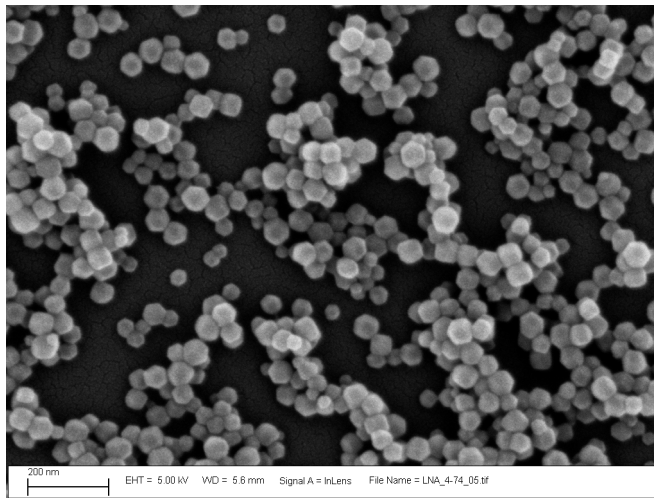


ZIF-8 Polymer Composite

SAND2012-9226P

Dielectric Films

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Current Capacitor Technology

Ceramic Capacitors

- Lower breakdown strengths
- Higher dielectric permittivity
- Go through hard failure
- Normally are much more brittle

Polymer Capacitors

- Very high breakdown strengths
- Lower dielectric permittivity
- Go through soft failure
- Normally are flexible

Project Goals

- To study the effects of metal organic frameworks (MOFs) on the dielectric properties of MOF-polymer composites.
- To compare how the addition of ZIF-8 particles, in a size range of 250 nm to 1 μm , effects the properties of the MOF-polymer composites.

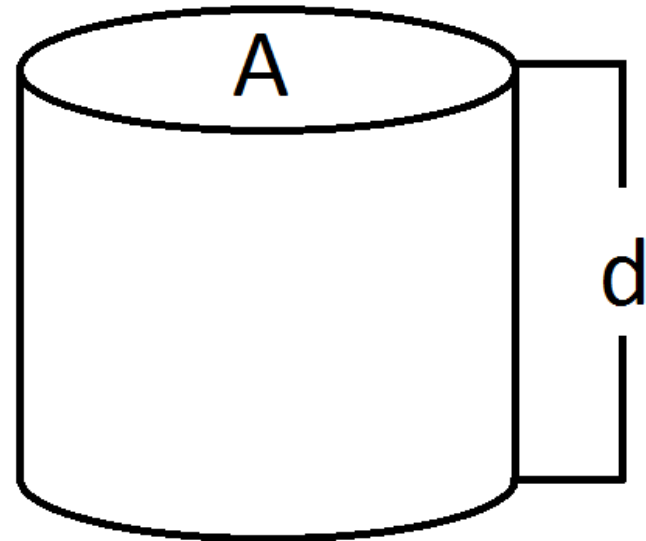
Permittivity Testing

- Used a 15 V AC LCR meter at 10 kHz to determine the capacitance (C) of the film.

- Then using the equation:

$$\epsilon_r \epsilon_0 = \frac{Cd}{A}$$

- C is the capacitance
- d is the thickness
- A is the area of the capacitor



Breakdown Testing

- The amount of voltage that makes the insulating material electrically conductive
- Tests were set to trip at 1mA
- Max voltage before trip is E_b



<http://capturedlightning.com/frames/lichtenbergs.html>

Energy Density

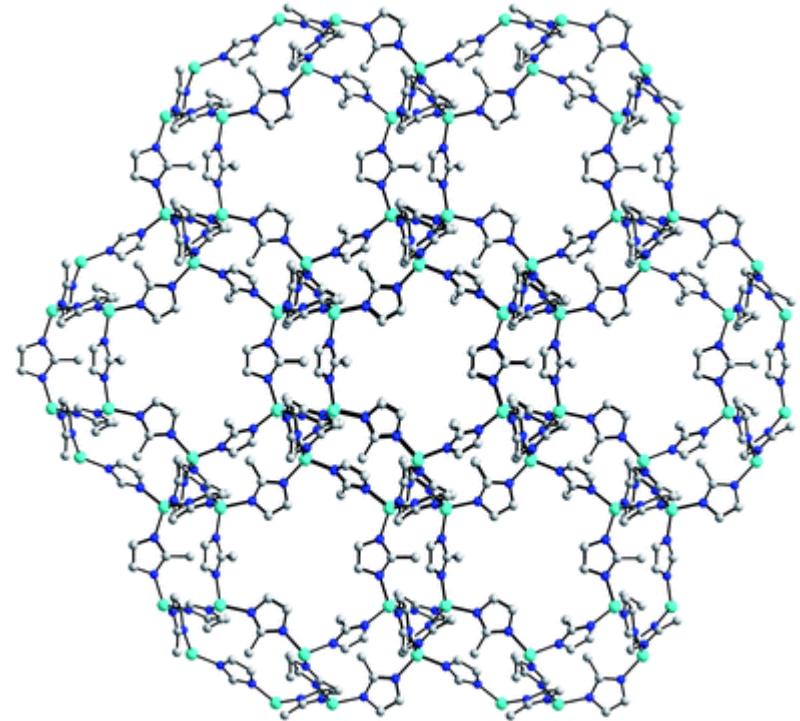
- Used as a way to compare capacitors:

$$U_e = \frac{1}{2} (\epsilon_r \epsilon_0 E_b^2)$$

- ϵ_r is the dielectric permittivity
- ϵ_0 is the vacuum permittivity (8×10^{-14} F/cm)
- E_b is the applied electric field at breakdown (V/cm)
- U_e is energy density (J/cm^3)

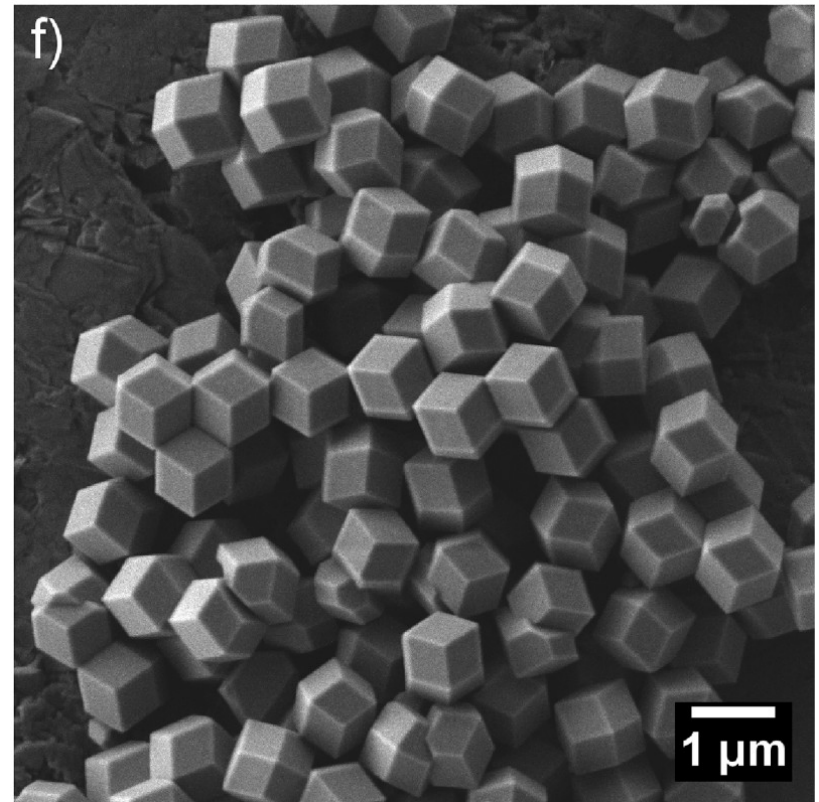
Metal Organic Frameworks

- Metal ion surrounded by an organic ligand
- CO₂ Capture
- Hydrogen Storage
- Hydrocarbon Separations



Zeolitic Imidazolate Framework (ZIF-8)

- Thermally and chemically stable
- Can vary particle sizing easily
- Easy particle sizing not common in MOFs



Wiebcke, *Chemistry of Materials*. 2011, 23 (8), pp. 2130-2140.

Altering Particle Size of ZIF-8

Zn/2-mim/1-mim/MeOH

- A high concentration of 2-methylimidazole (2-mim) relative to Zn^{2+} causes the nucleation rate to be high. This results in a small particle size.
- The addition of 1-methylimidazole causes a slower nucleation rate, resulting in a larger particle size relative to identical stoichiometry without added 1-mim.

Approach to Varying Particle Sizes

Varying Reaction Time

Zn/2-mim/1-mim/MeOH

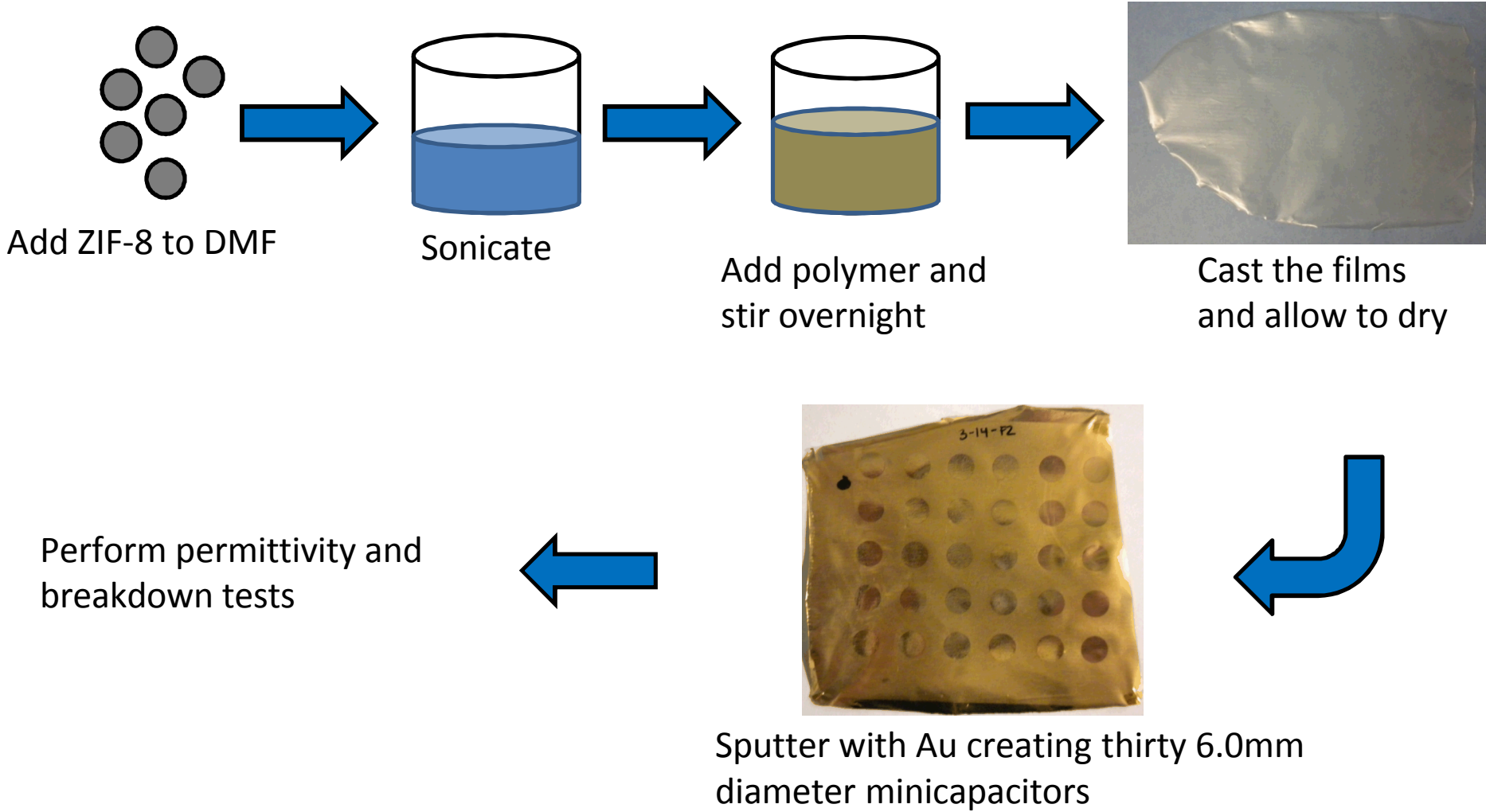
| | Time (hrs) | Particle Diameter (nm) |
|------------|---------------|---------------------------|
| 1/4/4/1000 | 6.5 | 375.8 |
| 1/4/4/1000 | 24 | 410.5 |
| 1/4/4/1000 | 96 | 636.6 |
| | | |
| 8/62/3000 | 2 | 64.17 |
| 8/62/3000 | 24 | 125.2 |

Varying Stoichiometry

Zn/2-mim/1-mim/MeOH

| | Time (hrs) | Particle Diameter (nm) |
|-----------------------|---------------|---------------------------|
| 1/4/ 0.8 /1000 | 24 | 102.7 |
| 1/4/ 1.9 /1000 | 24 | 151.8 |

Making the Films



Permittivity Results

Control Films

| | K at 10kHz |
|------------|------------|
| GDR1-37 F1 | 8.95 |
| GDR1-87 | 9.18 |
| GDR1-88 F1 | 9.18 |
| GDR1-88 F2 | 9.56 |

ZIF-8 Composite Films

| | Particle Diameter (nm) | K at 10kHz |
|------------|------------------------|------------|
| GDR1-36 F1 | 64.17 | 7.63 |
| GDR1-36 F2 | 64.17 | 8.88 |
| GDR1-17 | 102.7 | 9.34 |
| GDR1-82 F1 | 102.7 | 7.87 |
| GDR1-82 F2 | 102.7 | 8.09 |
| GDR1-83 | 102.7 | 6.91 |
| GDR1-86 | 140.8 | 7.75 |

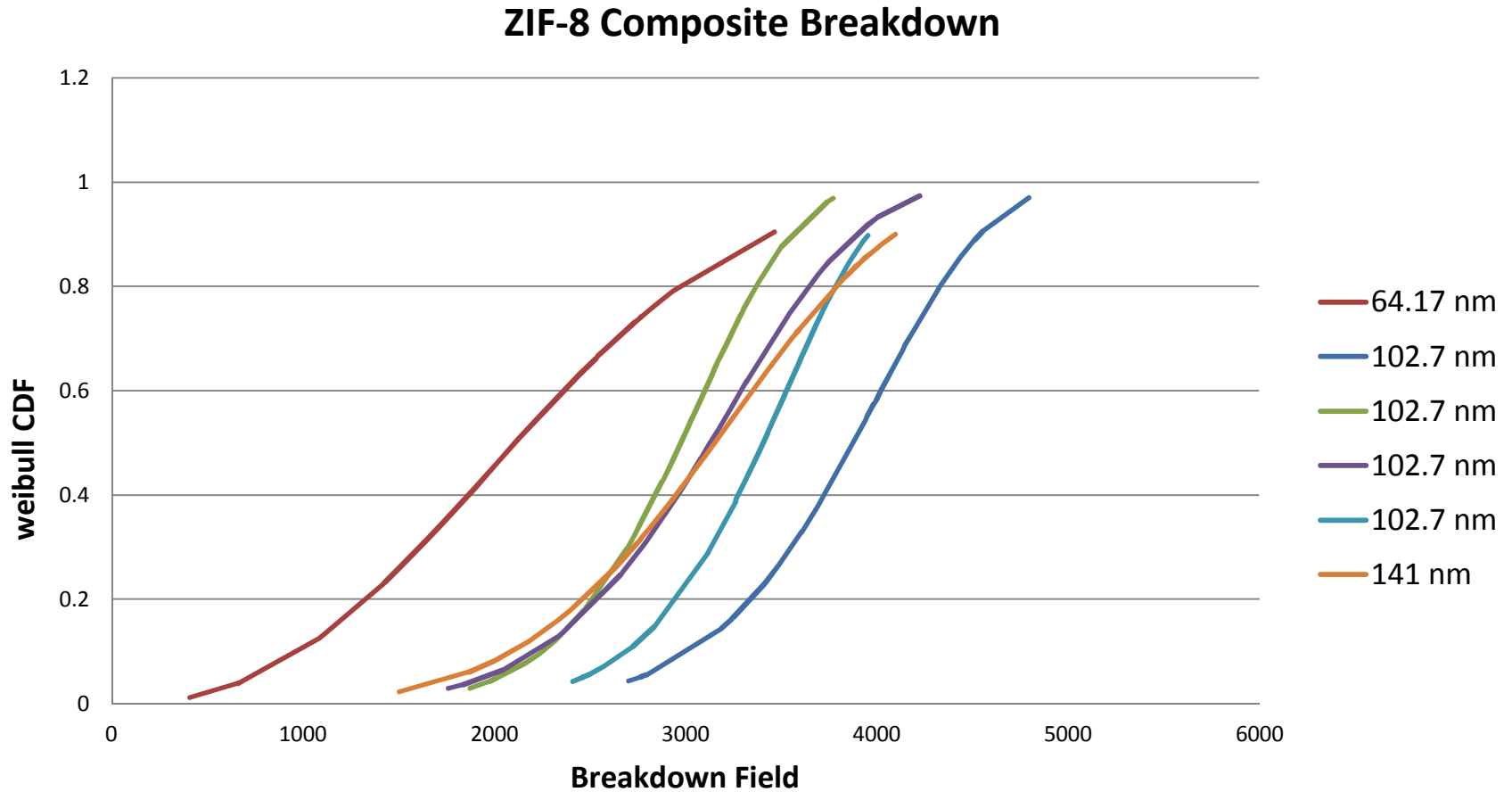
Weibull Distribution

- Used to describe the breakdown data

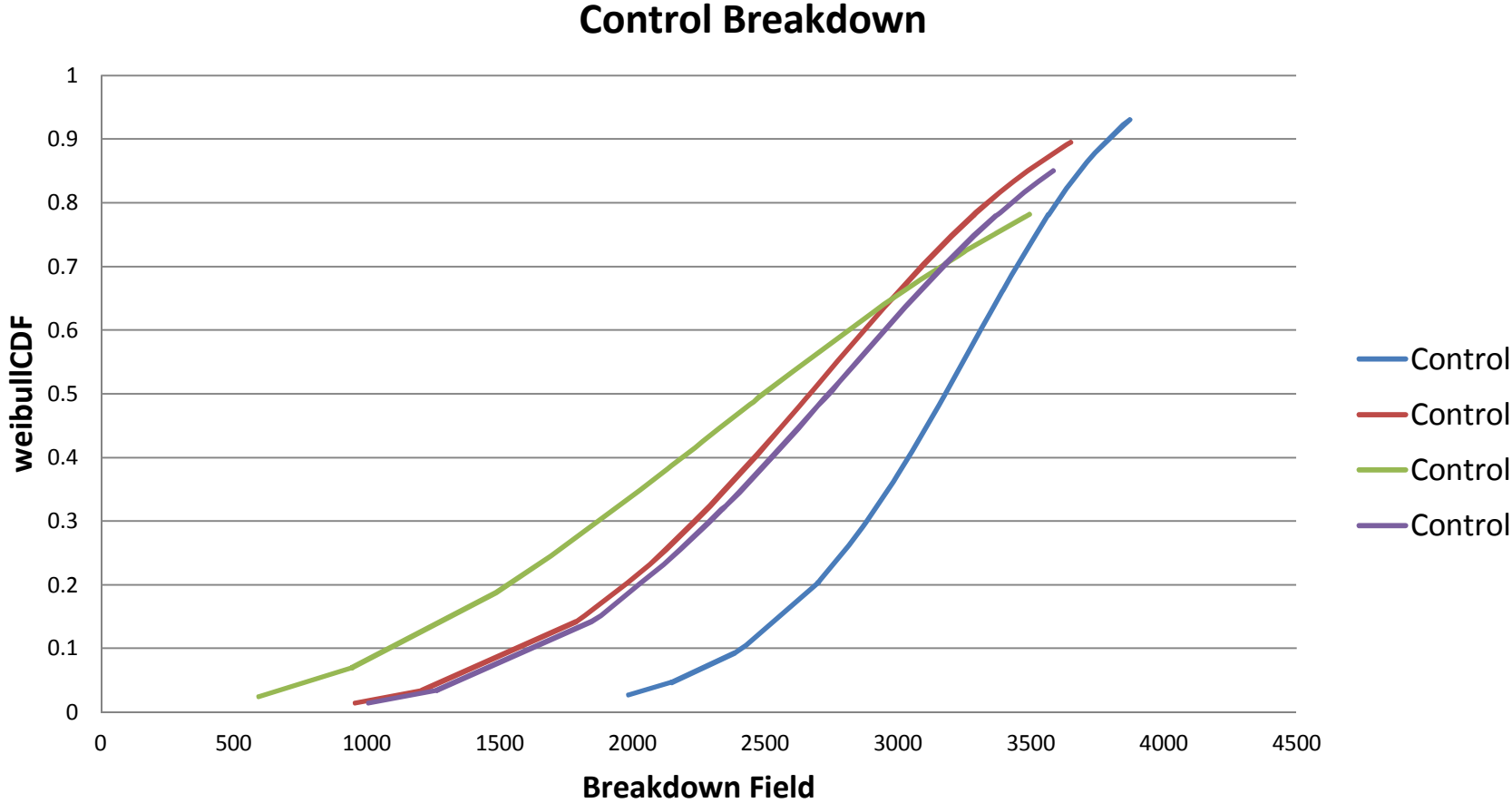
$$f(x; \alpha, \beta) = \begin{cases} \frac{\alpha}{\beta^\alpha} x^{\alpha-1} e^{-(x/\beta)^\alpha} & x \geq 0 \\ 0 & x < 0 \end{cases}$$

- Where α is the shape parameter
- Where β is the scale parameter
- Where x is the value to be determined, must be positive

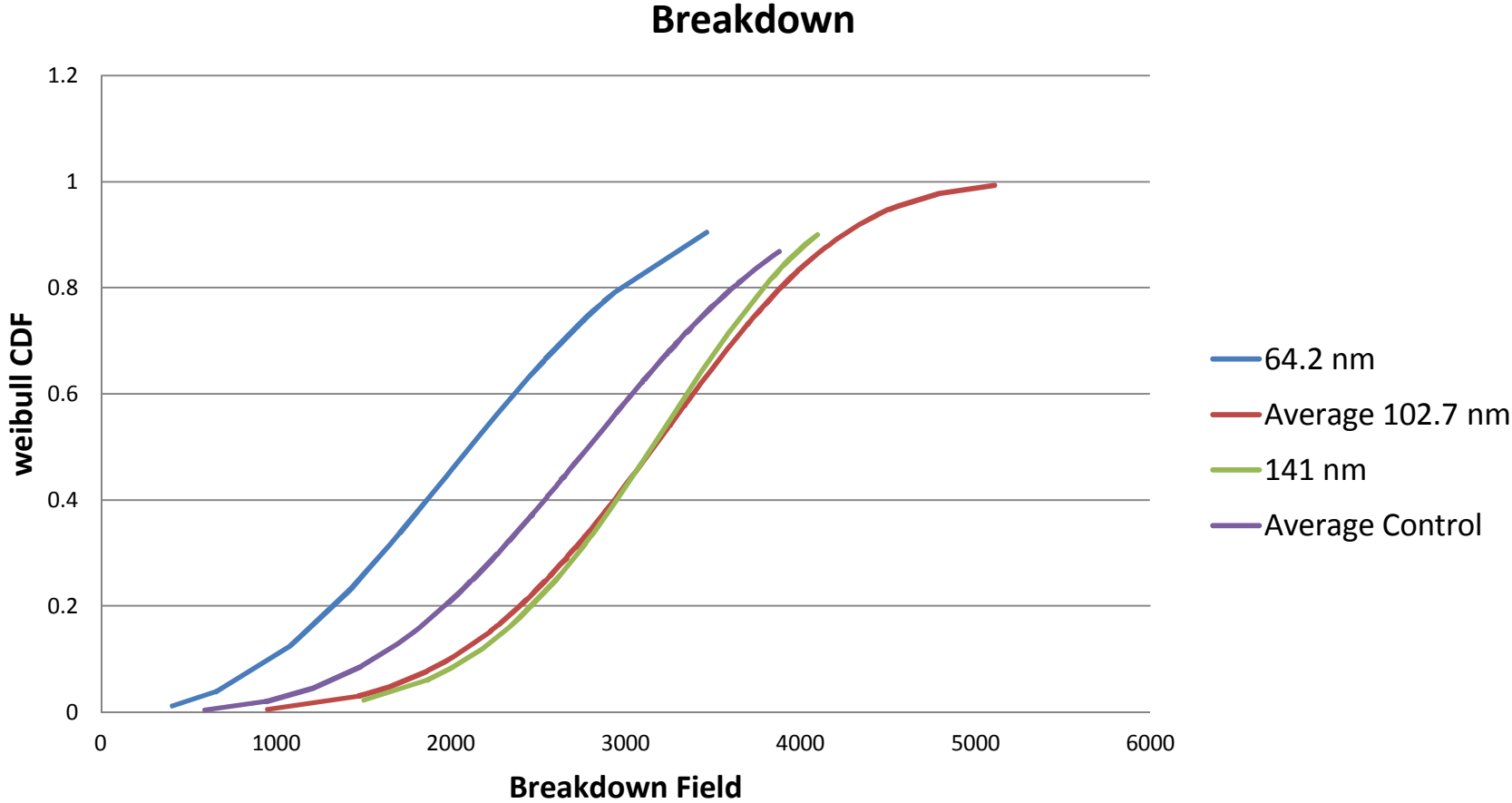
Breakdown of ZIF-8 Composite Films



Breakdown of Control Films



ZIF-8 Composite and Control Breakdowns



Energy Density Results

| ZIF-8 Composite | | | |
|-----------------|--------------|------------------------|-------------------------------------|
| Particle Size | Permittivity | Breakdown Field (V/cm) | Energy Density (J/cm ³) |
| 64.2 nm | 8.88 | 2.45×10^6 | 2.36 |
| 102.7 nm | | | |
| Average | 8.05 | 3.53×10^6 | 4.44 |
| 141 nm | 7.75 | 3.41×10^6 | 4.00 |
| All ZIF-8 | | | |
| Average | 8.14 | 3.33×10^6 | 4.09 |

| Control | Permittivity | Breakdown Field (V/cm) | Energy Density (J/cm ³) |
|---------|--------------|------------------------|-------------------------------------|
| Average | 9.22 | 3.04×10^6 | 3.77 |

Conclusions

- All particle sizes of ZIF-8 composites had a lower average permittivity than the controls
- 60 nm particle size ZIF-8 composites had a lower breakdown field and energy density than the controls
- > 100nm particle size ZIF-8 composites had, on average, a higher breakdown field and energy density than the controls
- Particle size does seem to have an effect on breakdown strength of ZIF-8 polymer composites, but larger sample sizes are needed

Problems and Future Work

- Due to casting problems (unrelated to particle size), films made with the larger synthesized ZIF-8 particles were unable to be used for dielectric testing.
- Due to high variability in both control samples and in composites with the same particle size a much larger sample size will be needed to provide conclusive results.
- Testing of additional samples at each particle size will determine if the differences observed in this work are due only to sample-to-sample variability, or if a true particle size effect exists.

Acknowledgements

- person who helped
- person who helped
- other people who helped?

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References

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