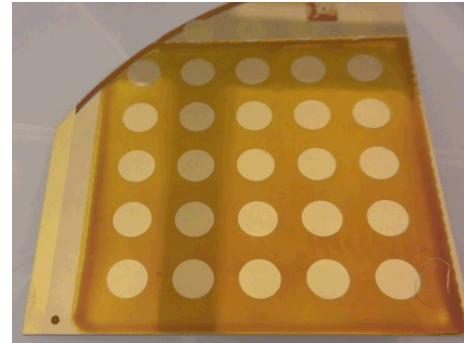
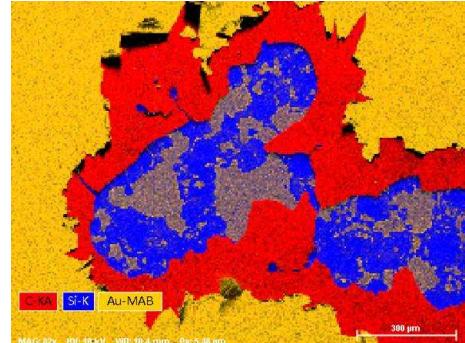
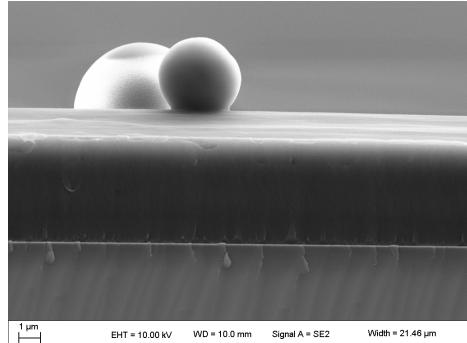
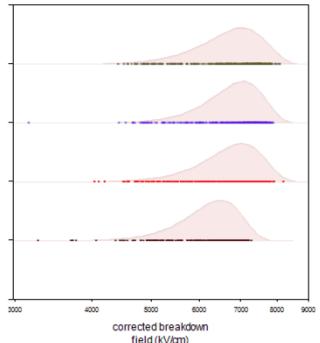


Exceptional service in the national interest



Dielectric Properties of Additively Manufactured vs. Solvent Cast Polyimide

Leah Appelhans*, David Keicher, Judi Lavin

Motivation and Approach



Use AM techniques to improve energy storage capabilities through development of '3-D' capacitors

- Explore additive manufacturing (AM) techniques for the production of polymer dielectrics for capacitors
- Understand origin of performance differences
 - Compare performance of AM films to solvent cast lab-made films
 - Compare both groups to commercial films
 - Differentiate between *process* and *scale* contributions to performance

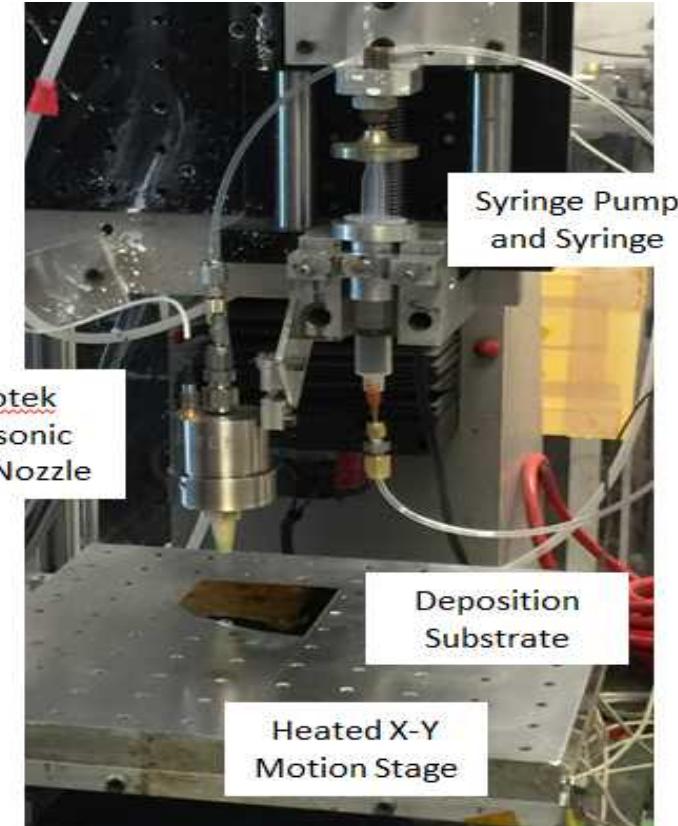
Additive Manufacturing

Advantages

- fewer design constraints
- easily customized/adaptable
- potential to fit capacitor to available space

Disadvantages

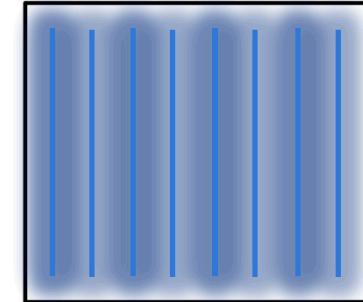
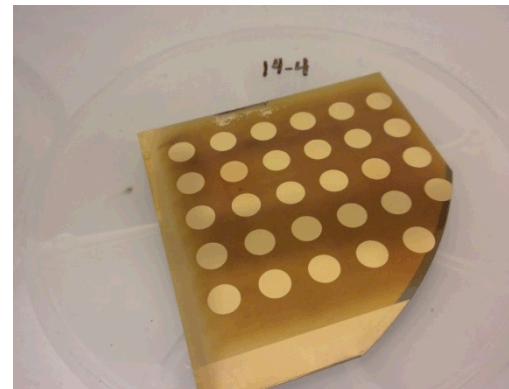
- deposition quality
- morphology/surface roughness
- defect density
- application to dielectric polymers



Additive Manufacturing

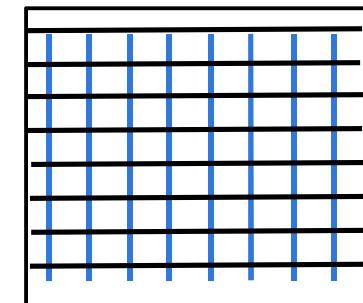
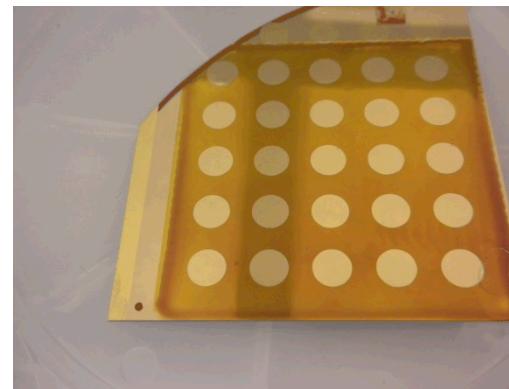
AM Spray

- **Sonotek ultrasonic spray nozzle**
- **staggered overlay**



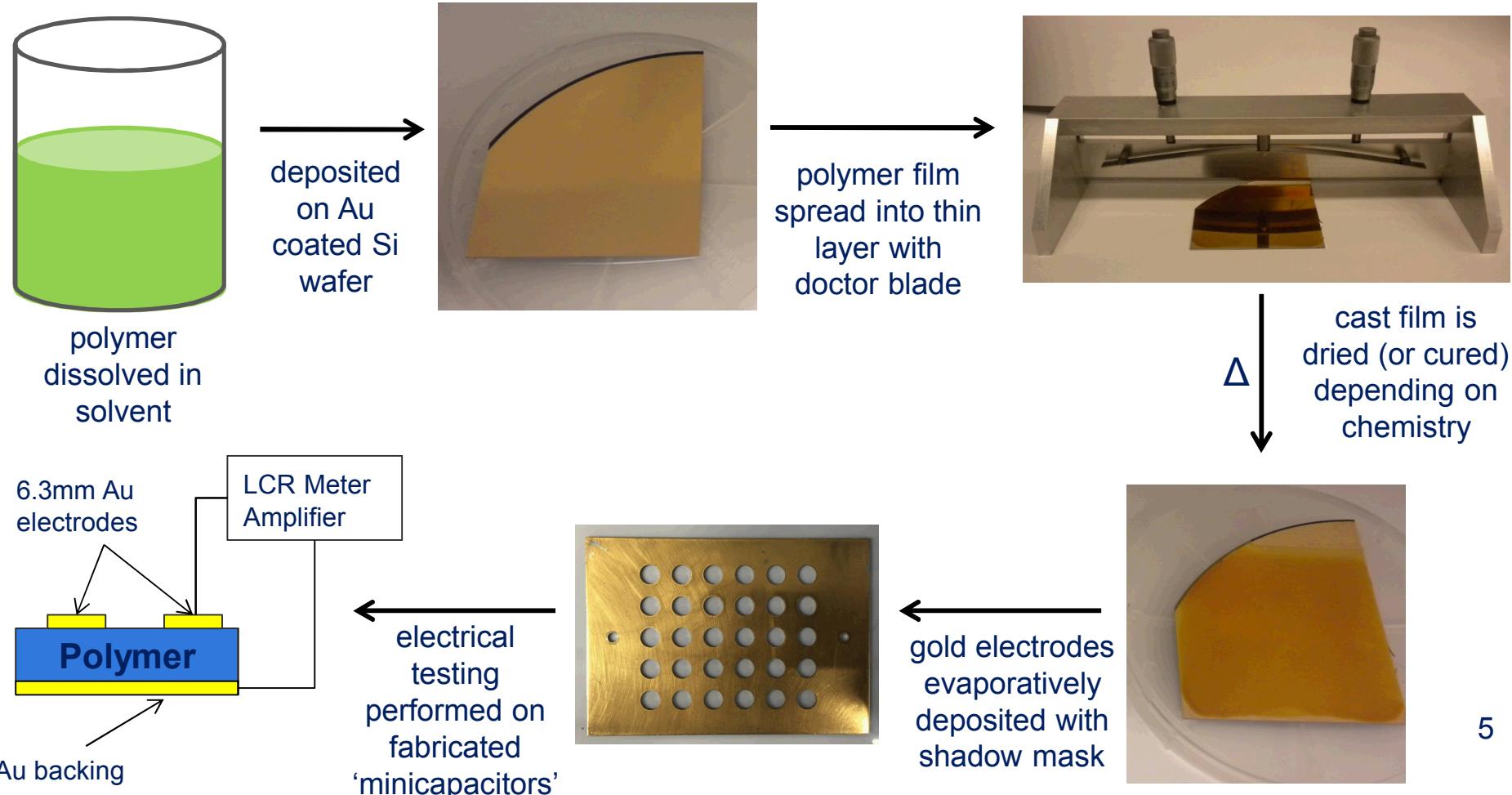
AM Syringe

- **250µm syringe tip**
- **250µm above substrate**
- **1 pass in X and Y**



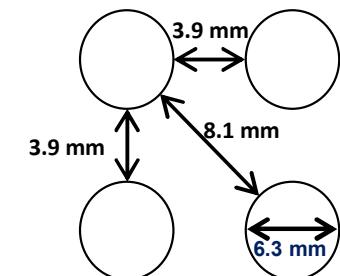
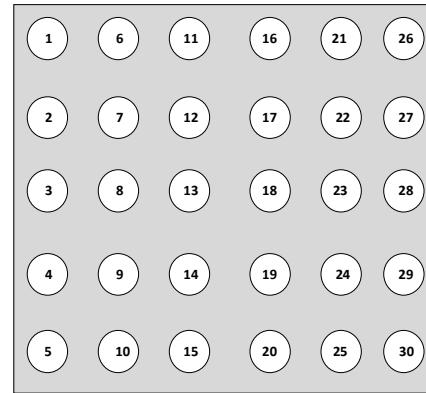
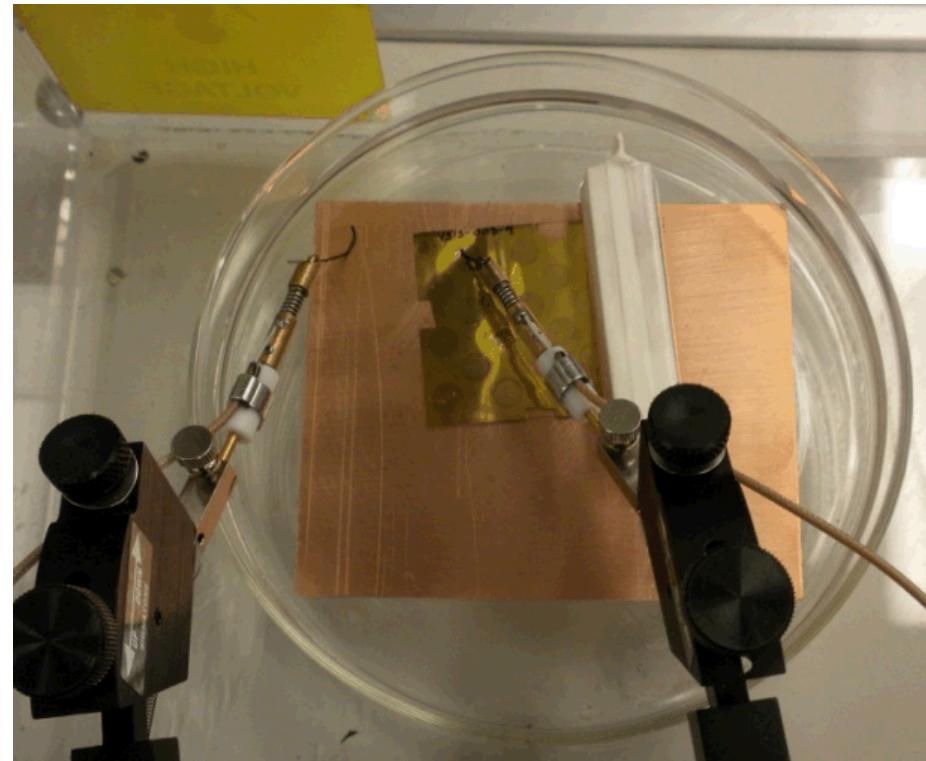
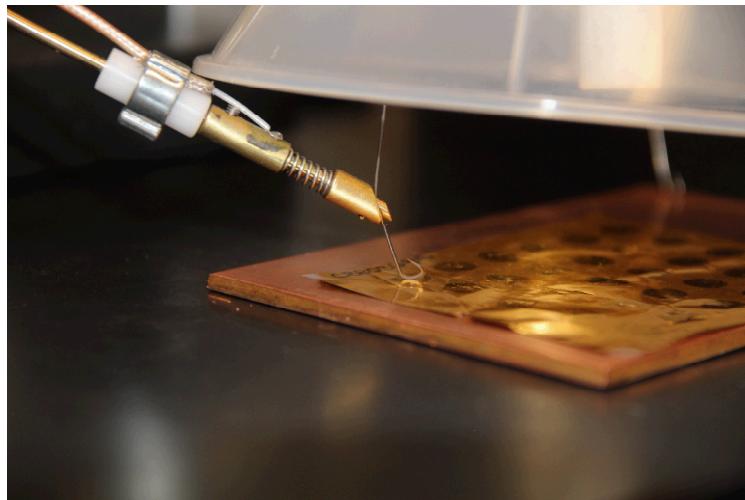
Solvent Casting

- Lab-made solvent cast films will be produced by doctor blade or spin-coating



Dielectric Testing

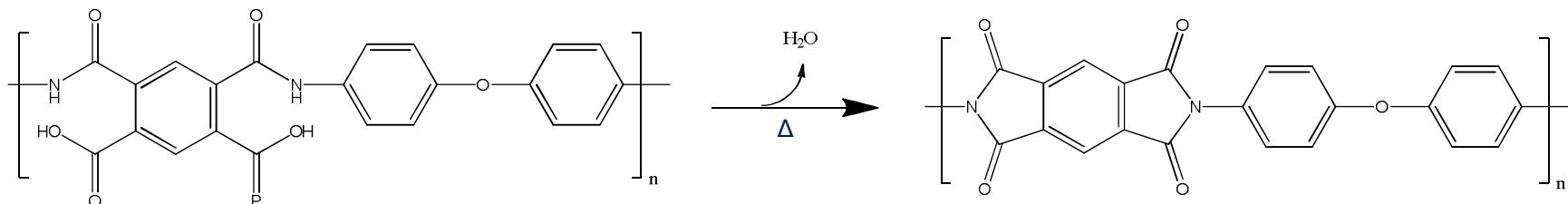
- κ/D_F : measure permittivity and loss from 100 Hz to 1 MHz
- **breakdown strength (E_B):** immerse film in Fluorinert and test ramp-to-fail DC breakdown, at ramp rate of 500 V/s



Polyimide

Polyimide: Polyimides are solvent cast or AM deposited as a solution of the polyamic acid. They must be thermally cured to be converted to the polyimide.

SA PI: poly(pyromellitic dianhydride-co-4,4'-oxydianiline) amic acid



Sigma-Aldrich 575828, 15wt% in NMP/aromatic hydrocarbons

UTD PI: UT Dots PI1-AJ polyimide precursor, in ethanol, proprietary formulation,

Commercial PI: Kapton® HN, 50G, American Durafilm

Data Analysis: Weibull Distribution

Weibull distributions are used to analyze dielectric breakdown strength or lifetime data. Samples are tested to failure and the time to failure is the measured value upon which the distribution is calculated.

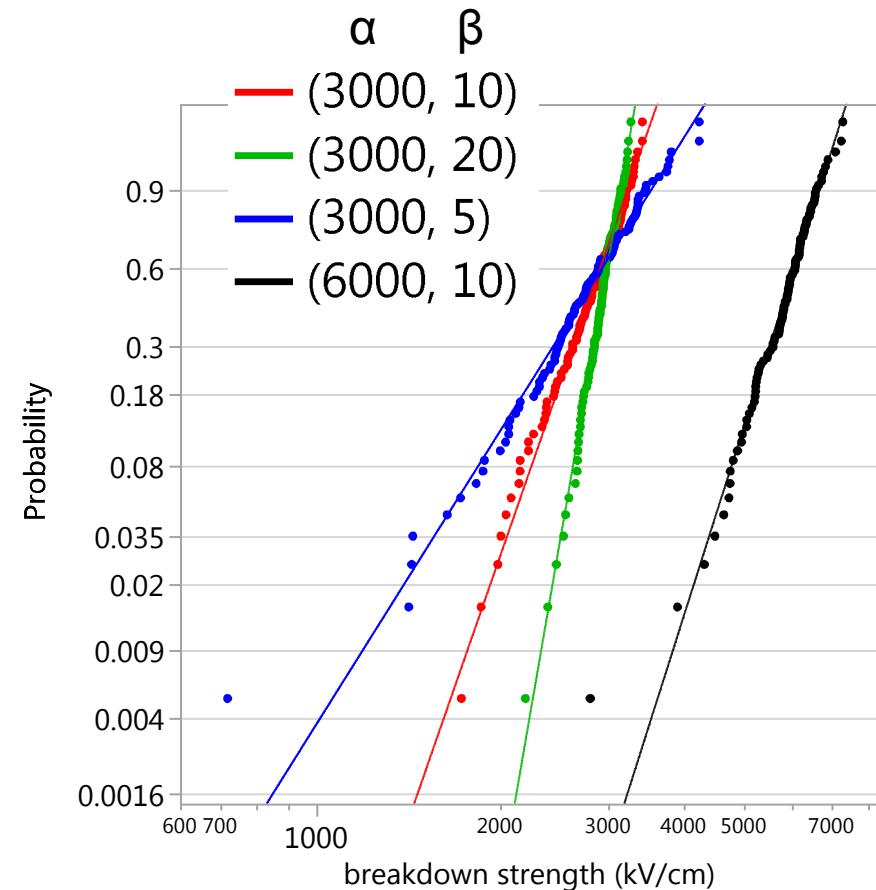
Weibull cumulative distribution function:

$$F(t) = 1 - e^{-\left(\frac{t-\gamma}{\alpha}\right)^\beta}$$

α parameter (scale): The α parameter is the value below which 63.2% of the sample population has failed.

β parameter (shape): The β parameter describes the shape of the Weibull distribution. For $\beta > 1$ a higher value indicates a narrower dispersion.

γ parameter (threshold): The γ parameter indicates a value below which no failures occur (not used in 2-parameter Weibull).



Experimental Details

Group	N_{total}	N_{ex} (κ/Df)	thickness μm (st. dev.)
AM spray SA PI	44	6	9.7 (2.5)
AM spray UTD PI	85	2	6.6 (1.8)
AM syringe SA PI	99	2	37.3 (14.7)
solvent cast SA PI	104	0	16.1 (6.2)
solvent cast UTD PI	53	11	2.6 (0.9)
commercial	90	0	13.3 (0.2)

Thickness Measurements

- Wyco NT9800
- Filmetrics F20 or F50-UV
- DektakXT contact profilometer

κ/Df Measurements

- Agilent E4980 LCR Meter
- shorts excluded from analysis

Breakdown Measurements

- Agilent E4980 as DC source
- Trek 30/20A amplifier
- 500 V/s ramp rate (50V step)
- current trip, 1mA

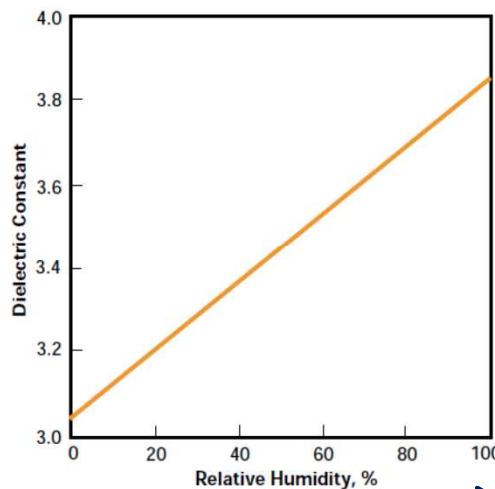
Humidity Control

Kapton® HN – with increasing RH

- increase in κ /DF
- decrease in E_B

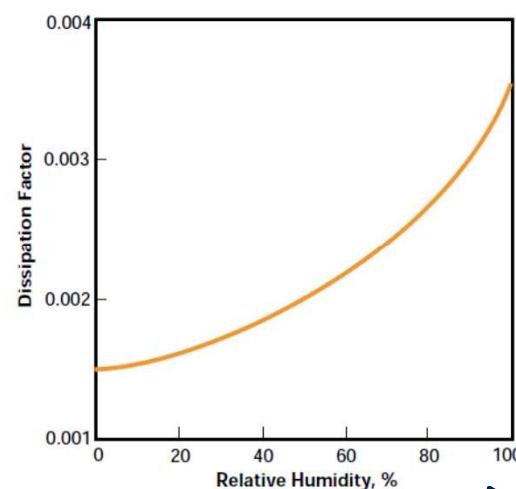
RH%	AC E_B (kV/cm)	κ	DF
0	3390	3.0	0.0015
30	3150	3.3	0.0017
50	3030	3.5	0.0020
80	2800	3.4	0.0027
100	2680	3.8	0.0035

Permittivity



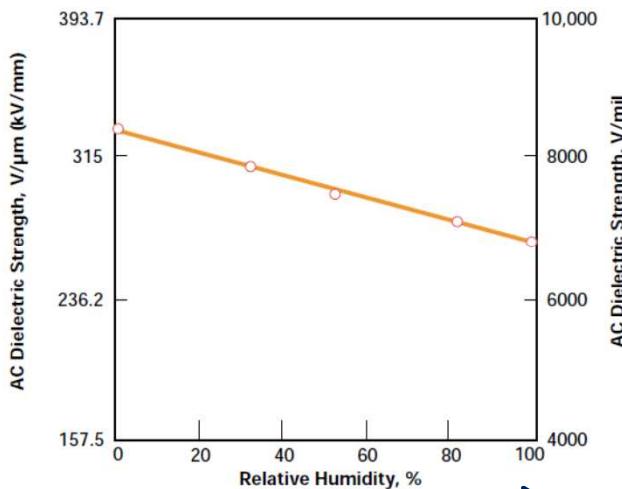
% relative humidity

Loss (DF)



% relative humidity

AC Dielectric Strength

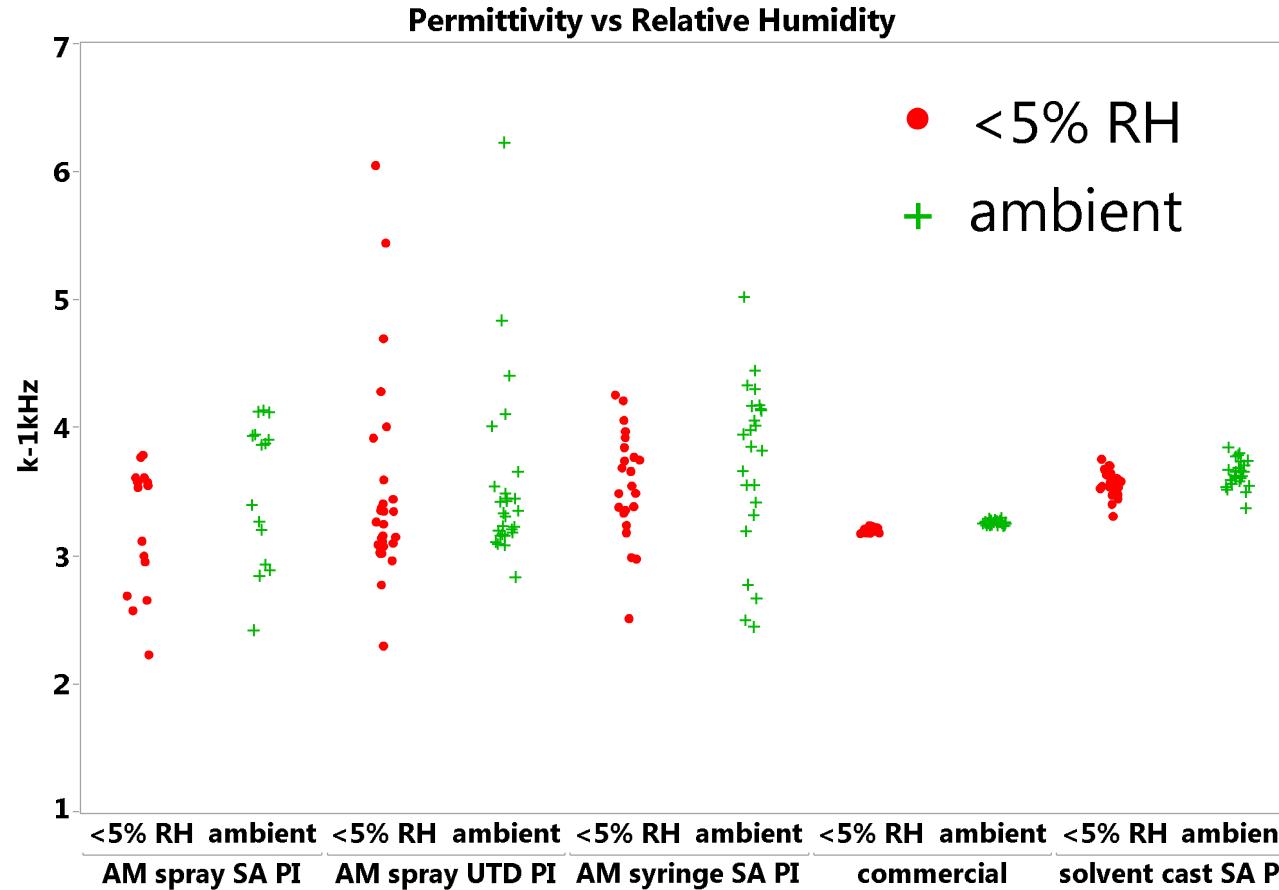


% relative humidity

Humidity Control: κ/DF

Test films under 'nitrogen blanket' (<5% RH) and at ambient.

Ambient humidity varied from 11-37% during test period.



Small differences but negligible compared to sample-to-sample variability
(except for commercial films)

Humidity Control

Permittivity

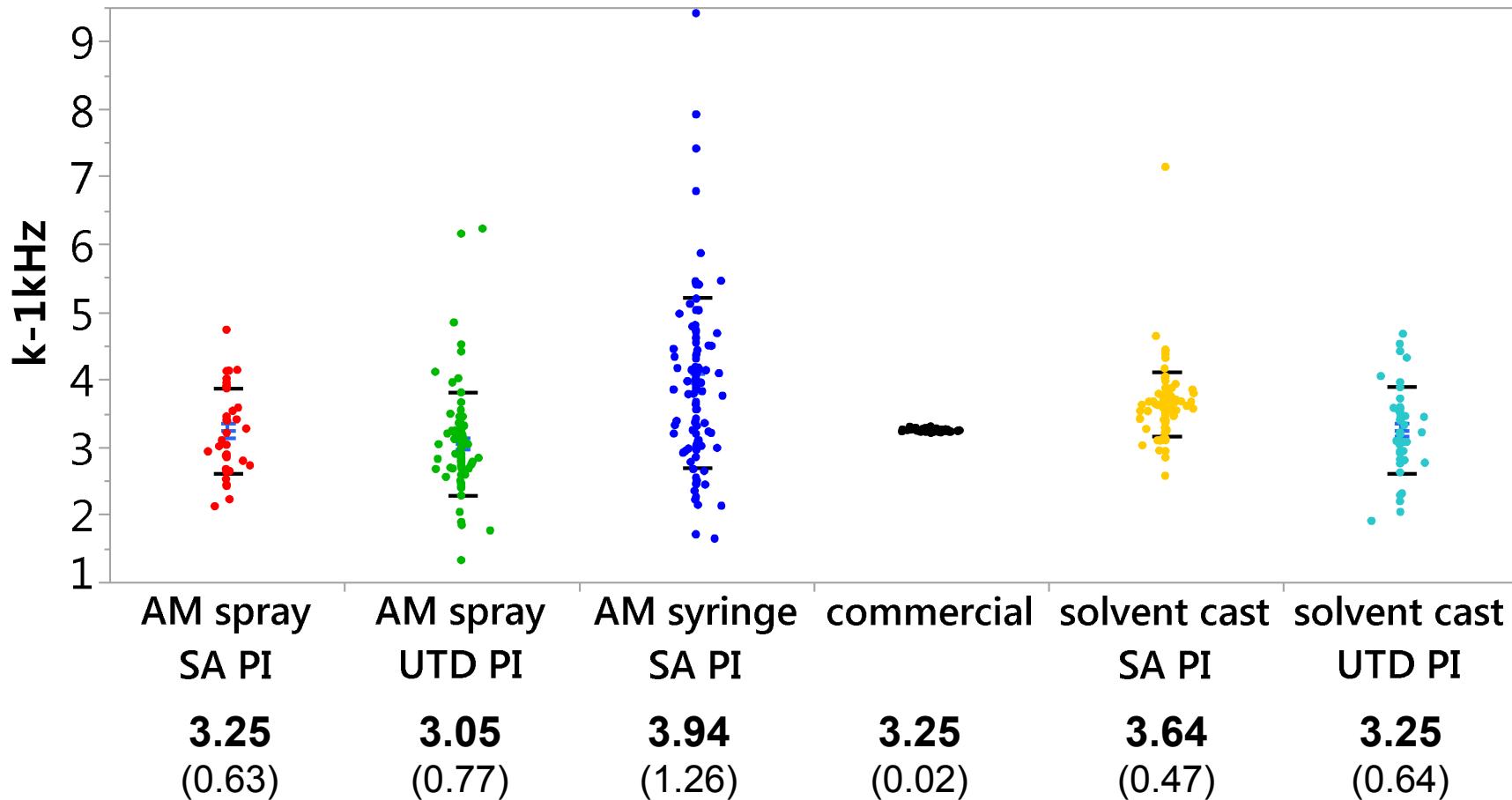
- Did not use any RH control for κ /DF testing
- Store and test at ambient

Breakdown Strength

- Use RH control for best β parameter measurement
- Dry films at 50 °C overnight
- Store in desiccator
- Test under Fluorinert immediately on removal from desiccator

Permittivity @ 1kHz

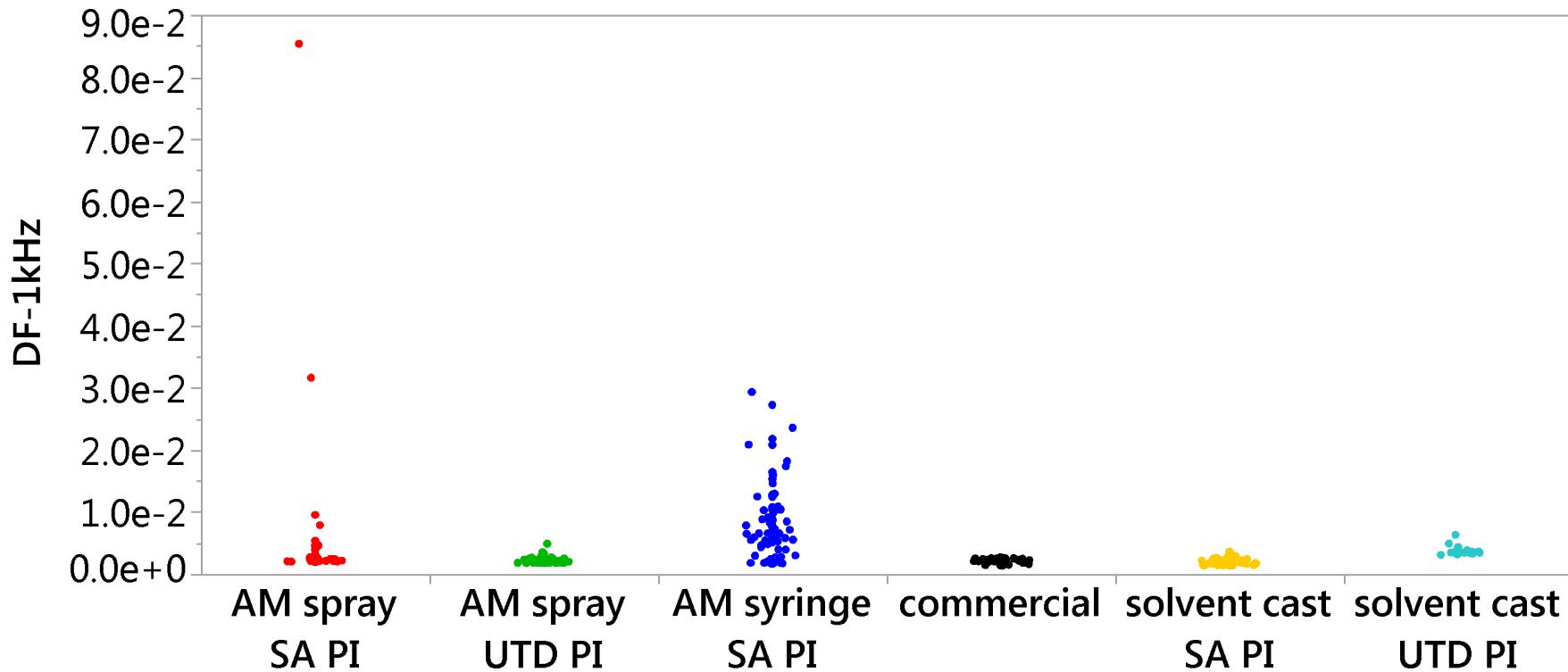
exclude shorts from all permittivity analysis



DF @ 1kHz

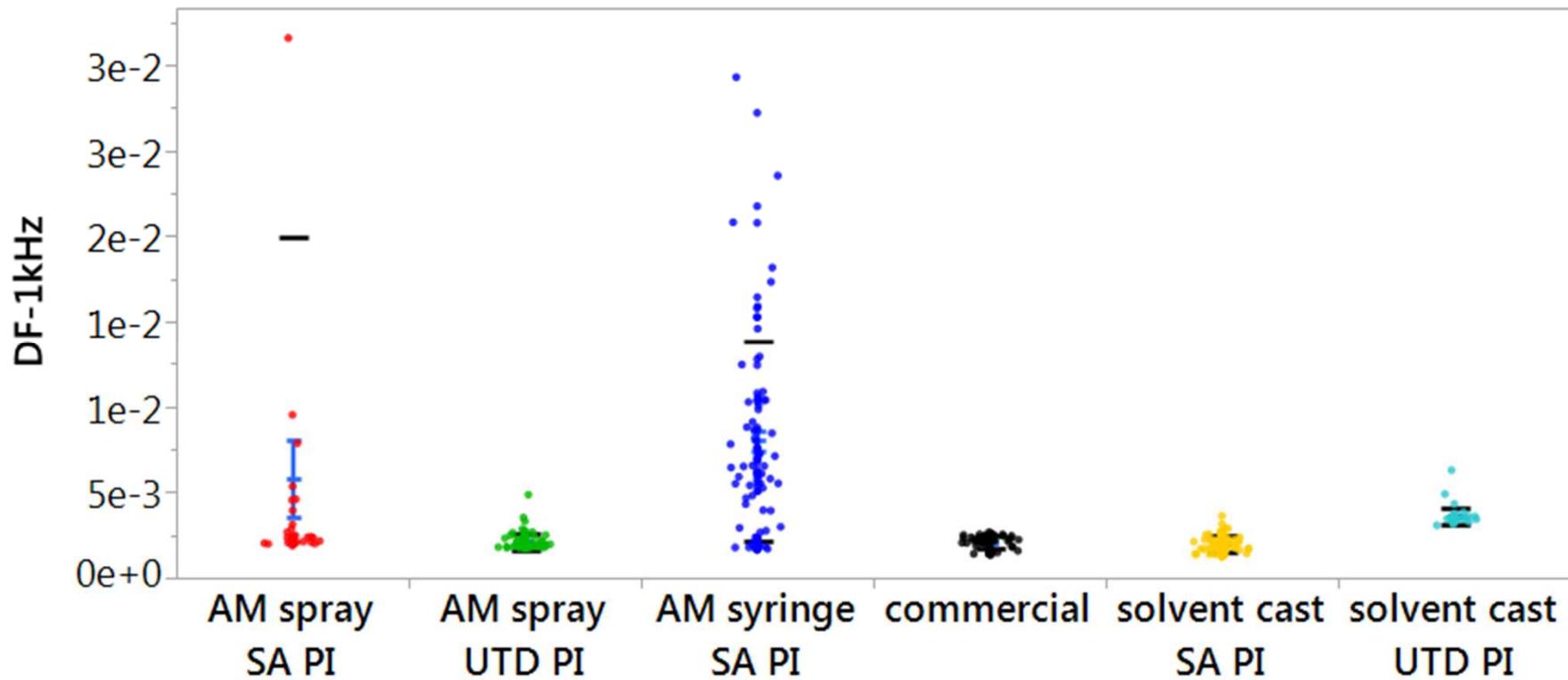


exclude shorts from all permittivity analysis



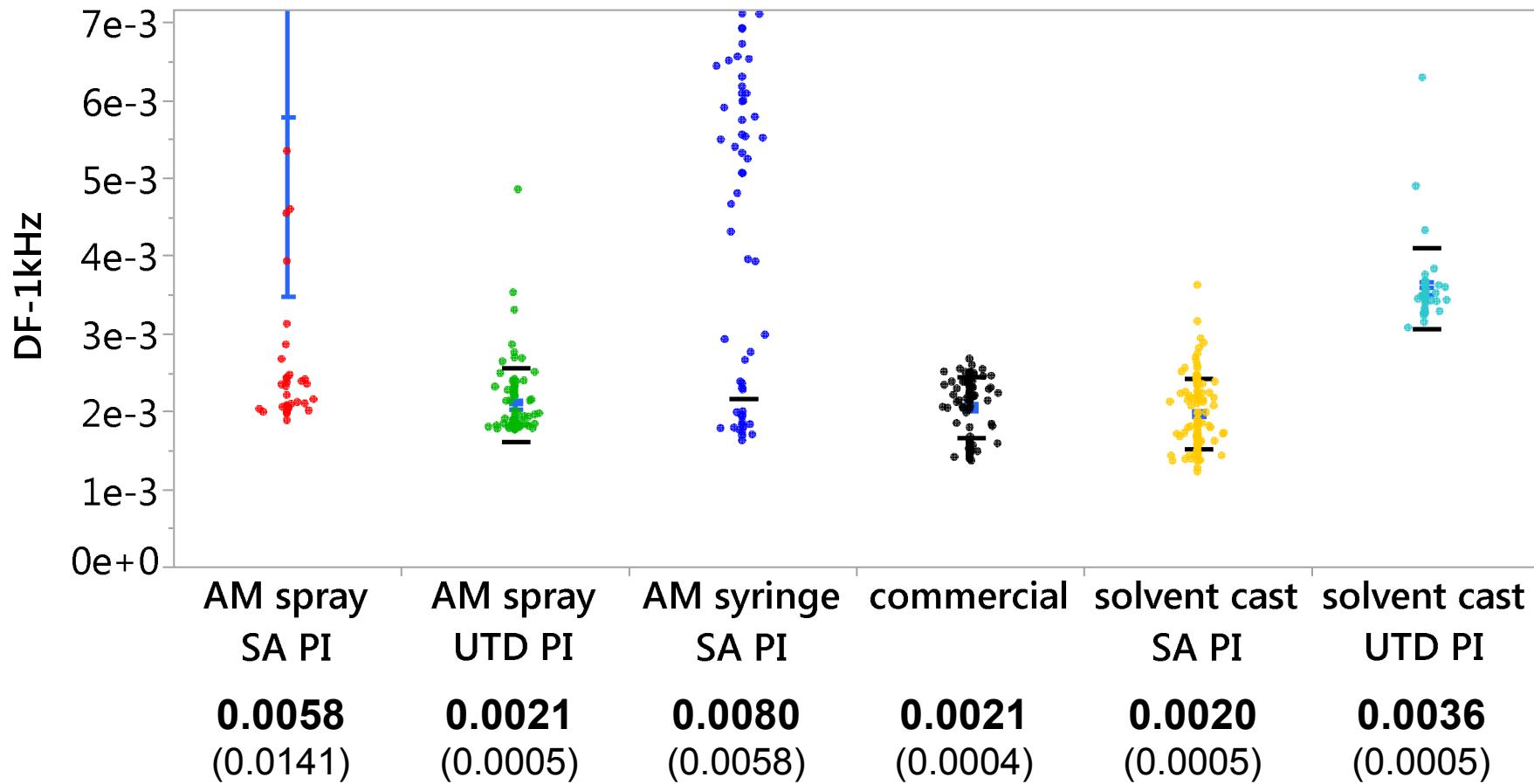
DF @ 1kHz

exclude shorts from all permittivity analysis



DF @ 1kHz

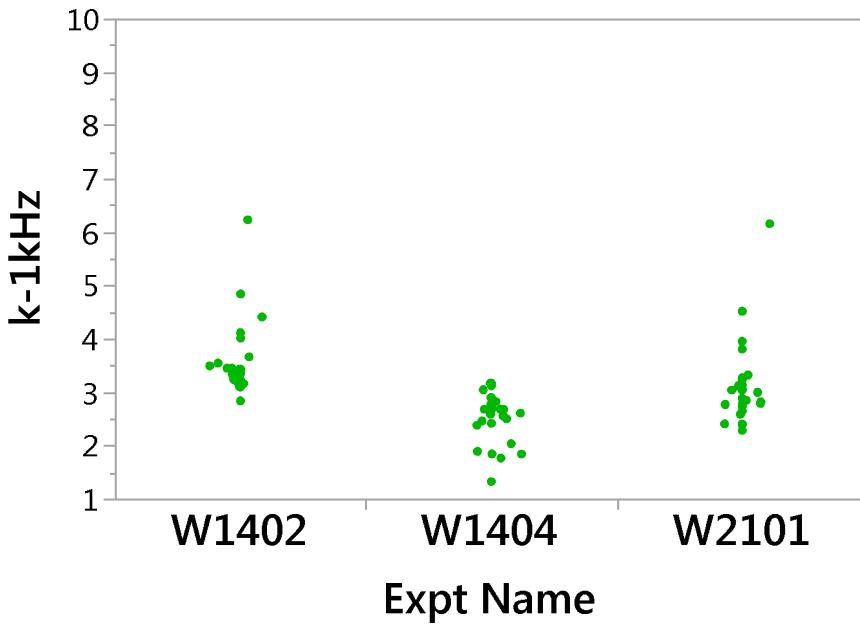
exclude shorts from all permittivity analysis



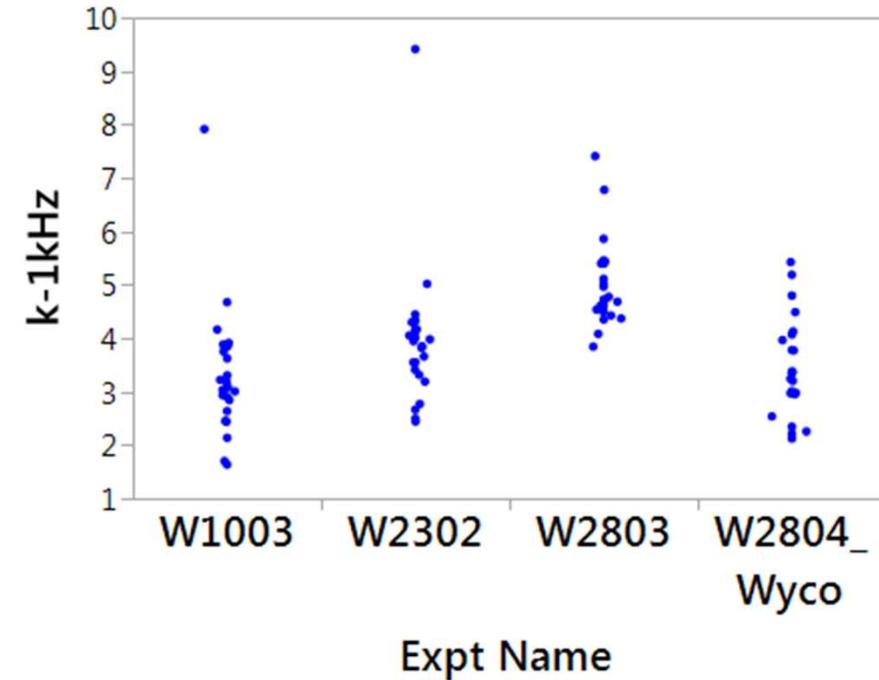
Permittivity @ 1kHz

Sample-to-sample variability

AM Spray UTD PI



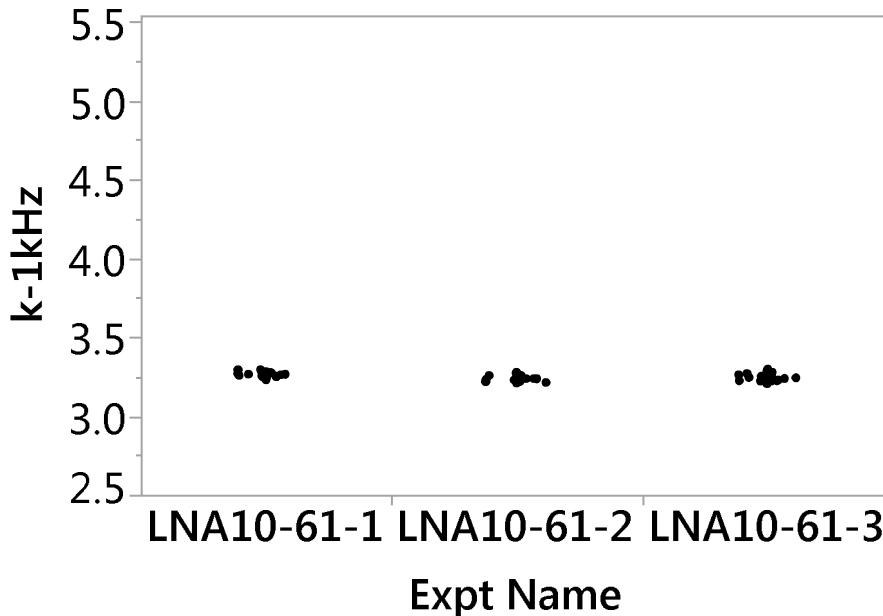
AM Syringe SA PI



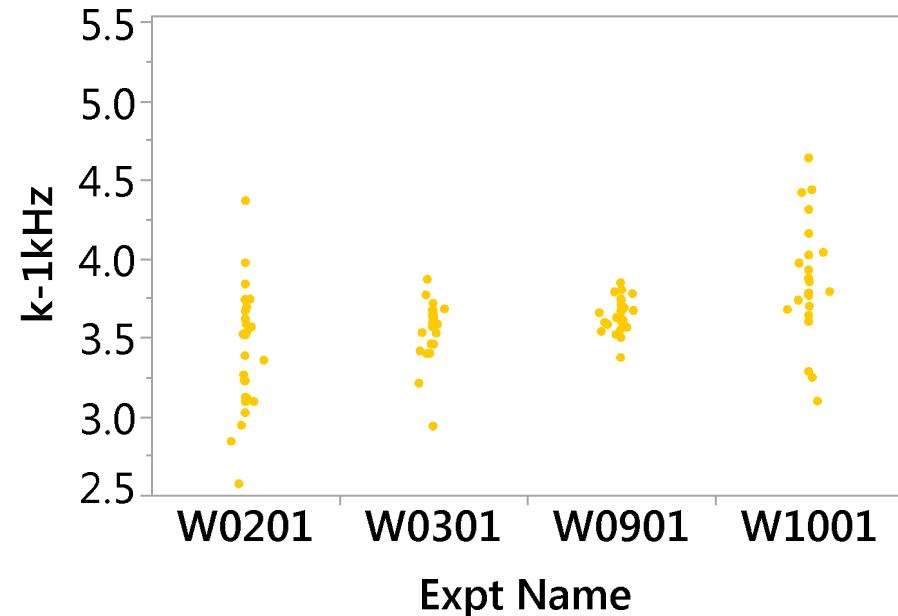
Permittivity @ 1kHz

Sample-to-sample variability

Commercial



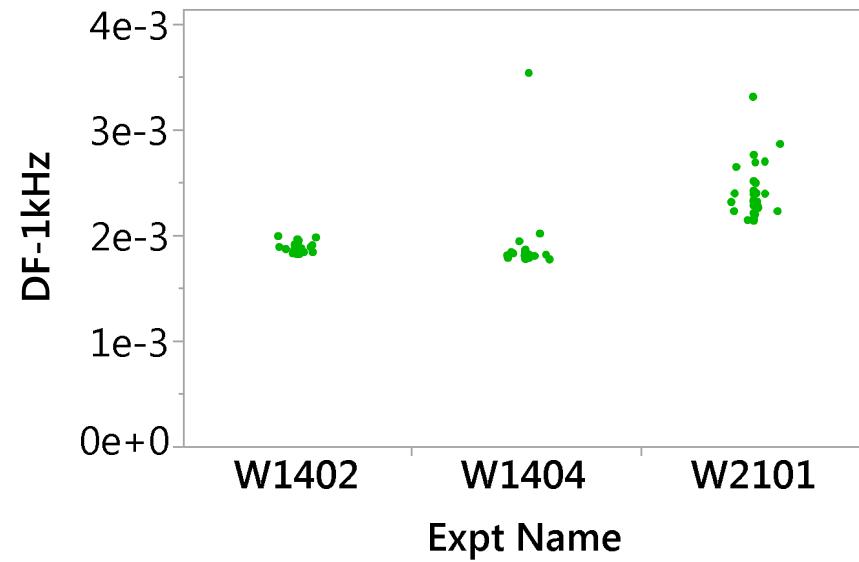
Solvent Cast SA PI



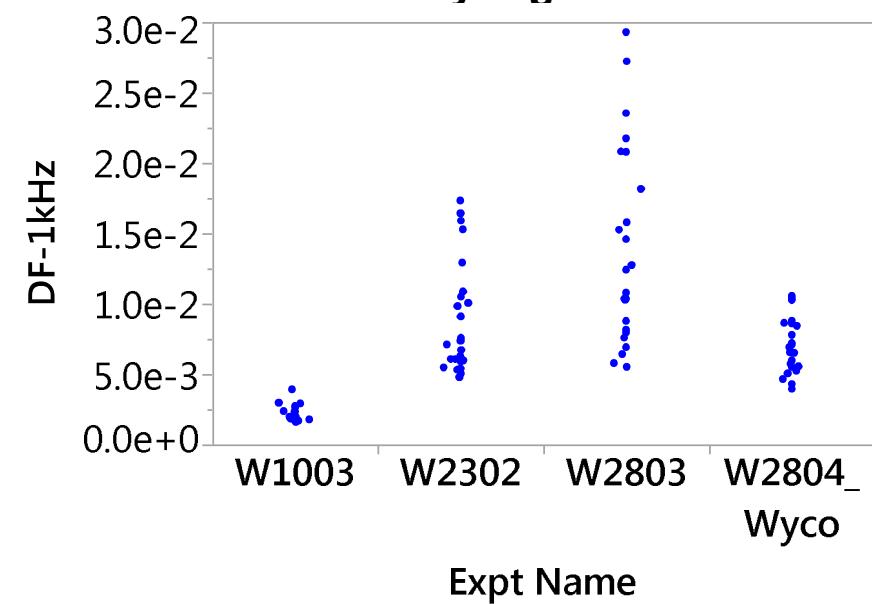
Loss @ 1kHz

Sample-to-sample variability

AM Spray UTD PI

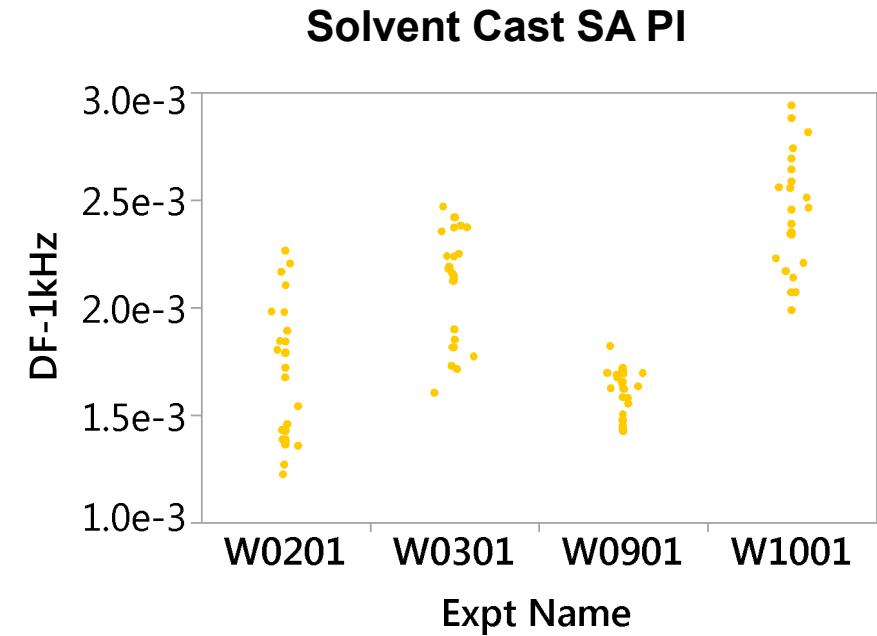
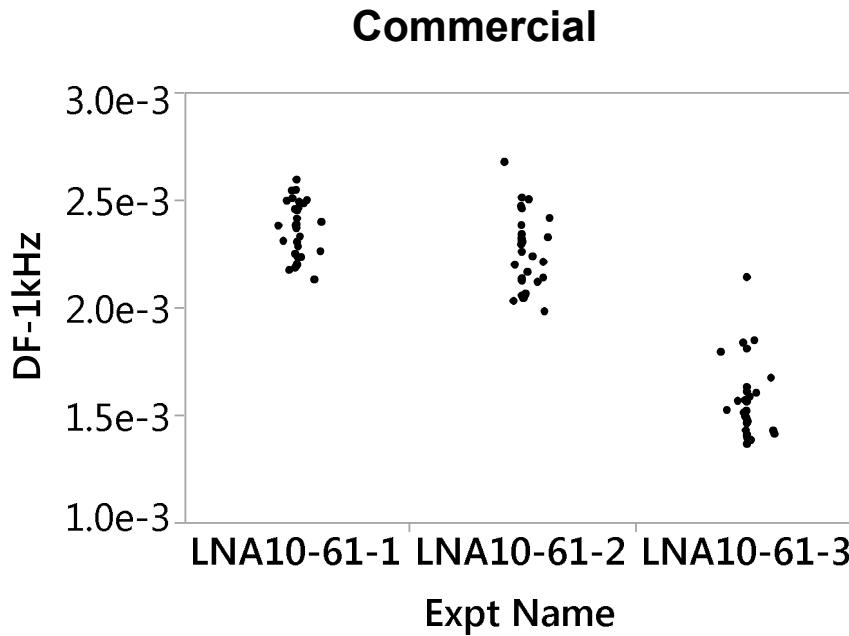


AM Syringe SA PI



Loss @ 1kHz

Sample-to-sample variability



Permittivity/Loss @ 1kHz



Sample-to-sample performance in both permittivity and loss is fairly consistent in all groups.

Permittivity

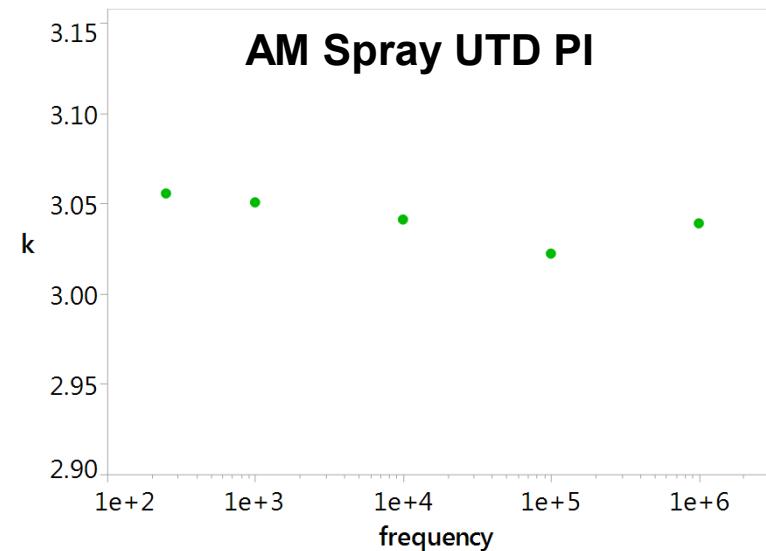
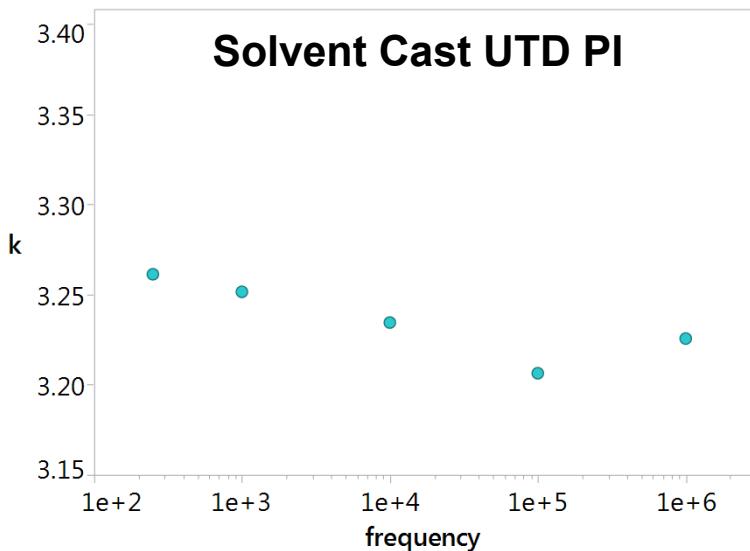
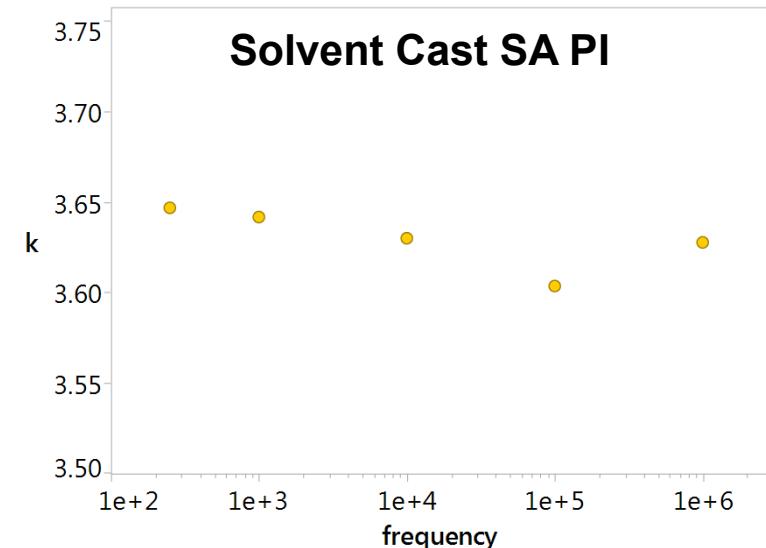
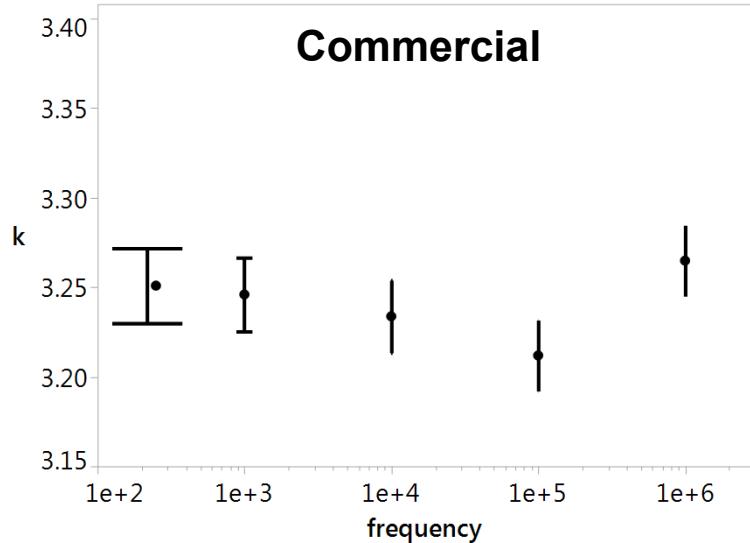
All films have much higher dispersion in permittivity than commercial

- Thickness variation
- Solvent trapping/poly(amic acid) conversion?

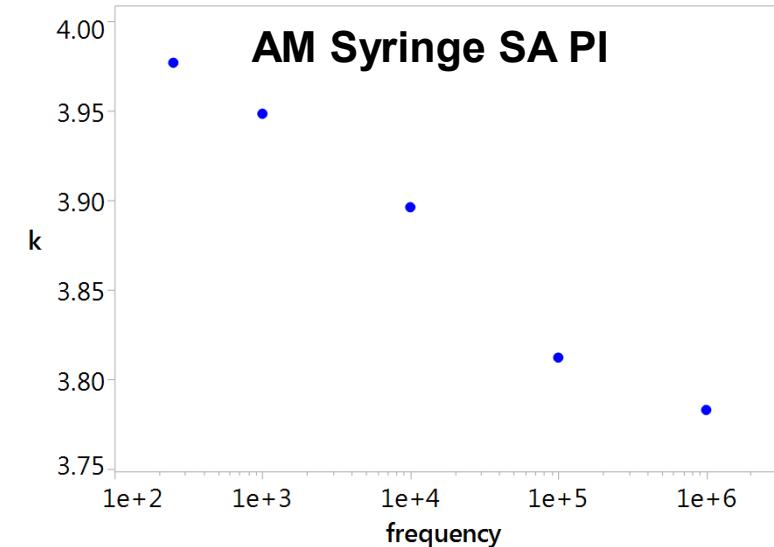
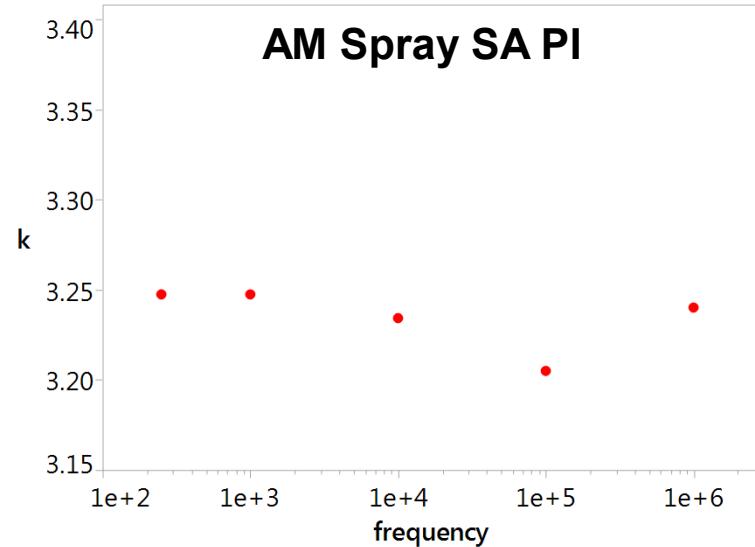
Dielectric Loss

- AM methods with SA PI have very high dispersion in the loss measurements
- Other groups have similar dispersion to the commercial films

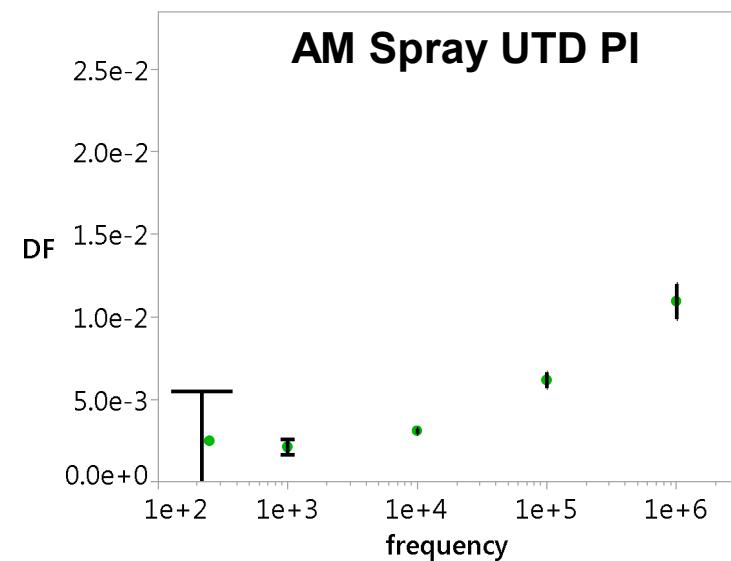
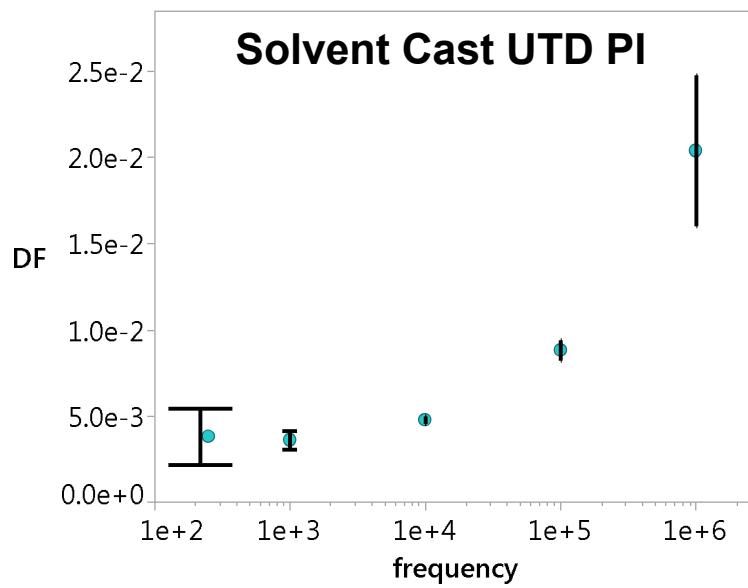
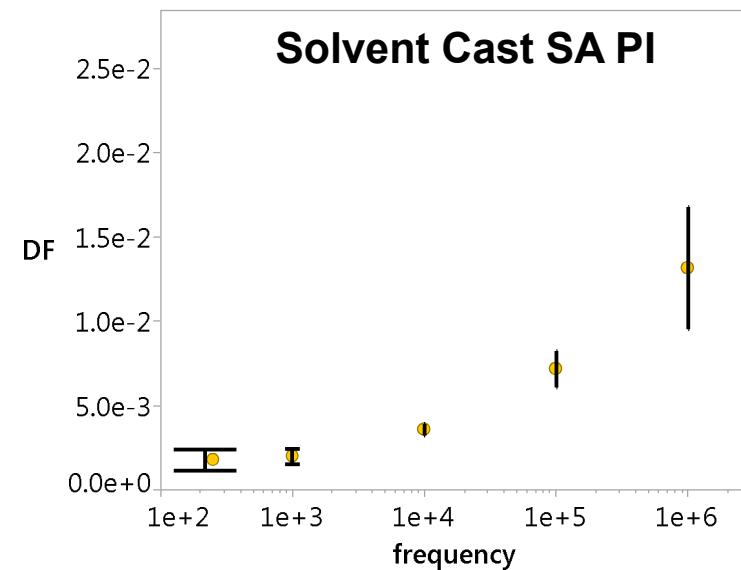
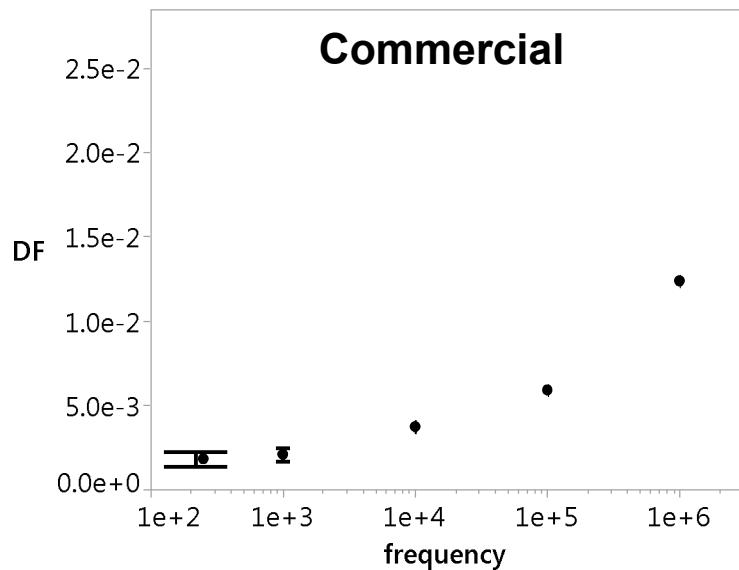
Permittivity vs. Frequency



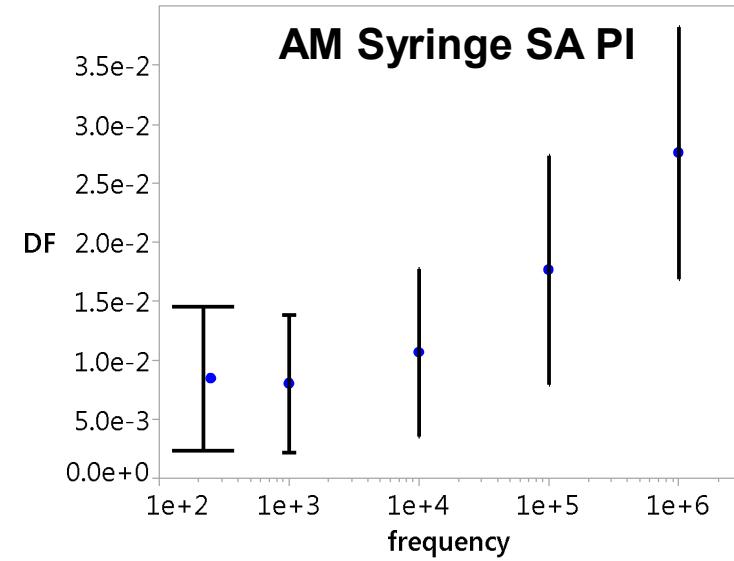
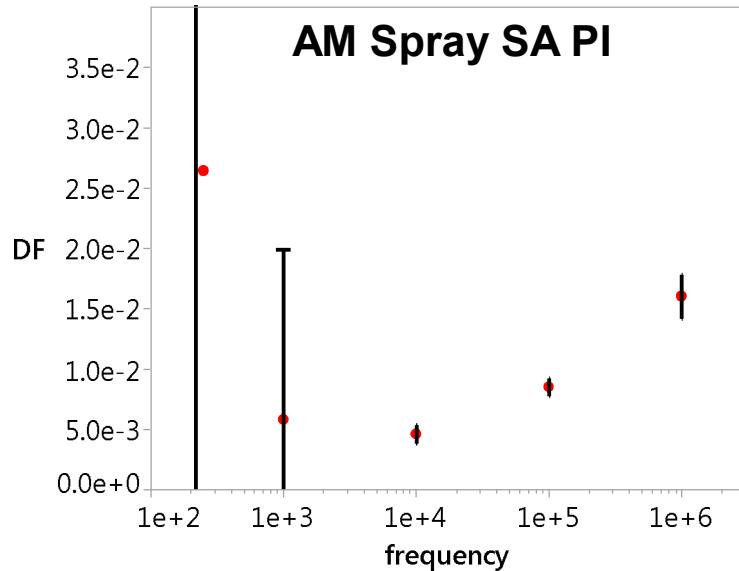
Permittivity vs. Frequency



Loss vs. Frequency

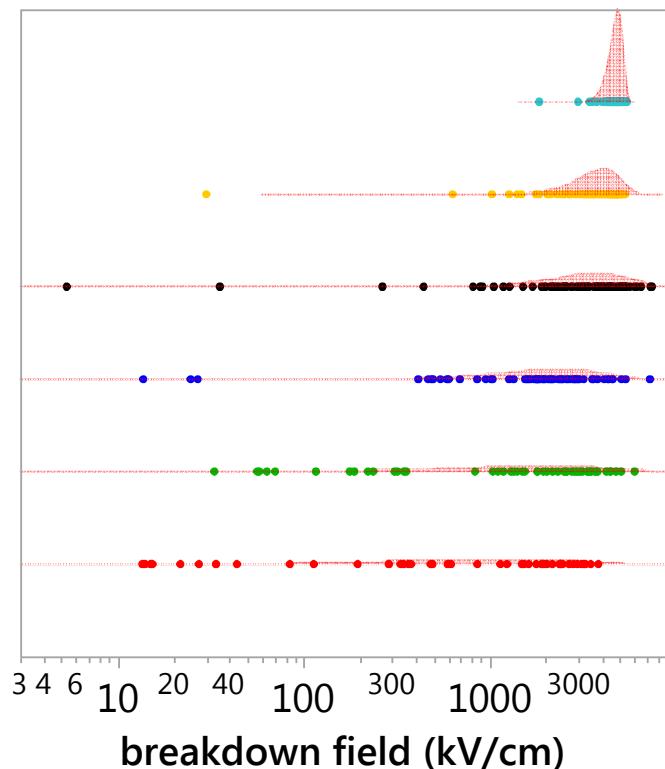


Loss vs. Frequency

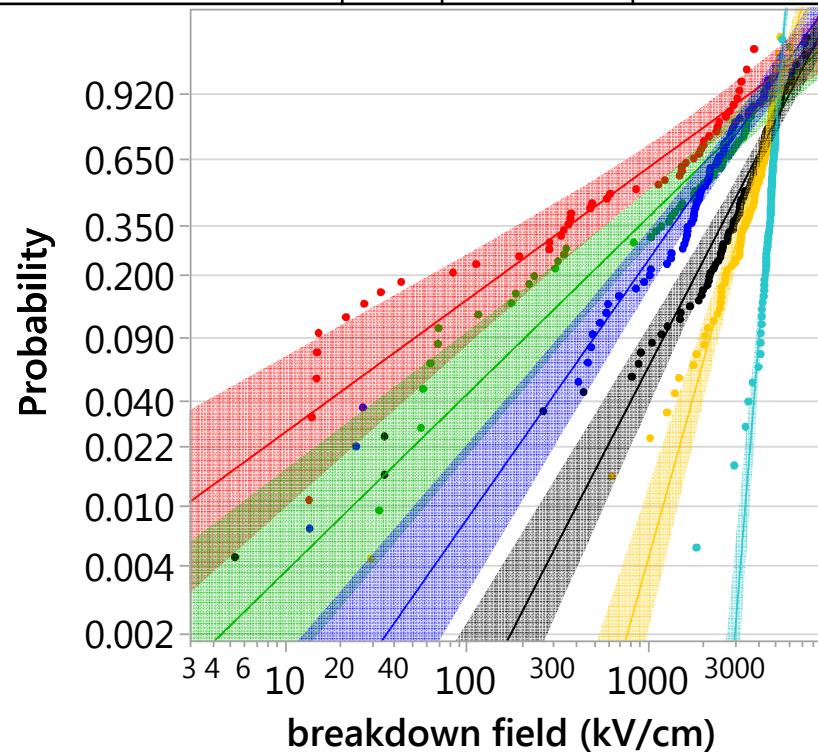


Dielectric Breakdown Strength

- AM spray SA PI
- solvent cast UTD PI
- AM spray UTD PI
- AM syringe SA PI
- solvent cast SA PI
- commercial

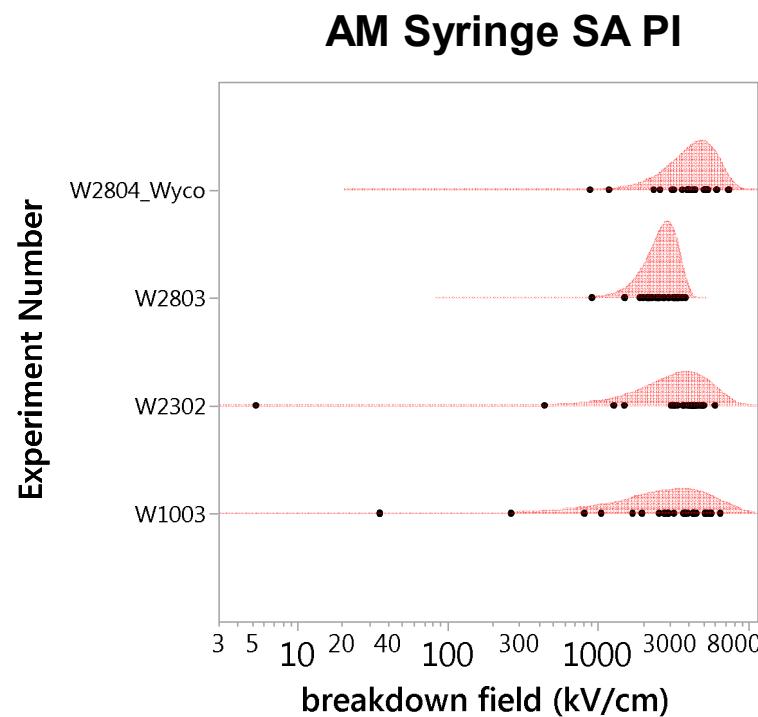
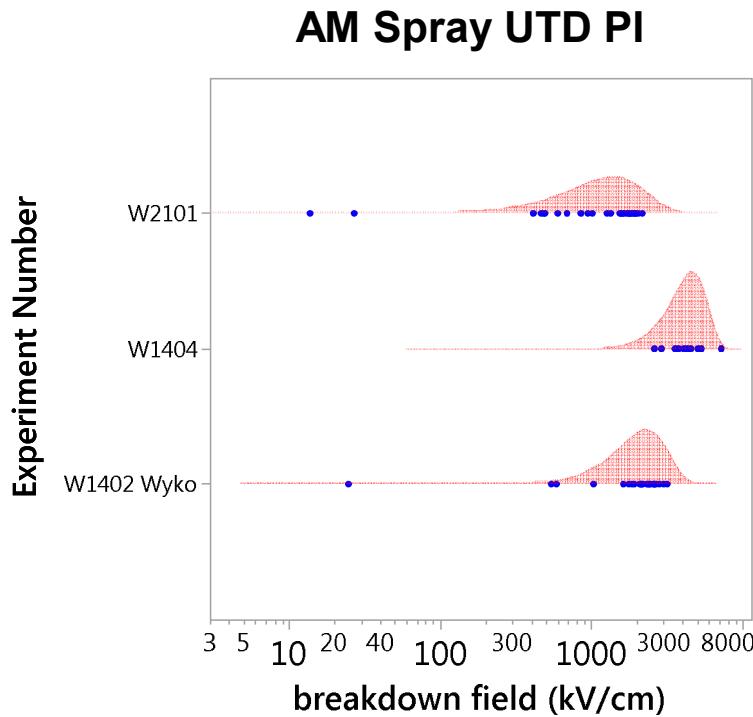


Group	N	Weibull α (kV/cm)	Weibull β
AM spray SA PI	47	1110	0.8
solvent cast UTD PI	54	2060	1.0
AM spray UTD PI	69	2402	1.5
AM syringe SA PI	101	3835	2.1
solvent cast SA PI	103	4072	3.8
commercial	89	4891	13.0



Dielectric Breakdown Strength

Sample-to-sample variability

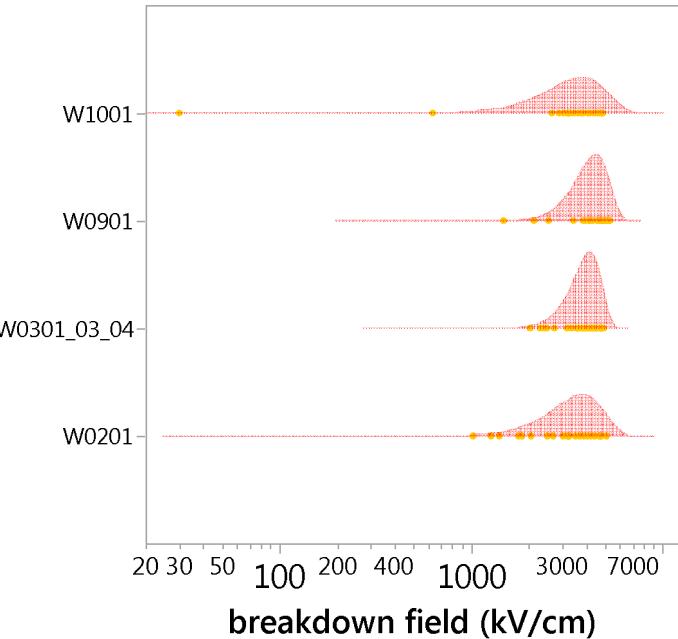


Dielectric Breakdown Strength

Sample-to-sample variability

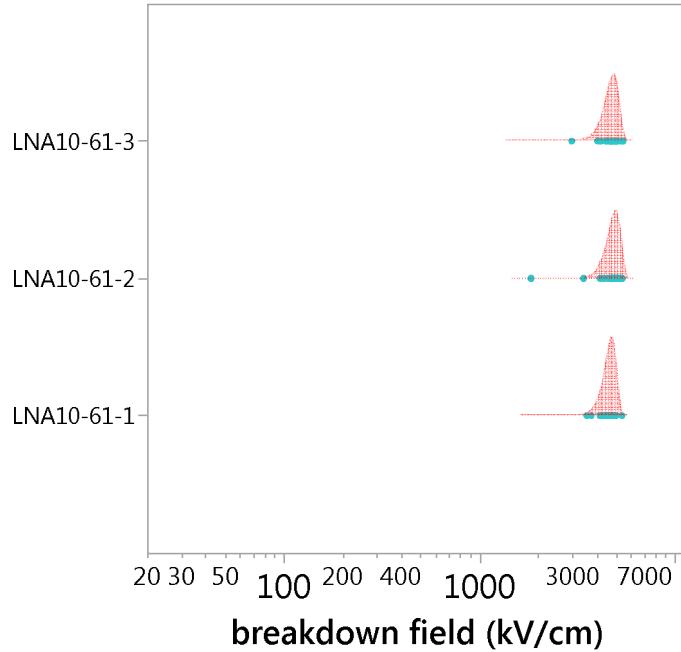
Solvent Cast SA PI

Experiment Number



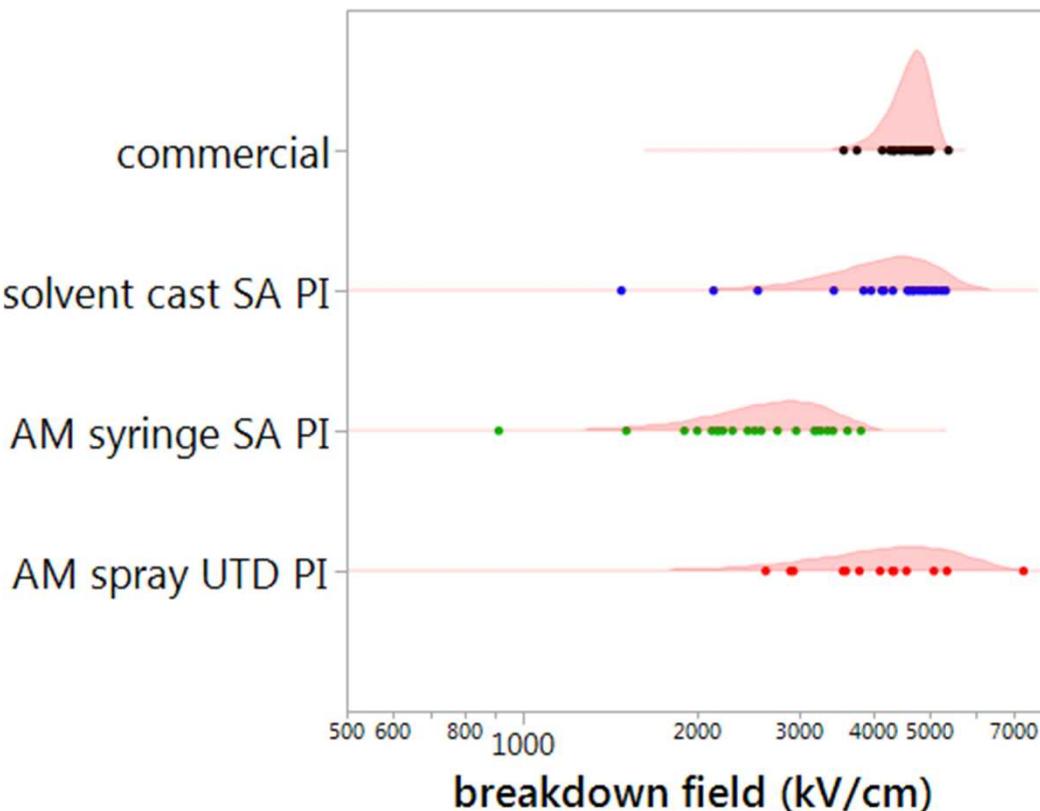
Commercial

Experiment Number



Dielectric Breakdown Strength

Single best film comparison



Group	Weibull α (kV/cm)	Weibull β
AM spray UTD PI	4659	3.7
AM syringe SA PI	2894	4.5
solvent cast SA PI	4482	5.2
commercial	4778	14.9

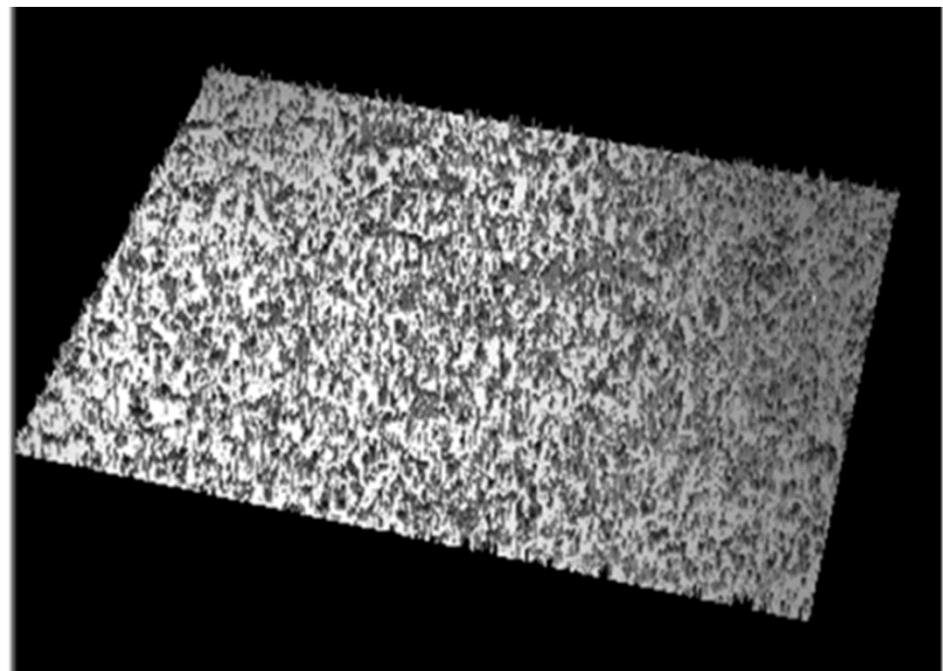
Origin of Performance Differences

Measurement Contributions

- thickness variability/measurement
- sample-to-sample variability

Sample Contributions

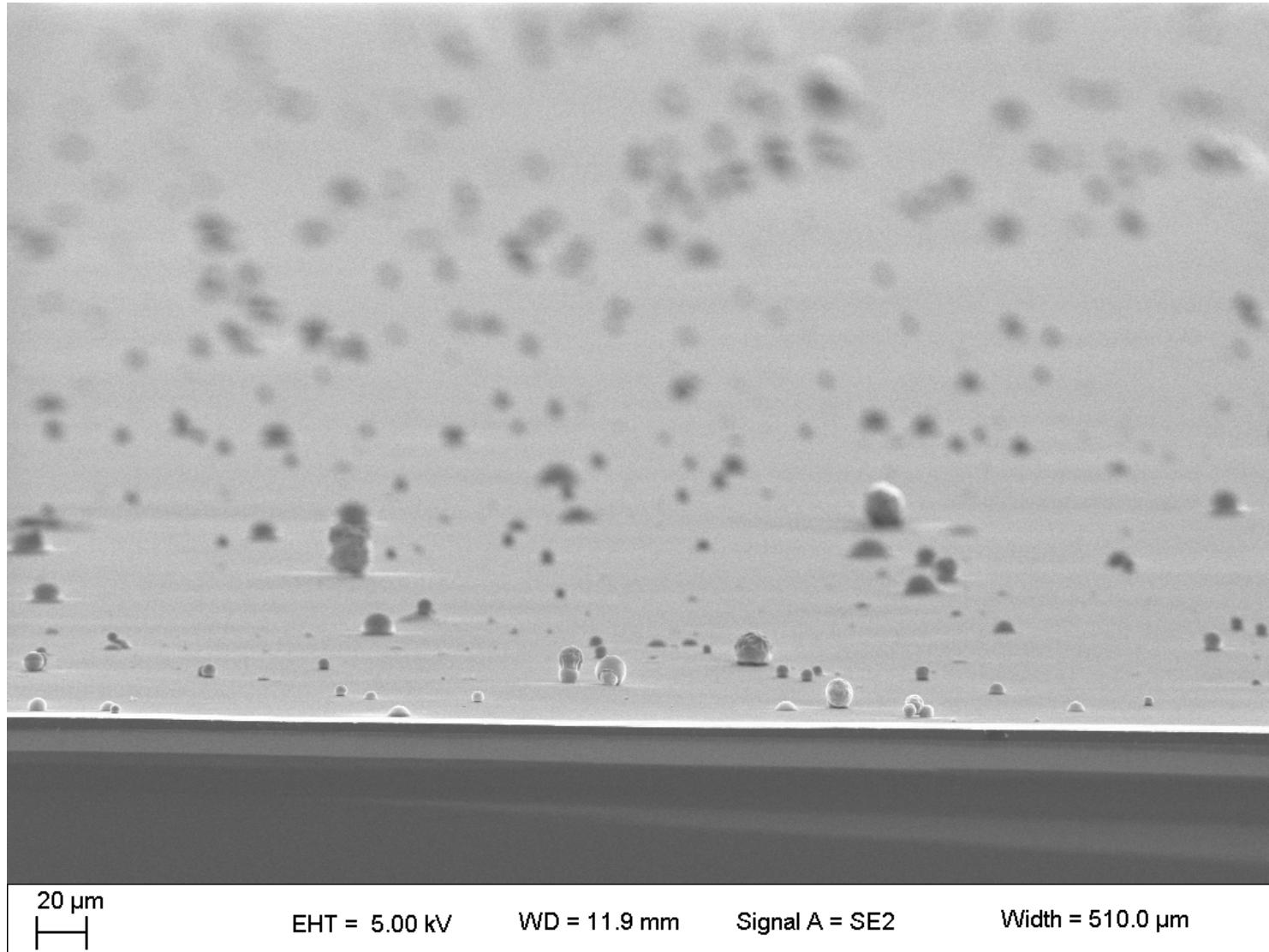
- surface roughness
- small molecule/solvent trapping
- deposition homogeneity



Films 5-6 μm thick have avg. surface roughness of 2.4 μm

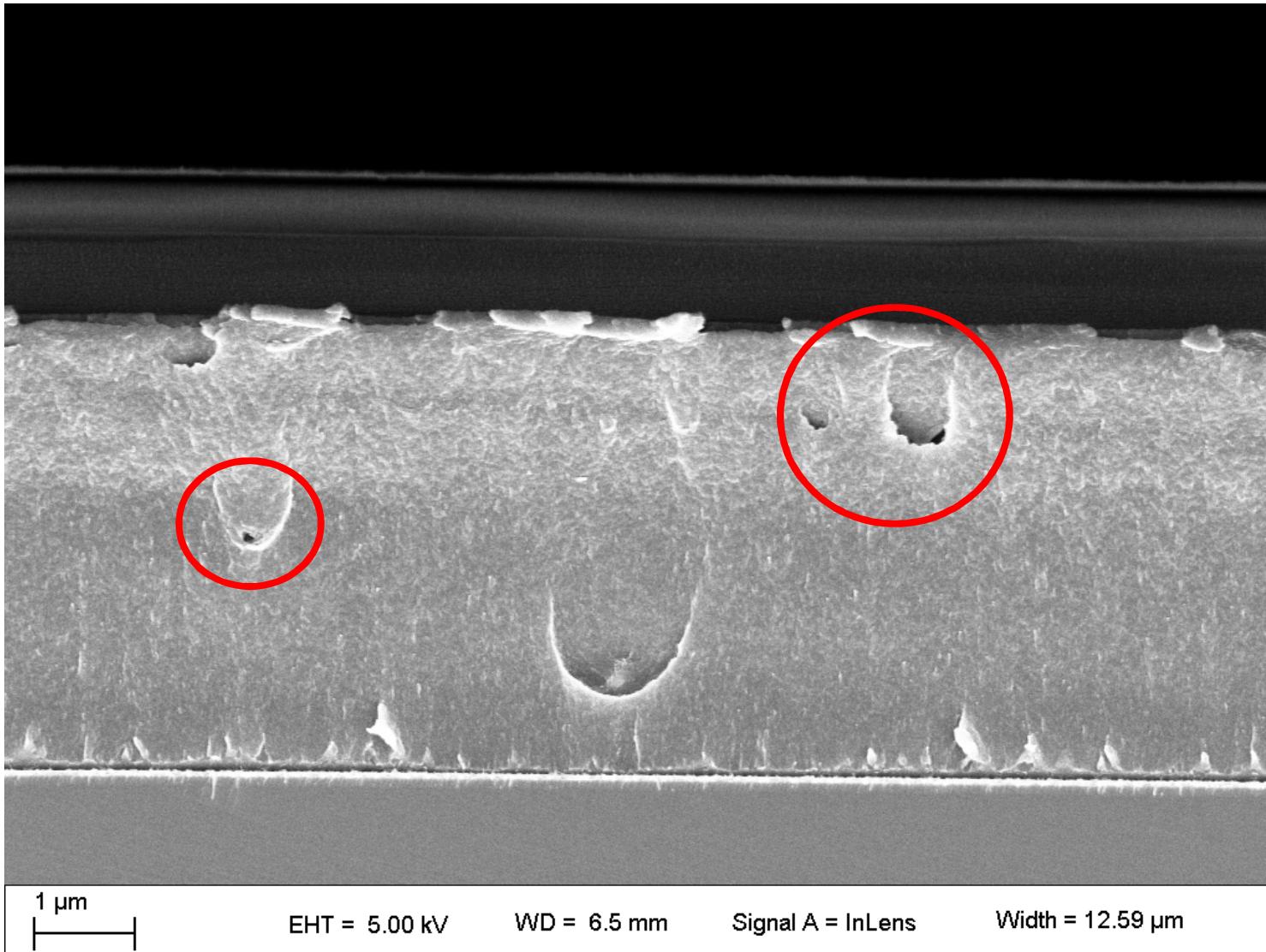
Origin of Performance Differences

SEM images of AM Spray UTD PI film



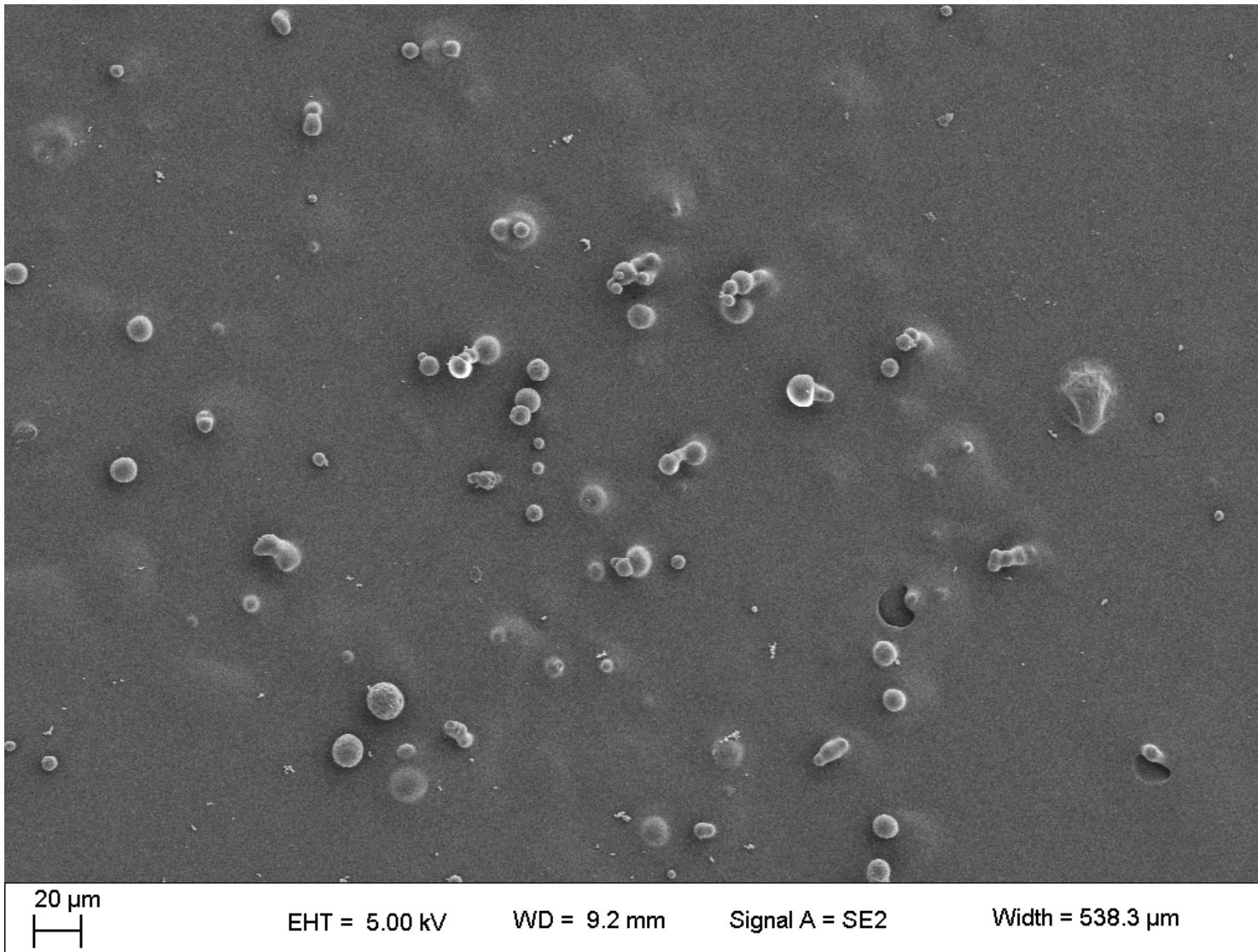
Origin of Performance Differences

SEM images of AM Spray UTD PI film



Origin of Performance Differences

SEM images of AM Spray UTD PI film



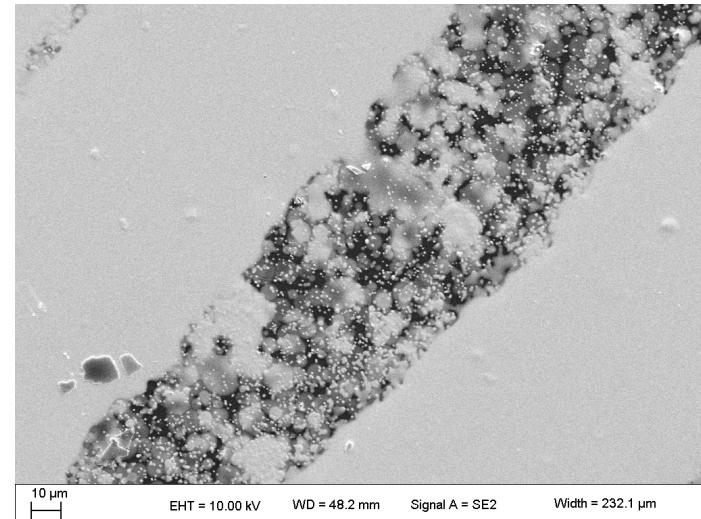
Conclusions



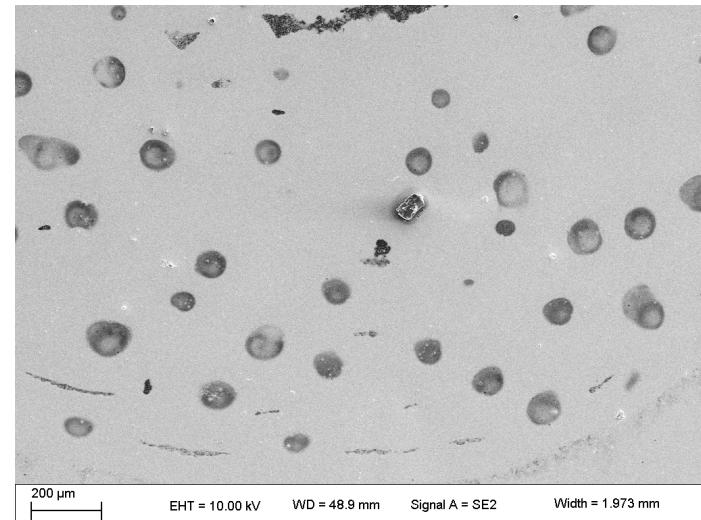
- The 'solvent cast SA PI' group performed the best of the lab-made films
- The 'AM spray SA PI' and 'solvent cast UTD PI' performed the worst
 - this may be partly due to mismatch between formulation/process
- The 'AM syringe SA PI' method performed the best of AM methods, in terms of breakdown strength, but had very high permittivity and loss. Furthermore it is not applicable to deposition on non-planar substrates.
- The 'AM spray' method seems the most promising method, but film quality will need to be improved

Future Work and Challenges

- Improve film deposition quality
 - surface roughness
 - film homogeneity
 - conversion/cure
- AM deposition of electrodes
- 3-D deposition (challenging!)
 - topography
 - field enhancement
- Other polymers (challenging!)
 - BOPET
 - BOPP



SEM images of defects in AM deposited Au electrodes



Acknowledgements



- Judi Lavin, Dave Keicher
- Patrick Finnegan
- Shaun Whetten, Mike Russell, Penny Moore, Sita Mani
- Marce Essien, Adam Cook
- Ron Goeke, Grant Grossete, Carl Smith
- Bonnie McKenzie
- Jerry Rejent, Shelley Williams

Supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.