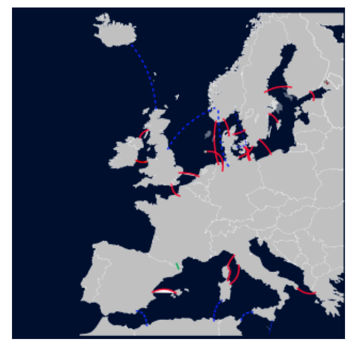
Top and Tail Transformation
A Grand Challenge in Energy Networks



Introduction:

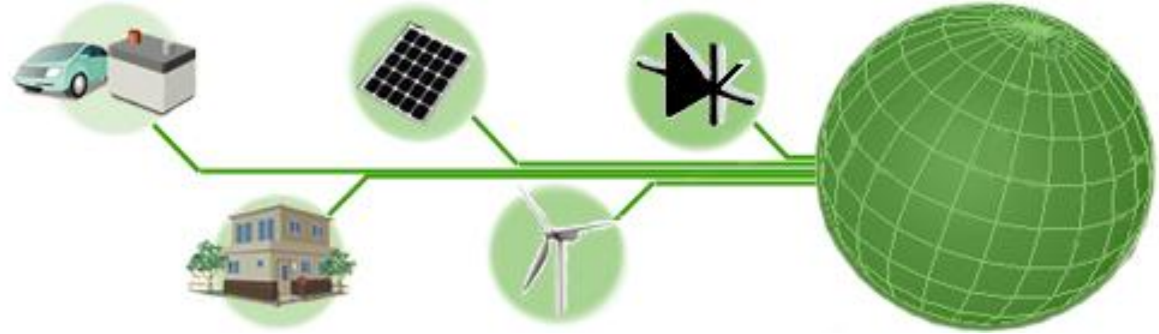
This work is part of an EPSRC funded project:
"Transformation of the Top and Tail of Energy Networks"

- Collaboration between 8 universities.
- And several industrial companies.



Top and Tail Transformation

A Grand Challenge in Energy Networks



Project Overview:

- The low carbon economy will challenge existing energy networks in two key areas:

  Tail :- Investigating the possibility of low voltage DC power delivery to the home.

  Top :- High voltage transmission to facilitate transcontinental energy exchange.

  - HVDC cable design and materials technologies.
  - Enabling future target ratings of 1 MV and 5 kA.

Current Aims for WP 1.3.1:

- We are currently investigating nano-filled dielectrics as a possible technology for high rating HVDC cable insulation.
- In particular, we aim to deepen understanding of the physical processes governing the action of nano-fillers;
- ...to enable engineering of better nano-dielectrics in the future.

Overview of Talk:

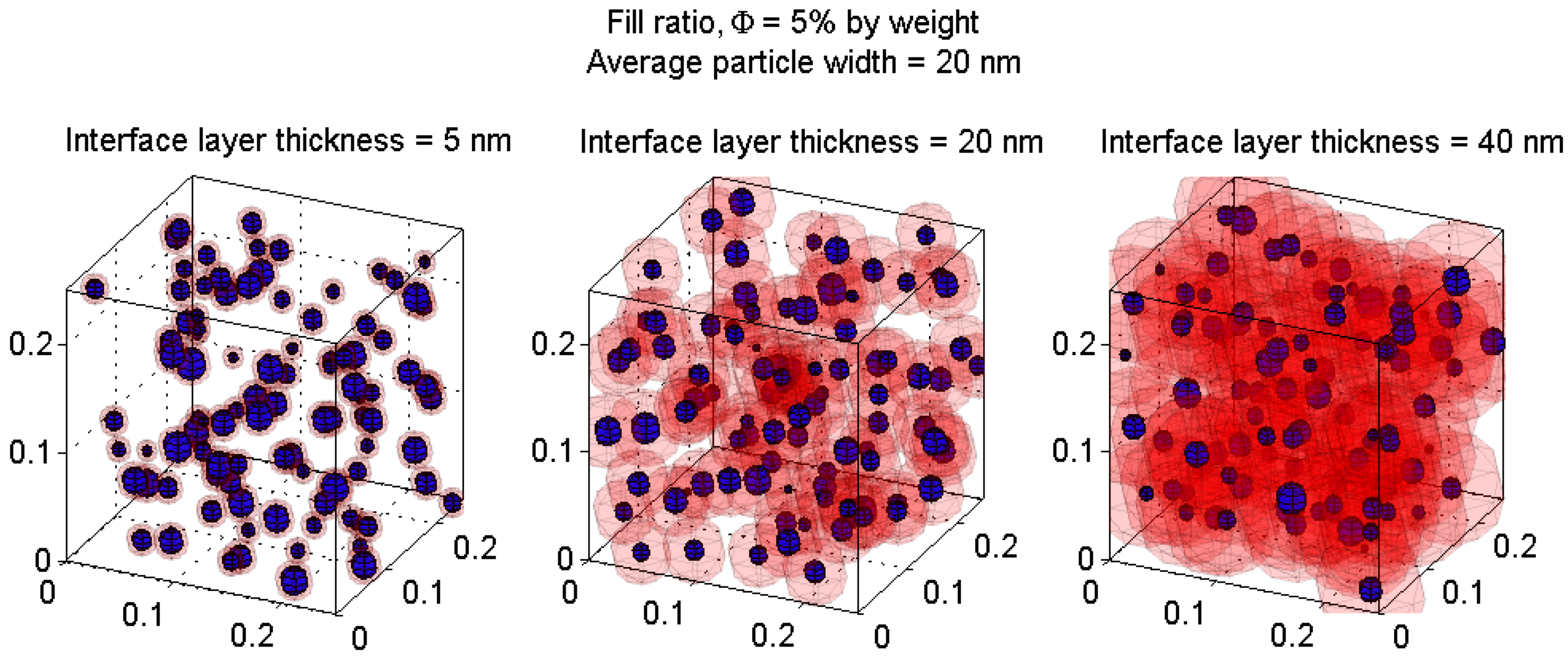
- ✓ Project overview and introduction.
- Some simple theoretical concepts for nano dielectrics.
- Overview of the present experimental work.
- Some initial results.
- Conclusion and future work.

Nano-dielectrics: (why they are interesting/strange).

- Add small quantities of nano-scale fillers to modify the material properties.
  - Relative Permittivity, Thermal Conductivity, etc.
- Simple predictions based on mixing ratios do not work:
  - Property X of A=1, Property X of B=2,
  - 50:50 Mixture of A and B has Property X ≠ 1.5.
- The properties are often a function of filler size.
  - Sometimes with a peak at low filler fraction.
- Nano-fillers potentially allow:
  - the production of materials with **extraordinary** properties,
  - ...or with properties **tailored** to particular applications.

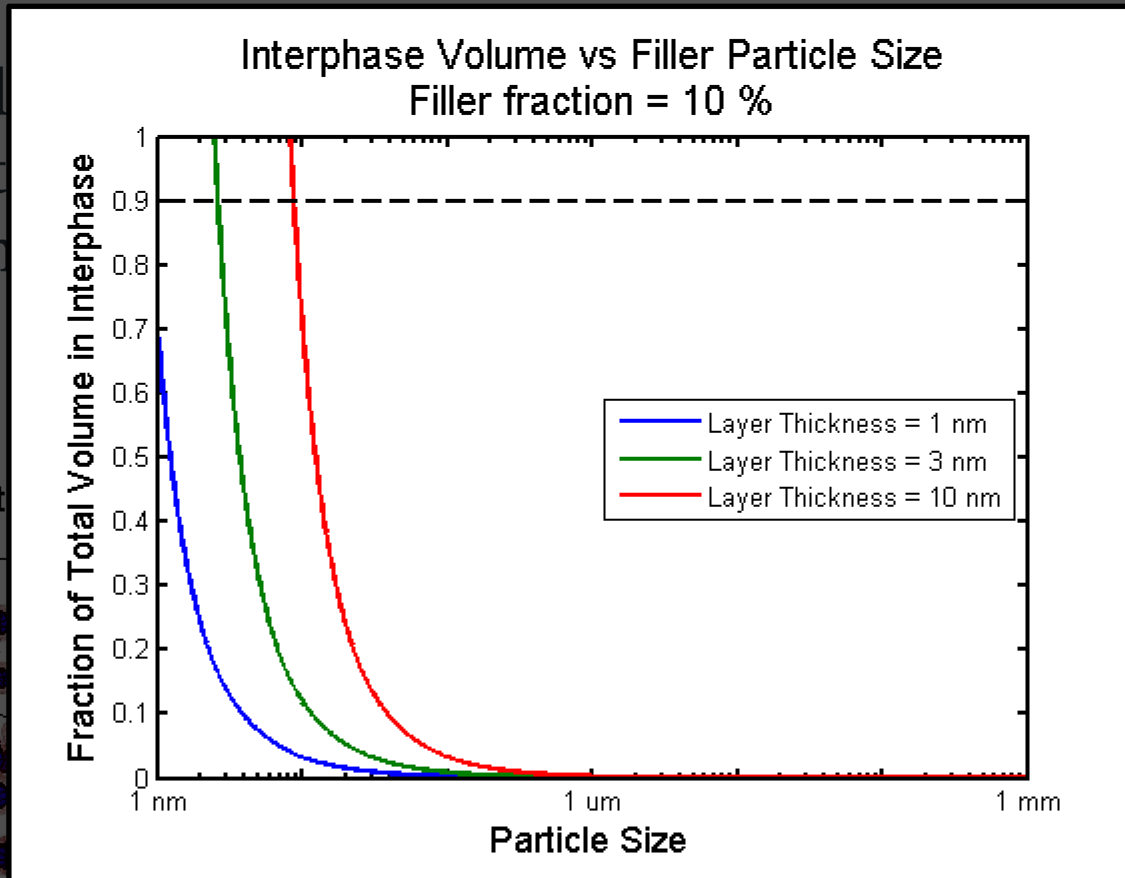
Nano-dielectrics 2: (Interphase)

- A possible explanation for some of the “strangeness” lies in the action of the interface region between the base polymer matrix and the nano-filler.

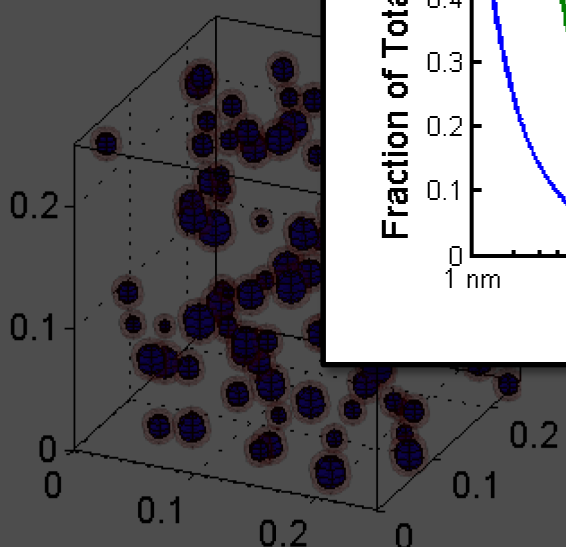


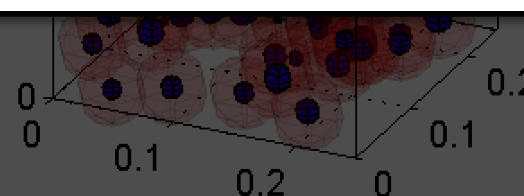
Nano-dielectrics 2: (Interphase)

- A possibl… the action of the int… matrix and the n…

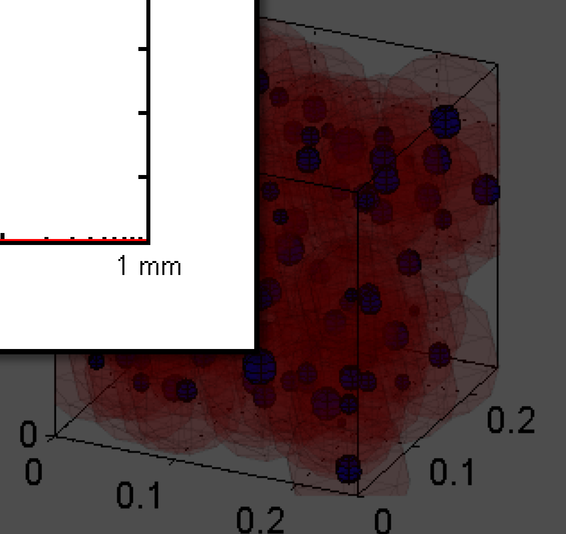


Interface layer t…

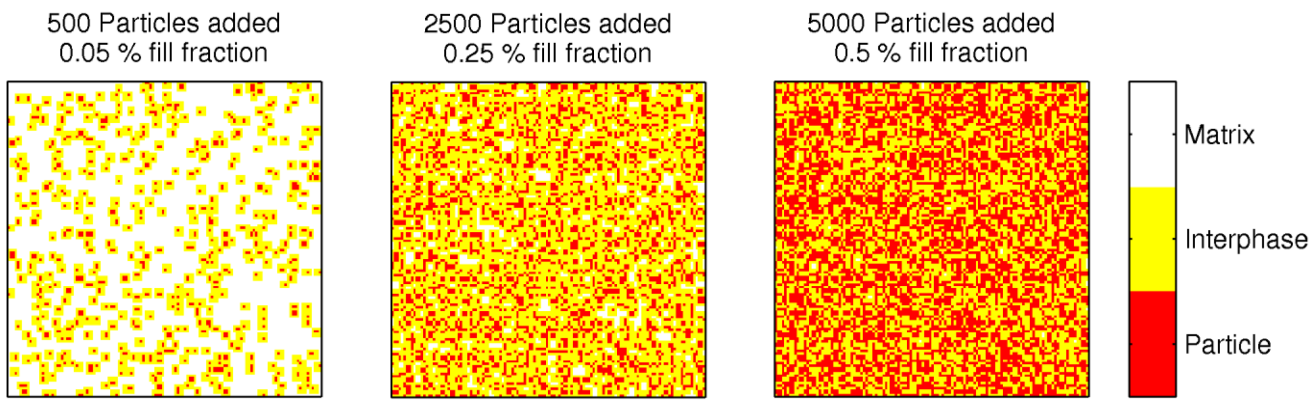




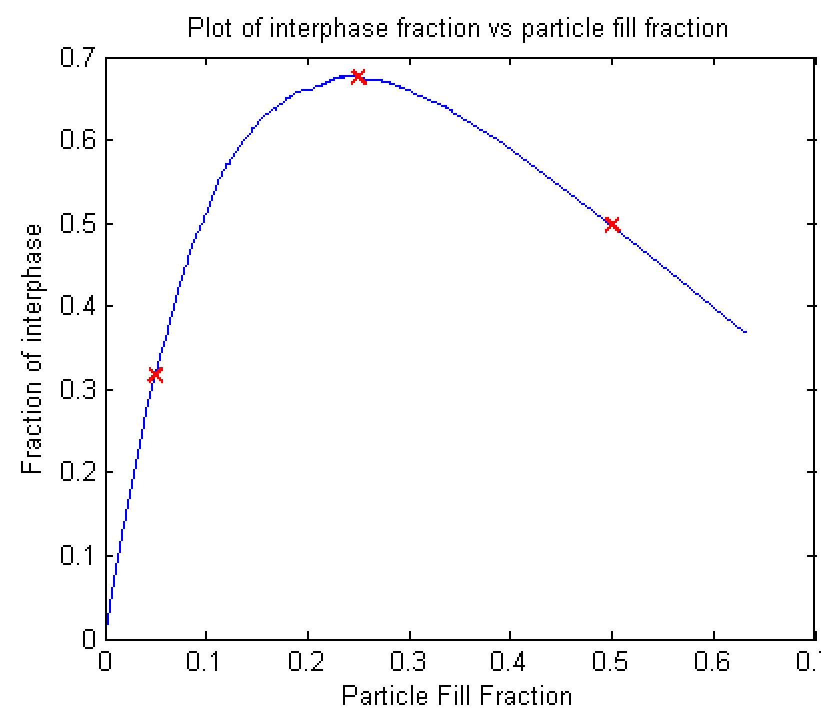
…r thickness = 40 nm



More filler is not always better:



- 2D "Monte Carlo" simulation:
- Progressively more filler is added.
- New particles can only occupy a matrix or interphase position.
- Unmodified filler is exhausted and the effect saturates.
- This produces a maximum in interphase volume at relatively low filler fractions.



Particle Dispersal:

- Agglomeration is serious issue for nano-dielectrics.
- When particles aggregate the effective particle size is much higher than expected.
  - Much of the benefit of the nano-filler can be lost.
  - Large aggregations may constitute significant defects in the base material which can make properties worse.
- Achieving good particle dispersal can be challenging.
  - This causes variability between experiments,
  - and has slowed the uptake of nano-fillers for industrial use.

Overview of experimental work:

"we aim to deepen understanding of the physical processes governing the action of nano-fillers;

...to enable engineering of better nano-dielectrics in the future."

- In the remainder of this section I will briefly present two studies:
  - DC breakdown.
  - SEM following Permanganic etching.
- We aim to correlate these results in order improve our understanding of the action of the nano fillers.
  - In particular we are interested in the effects of particle agglomeration.

Material System:

- For this initial study we have chosen **polystyrene** as the polymer matrix.
  - The amorphous matrix allows permanganic etching to reveal the nano fillers for SEM.
  - There are no lamella or crystal structures to complicate the analysis.

- The filler used is **nano-silica**:
  - Spherical porous type (637246 ALDRICH)
  - Typical particle size 5-15 nm

Very simple sample preparation:

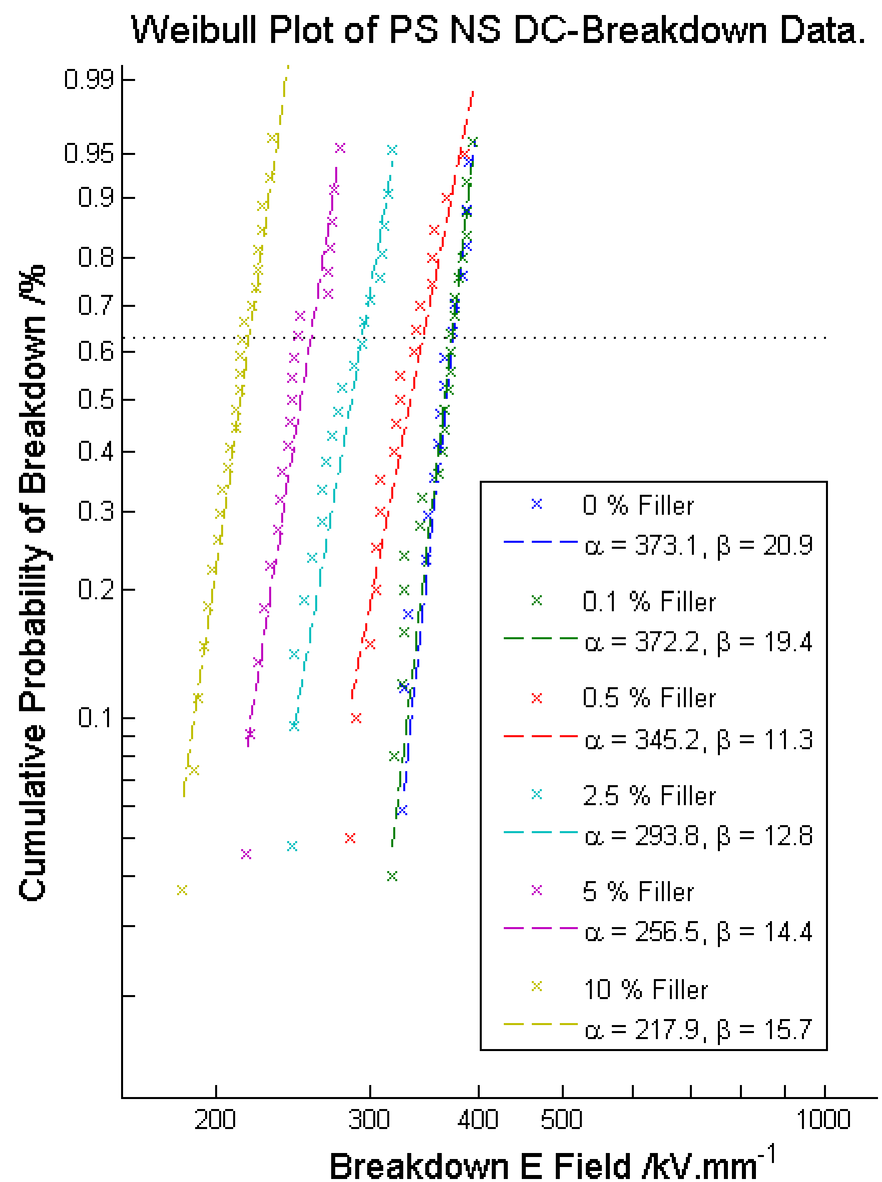
- Weight out PS and NS.
- Sonicate NS in DCM for 1 hour.
- Dissolve PS in DCM and add sonicated PS+NS.
- Shake samples for 1 hour.
- Evaporate DCM at room temperature.

- Samples are granulated and pressed 5 times at 175°C to remove residual solvent and bubbles.

DC breakdown:

- Breakdown tests carried out under silicone oil.
- Between two ball-bearings.
- Ramp rate of 100 V/s.
- Typical film thickness of 80 µm.

- These results clearly indicate a degradation of breakdown strength with the addition of nano filler.



DC breakdown:

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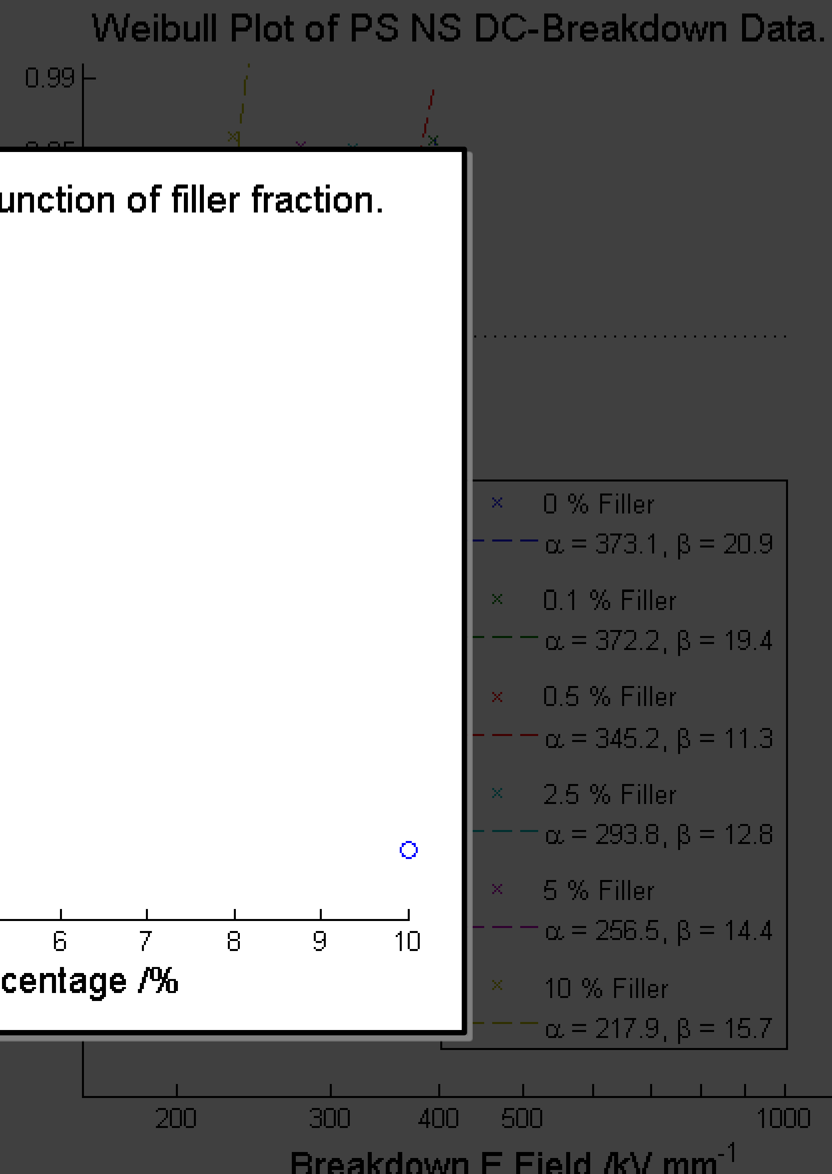
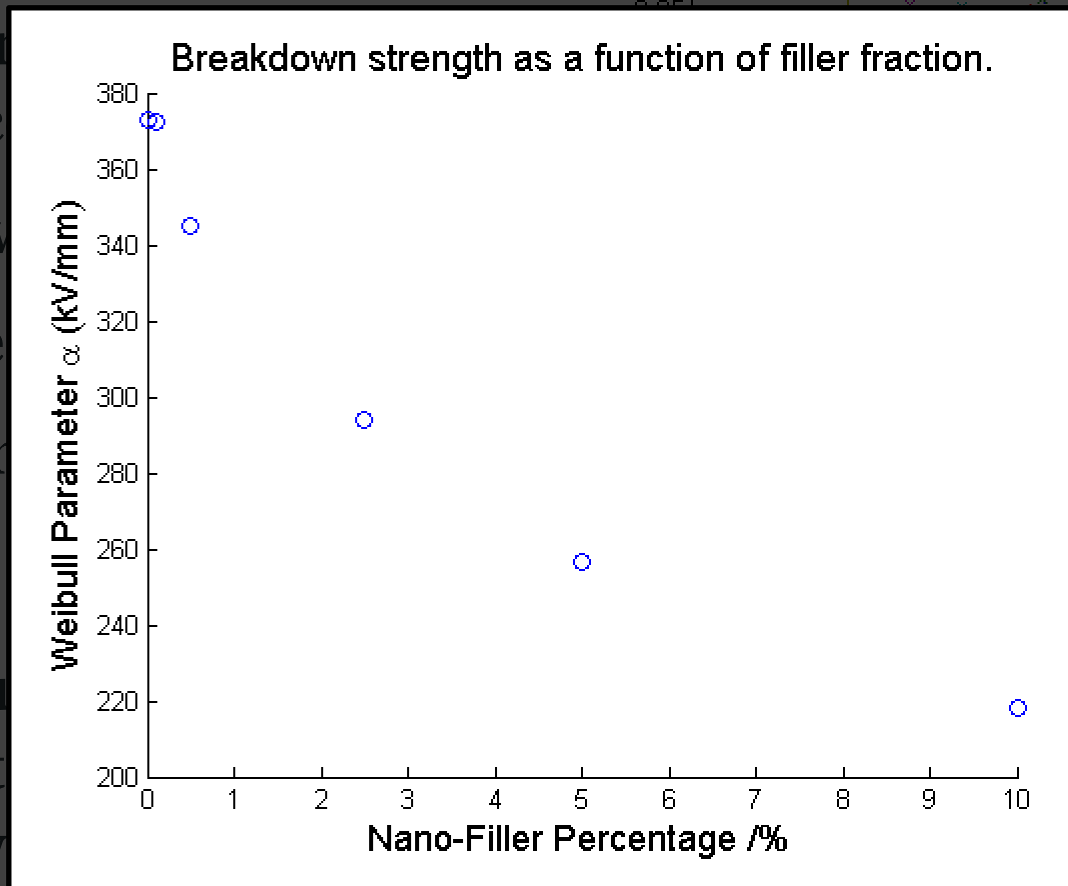




Permanganic Etch

- Etch solution:

$5\ H_2SO_4\ :\ 2\ H_3PO_4\ :\ 1\ H_2O\ +\ 1\%\ KMnO_4$

Sulphuric Acid : Phosphoric Acid : Water + Potassium Permanganate

- It is vital to agitate continuously during etch.

- Quench solution:

$2\ H_2So_4\ :\ 7\ H_2O\ +\ 20\%\ H_2O_2$

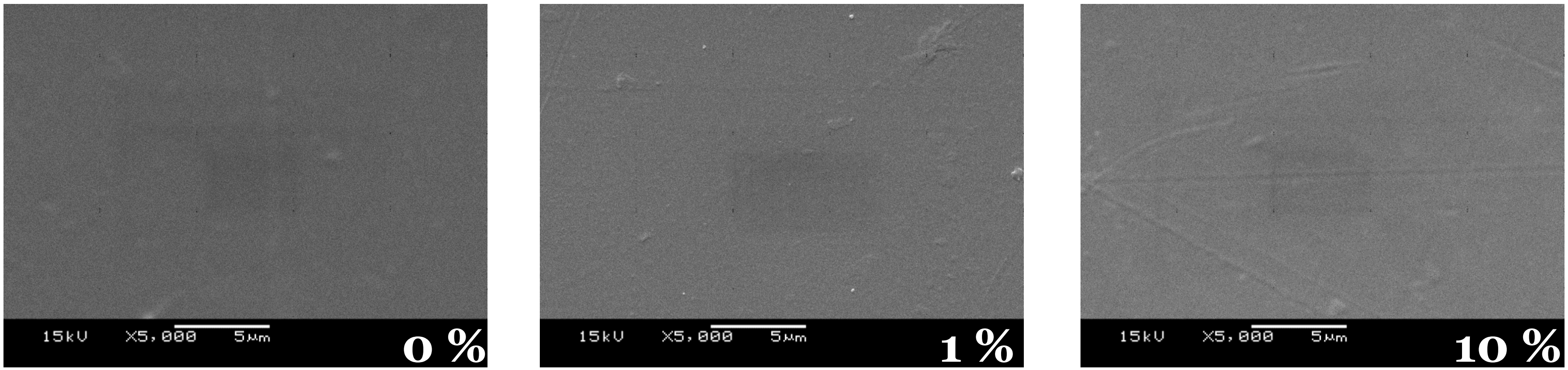
Sulphuric Acid : Water + Hydrogen Peroxide

- Caution: The etchant can be explosive if mixed incorrectly.

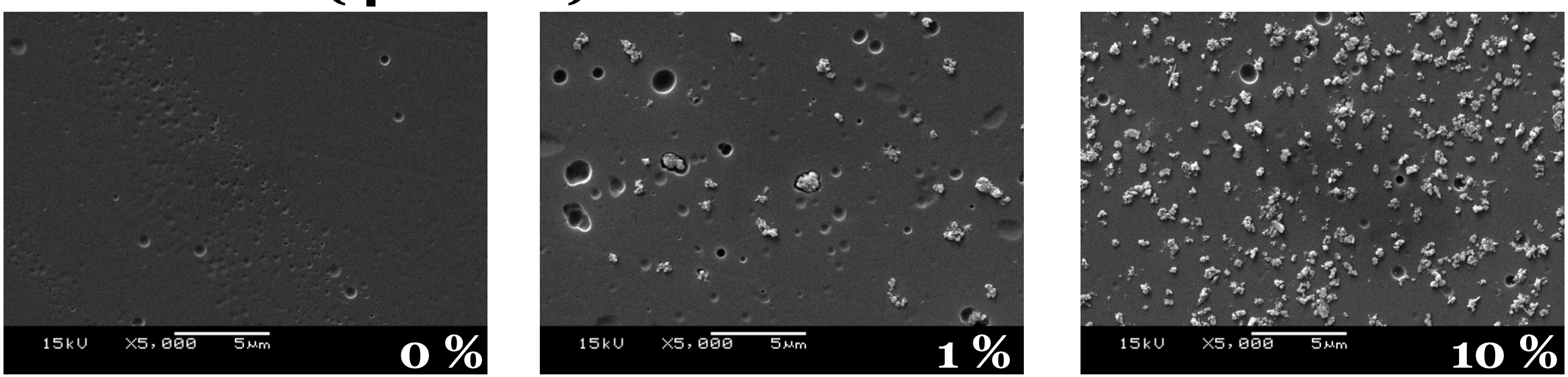
[1] R.H. Olley, D.C. Bassett, An improved permanganic etchant for polyolefines, Polymer, Volume 23, Issue 12, November 1982, Pages 1707-1710

SEM imaging:

Before Etch:



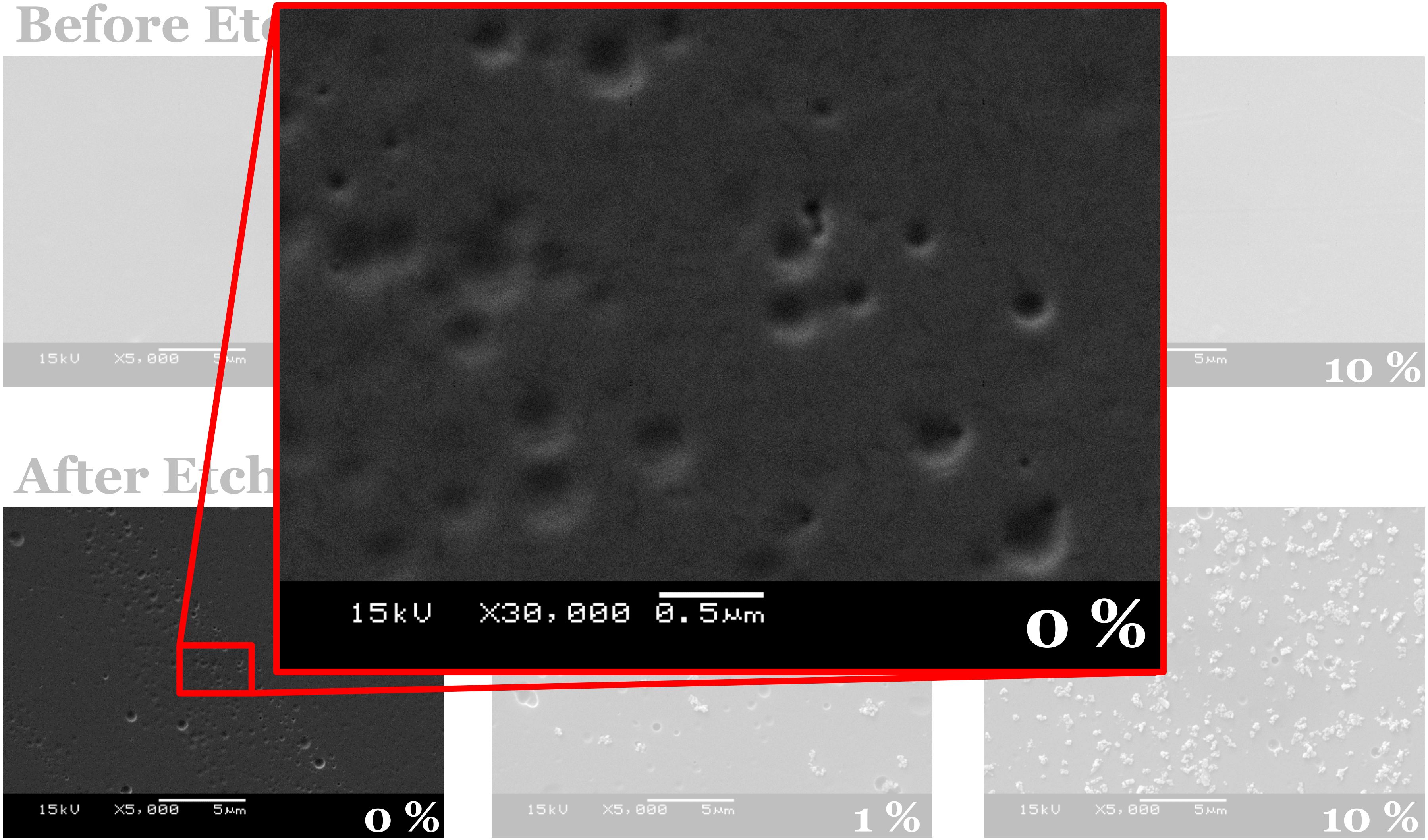
After Etch (4 hours):



SEM imaging:

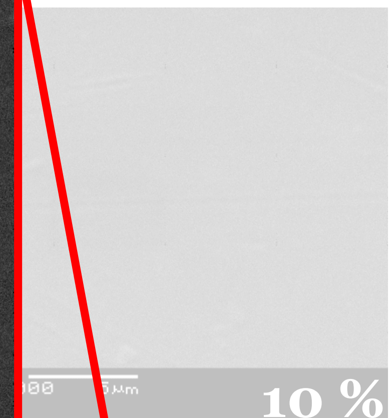
Before Etch

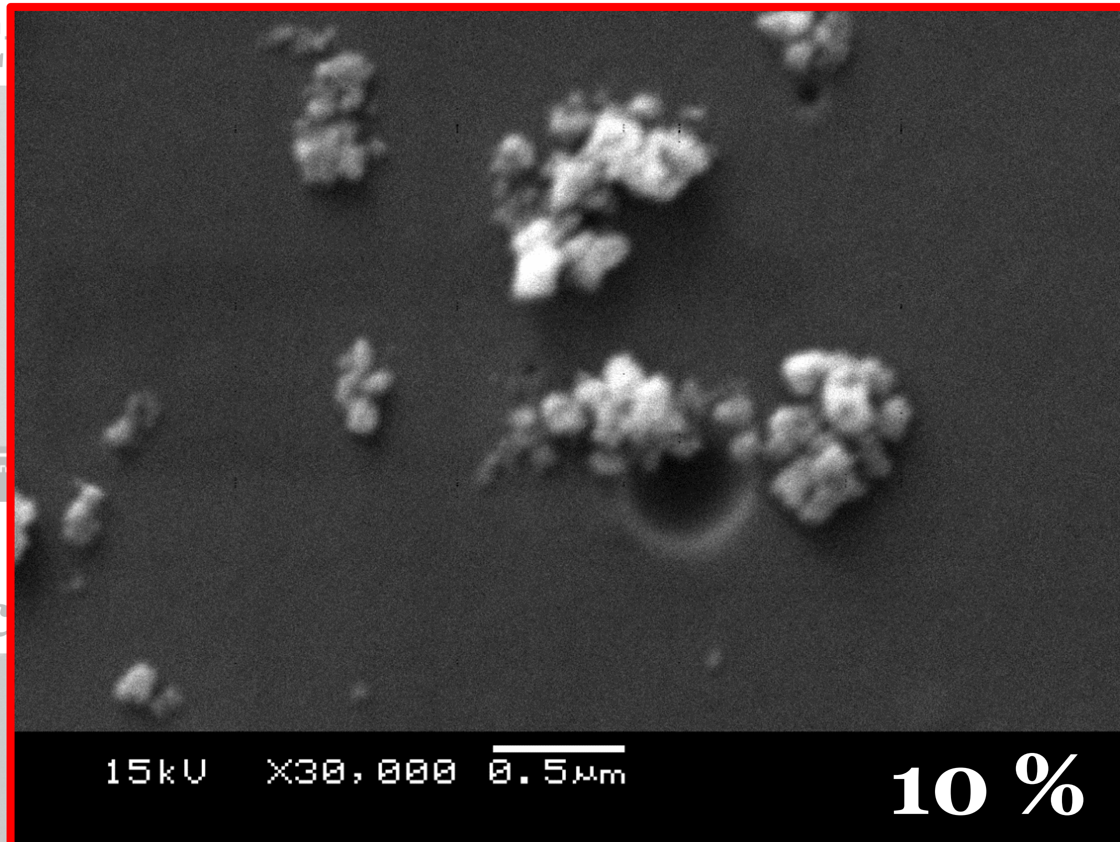
After Etch



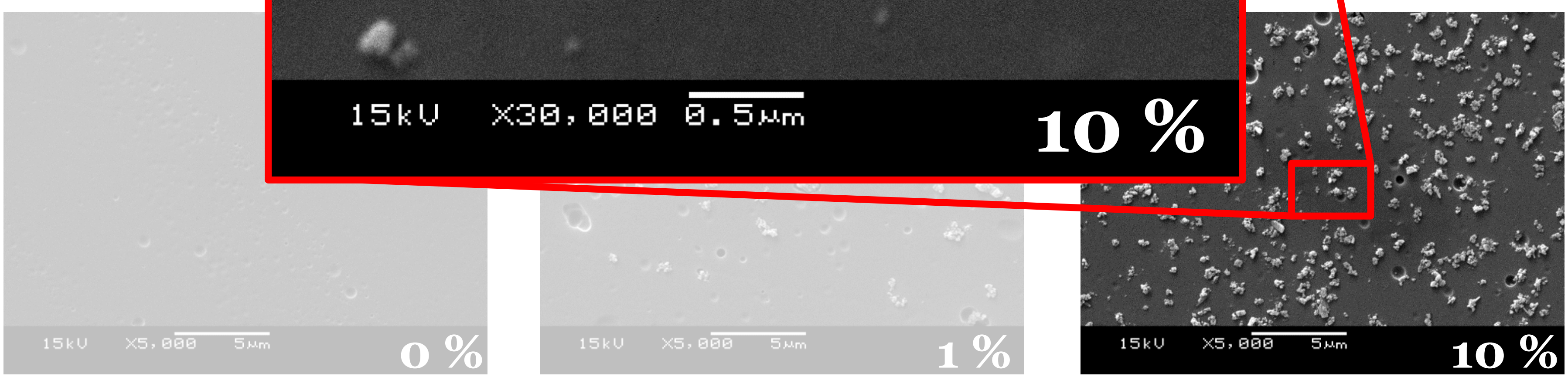
SEM imaging:

Before E



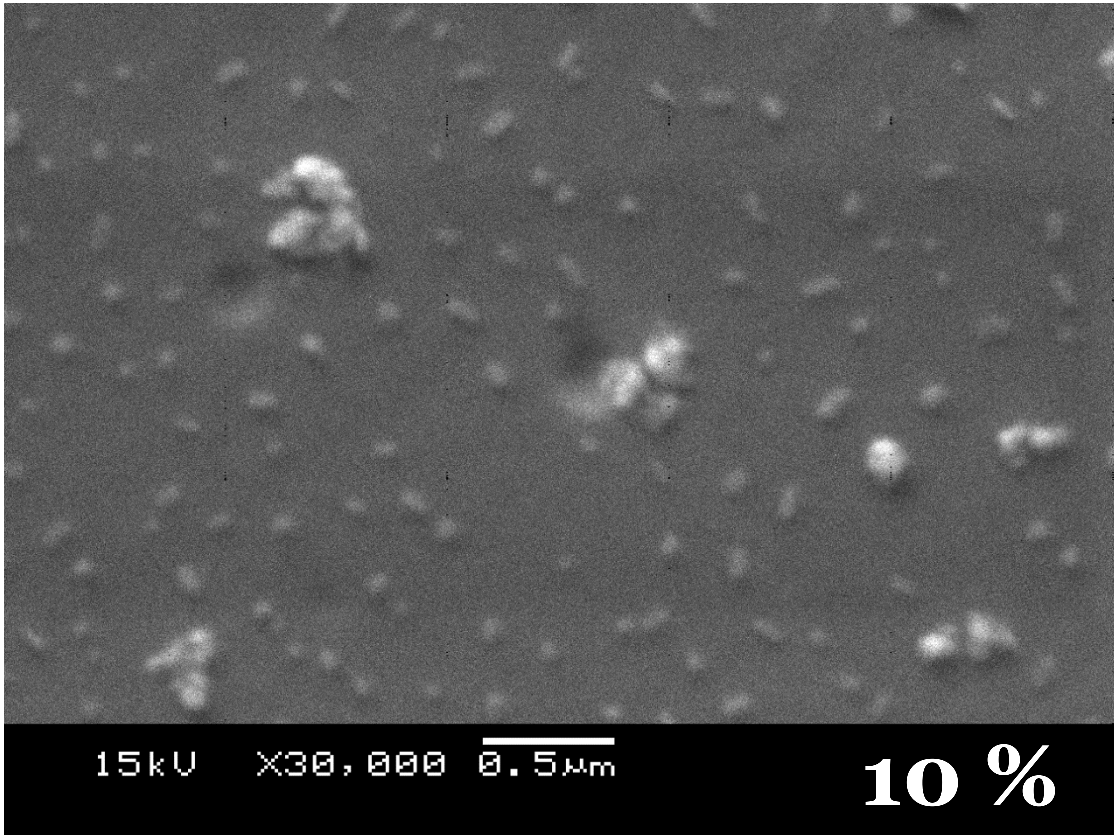


After Etc



Some regions have better filler dispersal:

1 Hour Etch:



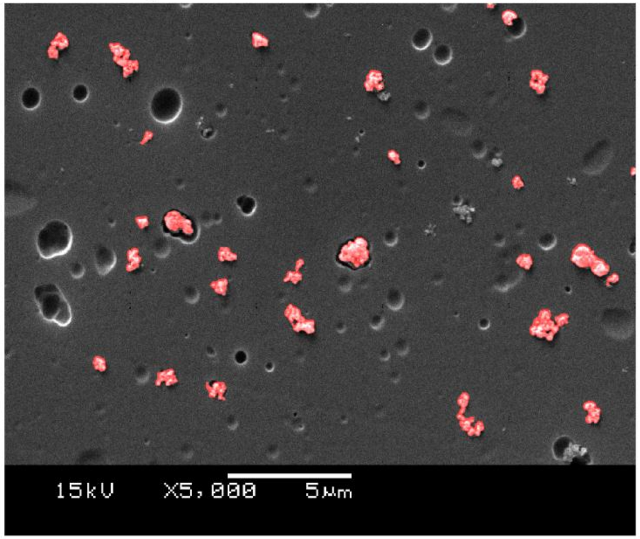
Conclusions:

- The simple sample preparation protocol tested resulted in significant nano-filler agglomeration.
- The agglomerated nano-filler decreased the DC breakdown strength.
- Permanganic etching of polystyrene provides excellent contrast between the nano-filler and the matrix.
- This technique successfully reveals the agglomeration of the filler.

Future Work:

- We now need to repeat the experiment with a protocol that achieves better nano-filler dispersion. (Coupling agent).
- Other material properties such as thermal conductivity or relative permittivity could also be measured and correlated with the degree of agglomeration.
- Image analysis of the SEM data is underway:
  - It is hoped this will yield useful statistics such as mean particle size for correlation with the breakdown data.

Resulting Selection: Mean particle area = 0.397 μm²

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