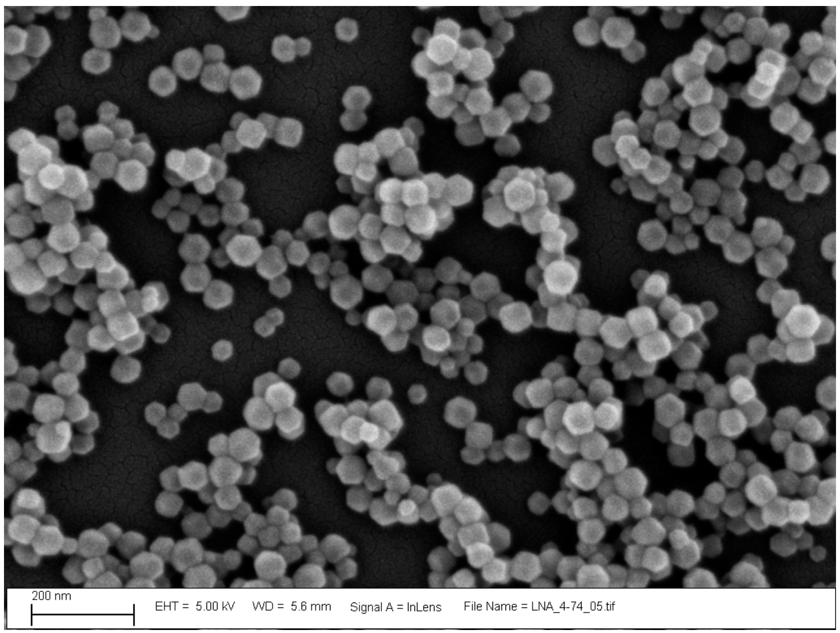
SAND2011-2739C

Polymer-MOF Composites as Dielectric Materials

Leah N. Appelhans

Sandia National Laboratory



Sandia National Laboratories is a multi-program 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.

High Energy Density Capacitors

relative permittivity (ε_r or κ): high, stable
breakdown strength (E_b): high
dissipation factor (Df): low, <2%

Energy Density

$$U_e = \frac{1}{2} \varepsilon_r \varepsilon_o E_b^2$$

Advantages of Polymer Dielectrics

- high breakdown strengths
- soft failure
- cost
- flexibility
- ease of processing
- control of properties

but…

- low relative permittivities
- low energy densities
- small T operating ranges
- high performance polymers expensive

Polymer Composite Dielectrics

- higher permittivity
- lower breakdown strengths

- polymer/additive incompatibility
- poor dispersion
- field inhomogeneity

Improve Compatibility

- organic functionalization
- covalent particle integration
- polymer/insulator coating
- MOFs?

Metal-Organic Frameworks

MOF-Polymer Composites

- intrinsic organic functionality to improve dispersion and polymer compatibility

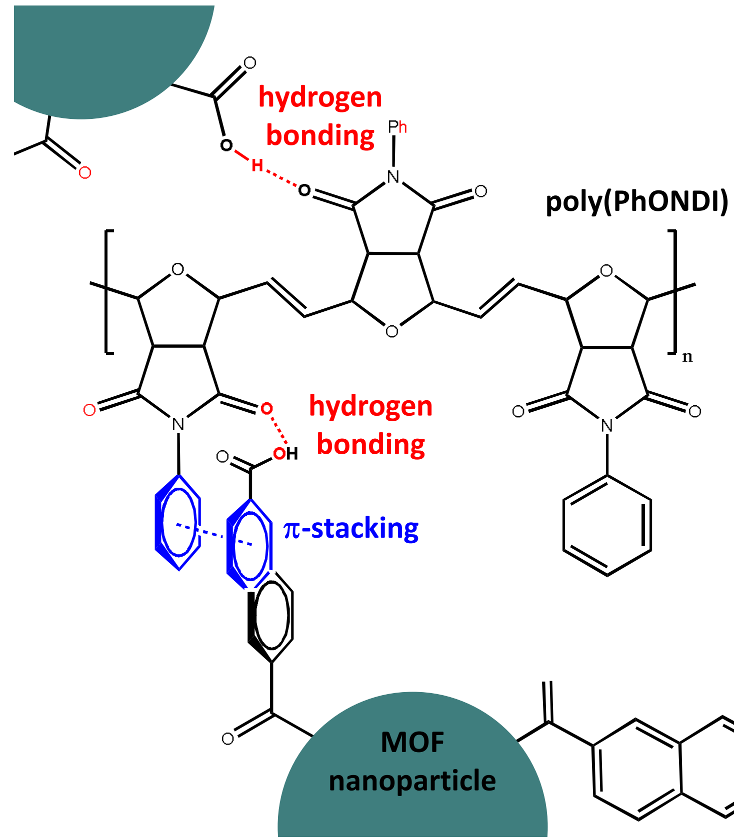
- modify/control properties by appropriate selection of metal and ligand (chiral/polar frameworks)

- postsynthetic modification to improve/alter compatibility or covalently integrate into polymer

- high dielectric permittivity materials (T stability?)

- wealth of materials with unique properties

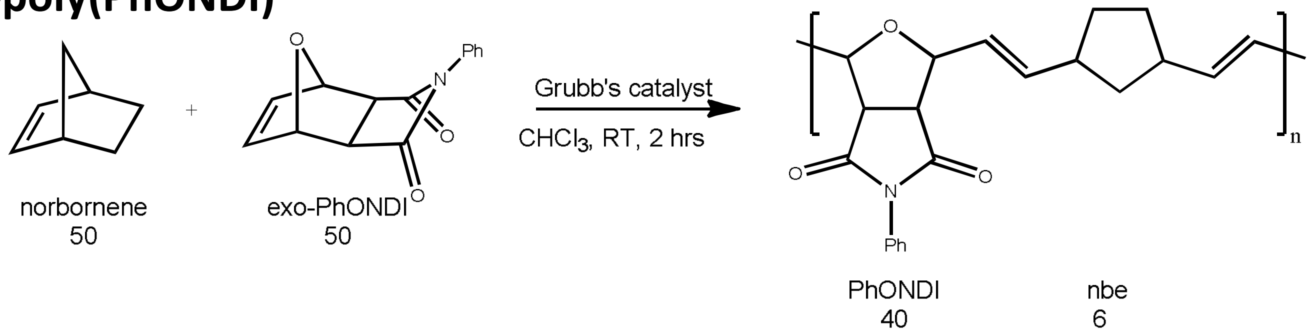
- applications in other areas (need previous work etc)

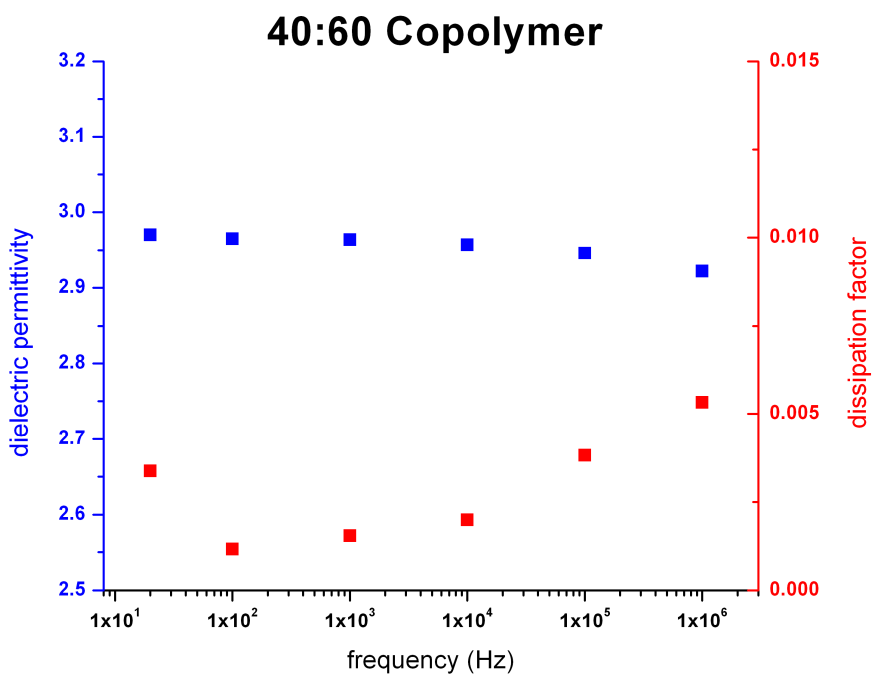


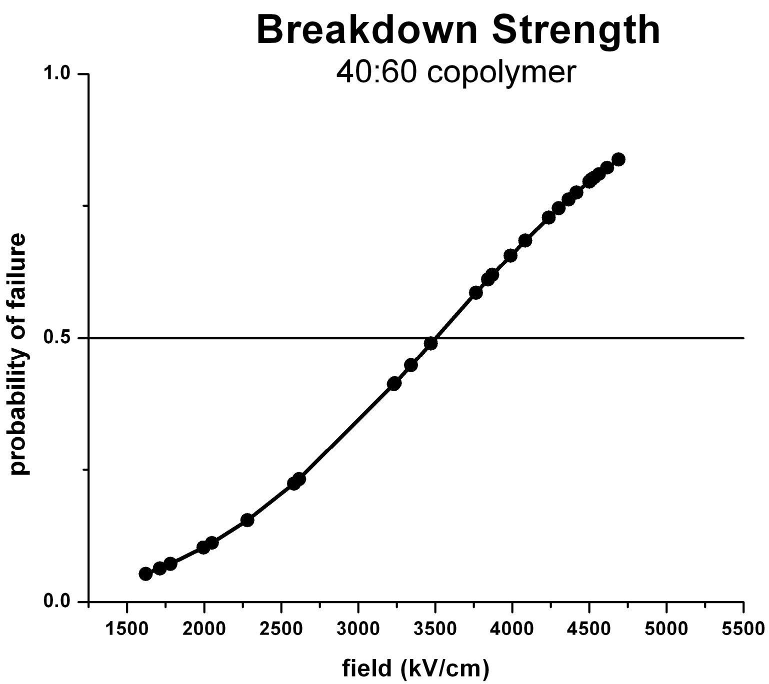
ROMP Polymers

Sandia National Laboratories

co-poly(nbe)-poly(PhONDI)







WW11.7. Hydrogenated ROMP Copolymers as Novel High Temperature Dielectric Materials with Improved Processing Characteristics.

S. M. Dirk; L. N. Appelhans; K. N. Cicotte; R. S. Johnson

ZIF-8 Nanoparticles

Zeolitic Imidazolate Framework

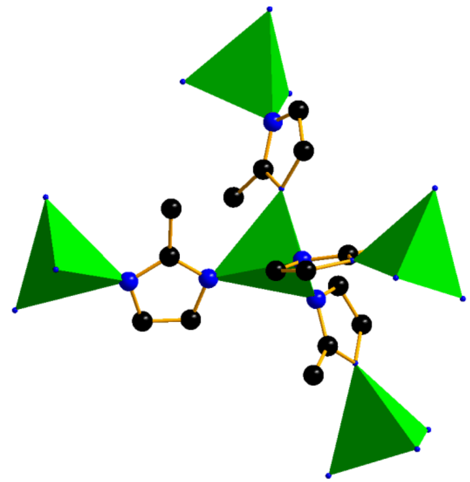
ZIF-8: $[Zn(mim)_2.2S]_\infty$

Zn tetrahedral node

sodalite-type structure

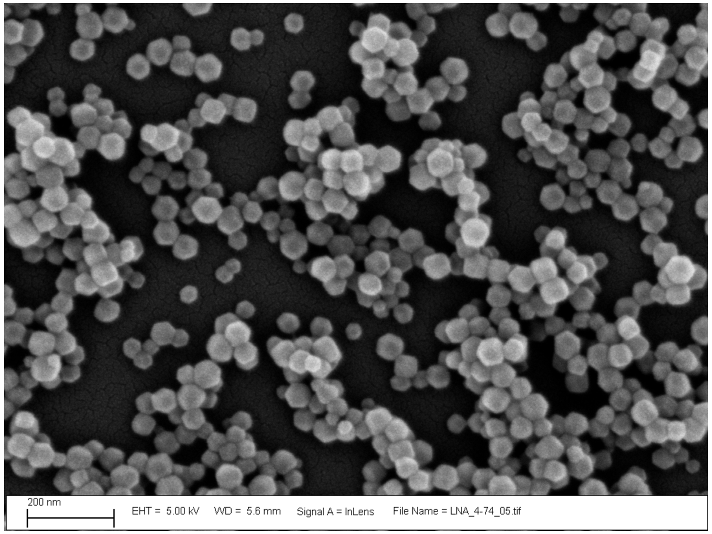
11.6 Å cages, 3.4 Å 'windows'

ε_r = 1.98 (Herrmann)



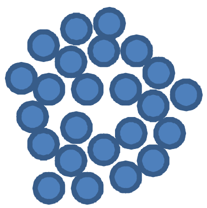
$Zn(NO_3)_2$
2-methylimidazole (8 eq)

$\xrightarrow{\text{MeOH}}$

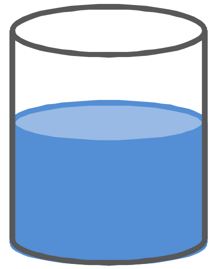


Chen, *Angew. Chem. Int. Ed*. **2006**, *45*, 1557 Yaghi, *PNAS*, **2006,** *27*, 10186
Wiebcke, *Chem. Mater.* **2009,** *21,* 1410–1412 Herrmann, *App. Phys. Lett.* **2010,** *97,* 251905

ZIF-8 Composites



ZIF-8 particles →



dichloroethane

$\xrightarrow{\text{sonication}}$ $\xrightarrow{\text{add polymer}}$

composite solution

$\xrightarrow{\text{stir}}$

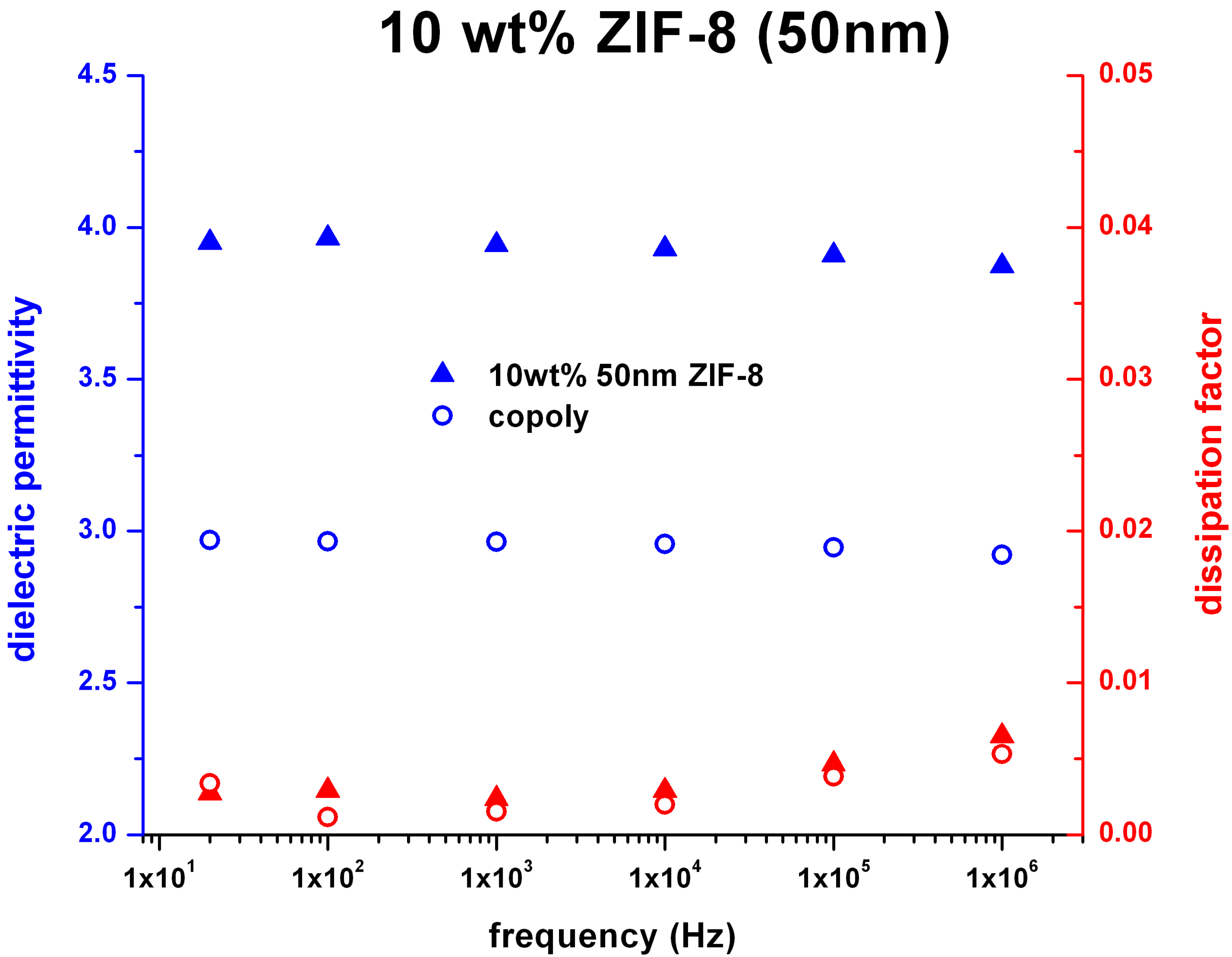
$\xrightarrow[\text{drawdown machine}]{\text{solvent cast}}$

plain poly picture

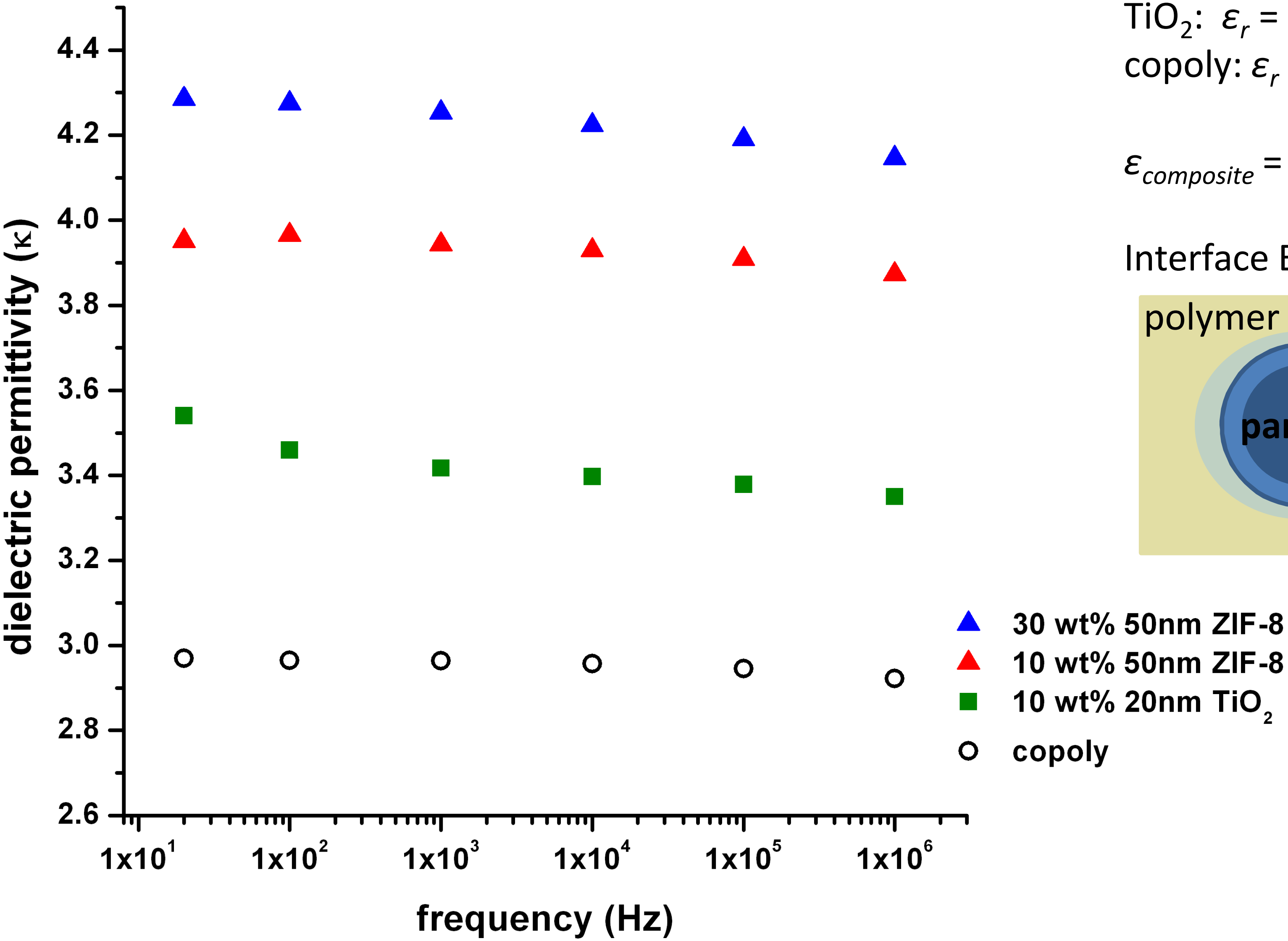
dry, vac oven, 60 °C

$\xrightarrow[\text{6.0mm Au electrodes}]{\text{sputter coat}}$

Electrical Characterization



Comparison to TiO_2 Composite Permittivity



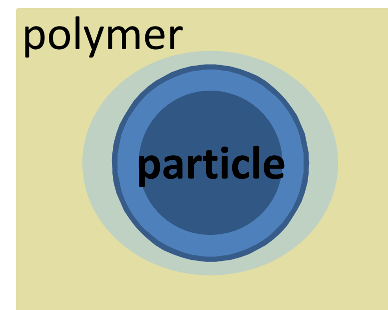
ZIF-8: ε_r = 1.98

TiO_2: ε_r = 41

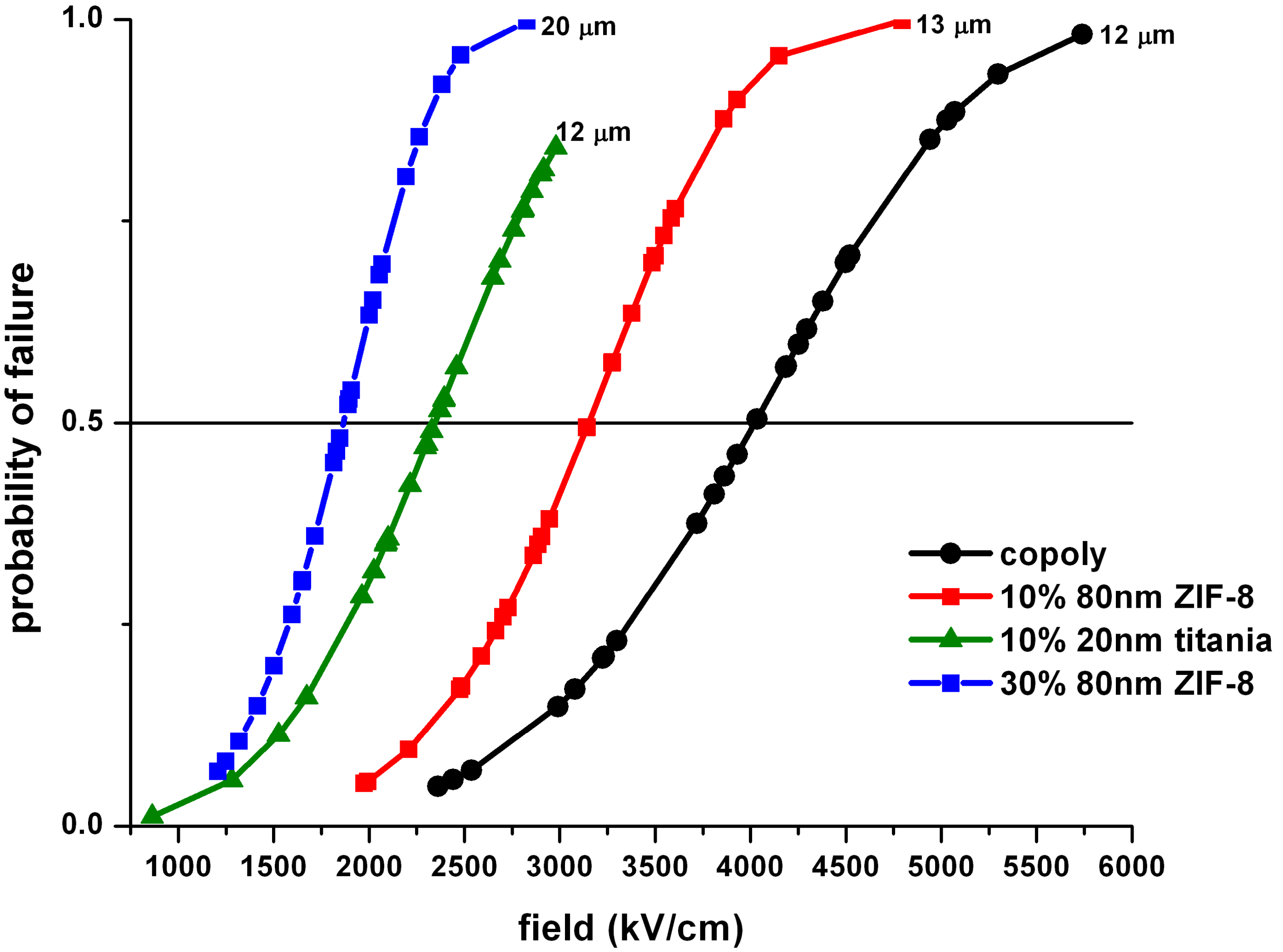
copoly: ε_r = 2.98

$$\varepsilon_{composite} = \varepsilon_1(f_1) + \varepsilon_2(f_2)$$

Interface Effects!

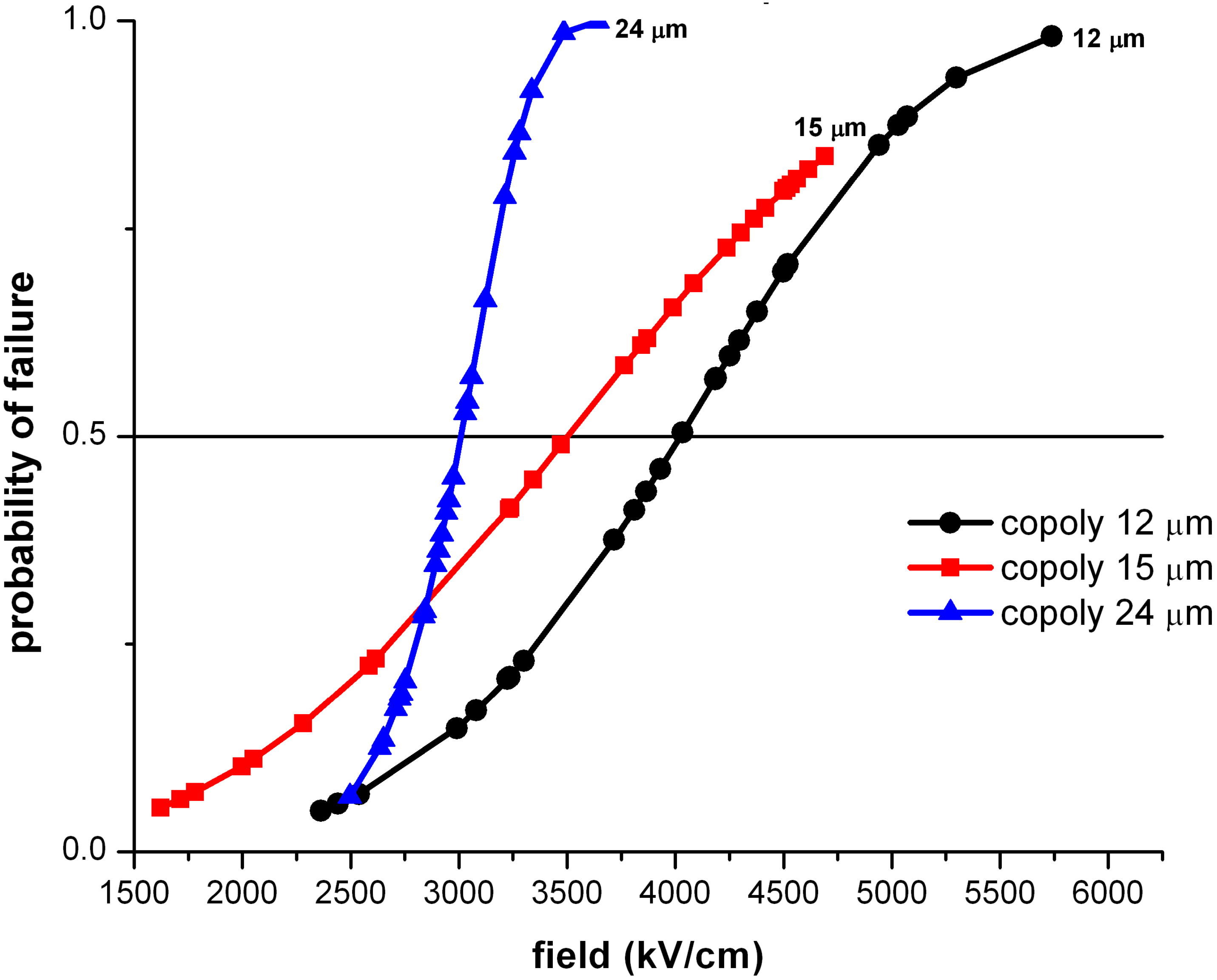


Comparison to TiO_2 Composite Breakdown Strength



Breakdown Strength

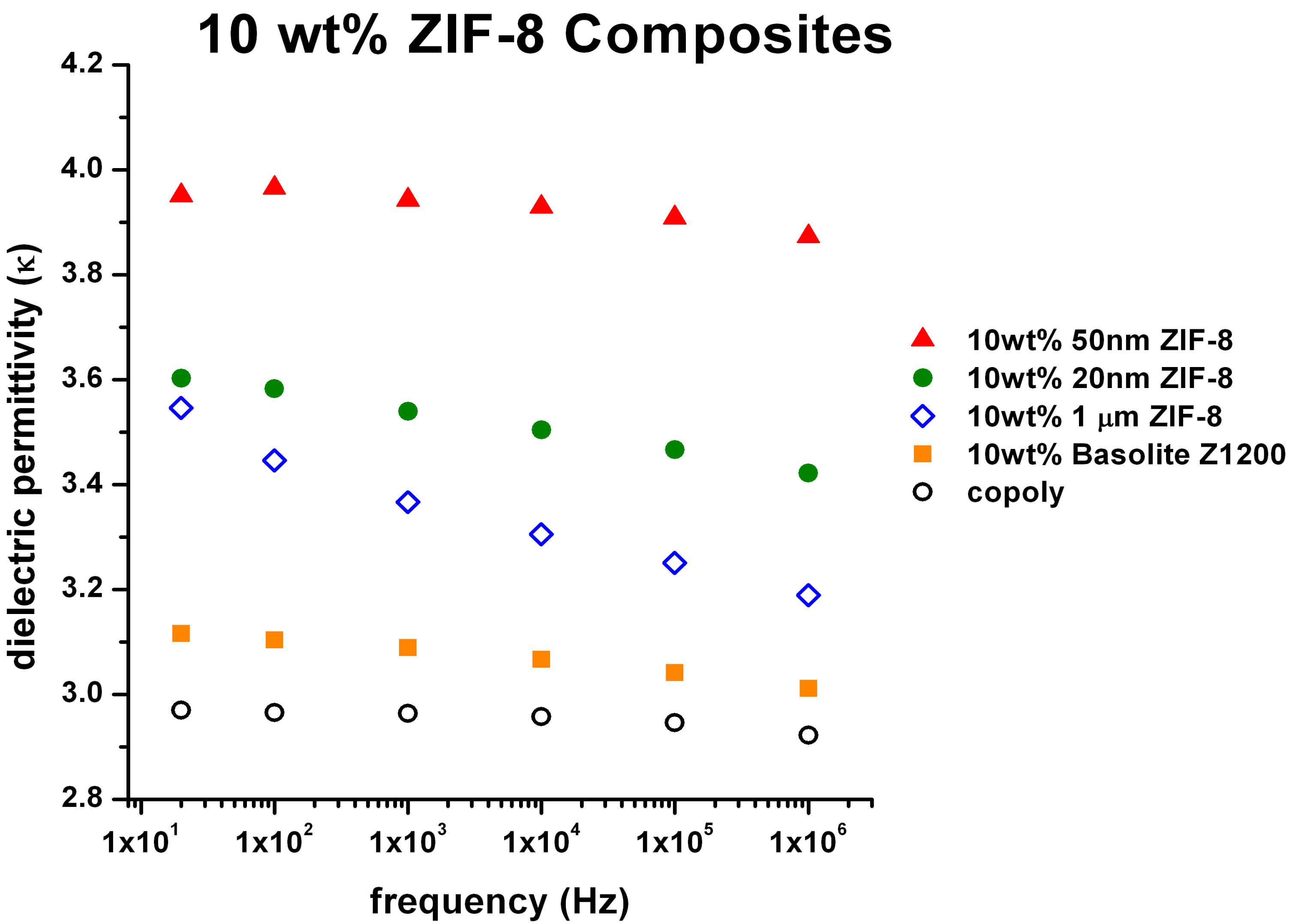
Thickness Dependence



ZIF-8 Composite

- 10 wt% 50nm ZIF-8 composite has improved permittivity relative to copolymer alone, but lower breakdown strength.
- ZIF-8 composite has higher permittivity and breakdown strengths than TiO_2 composite.
- Higher ZIF-8 loading (30wt%) increases permittivity but further decreases breakdown strength.
- 10wt% 50nm ZIF-8 composite dissipation factor is unchanged relative to the copolymer alone.

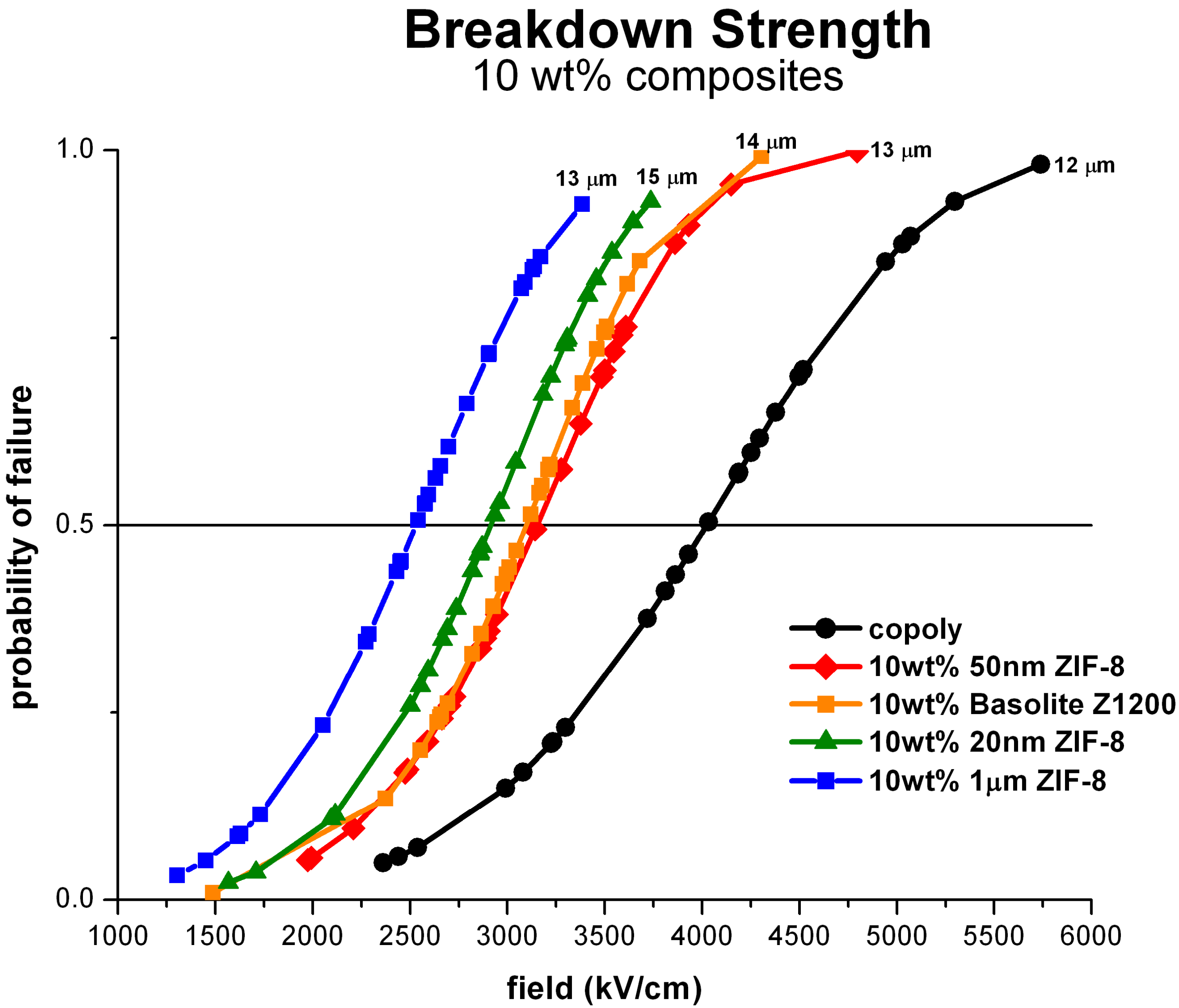
ZIF-8 Particle Size



Wiebcke, *Chem. Mater.* **2009,** *21,* 1410–1412 Wiebcke, *Chem. Mater.* **2011,** *23,* 2130

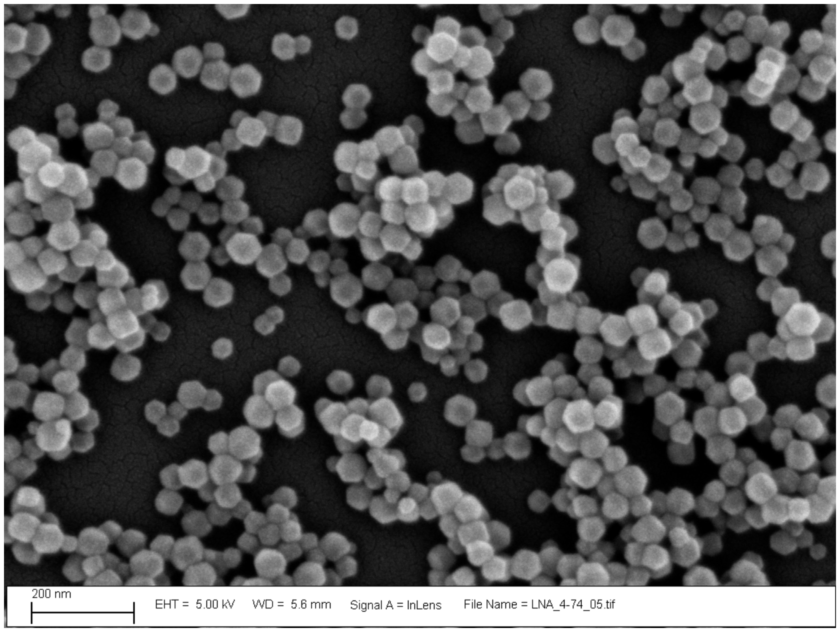
* nominal particle sizes

ZIF-8 Particle Size



ZIF-8 Particle Size

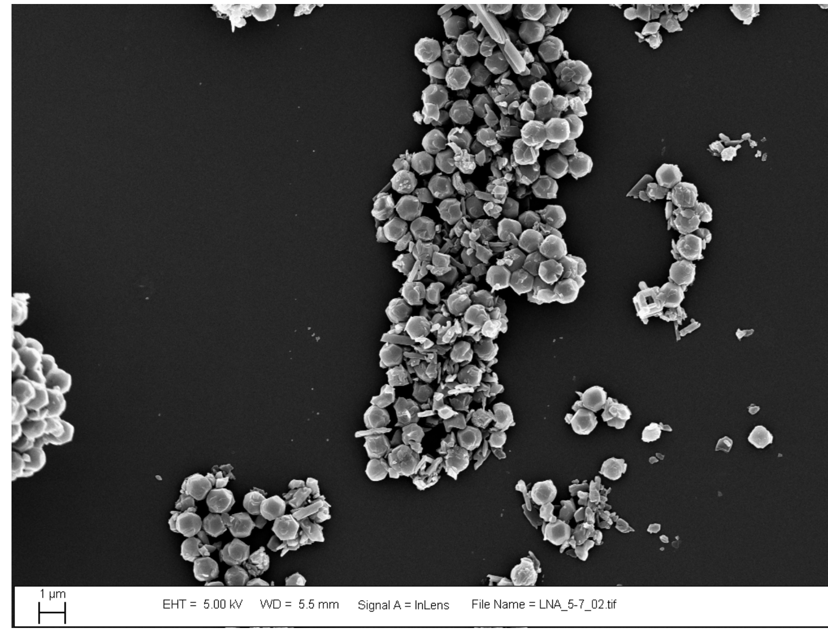
50 nm



200 nm

DLS (MeOH): 60 nm

1 μm

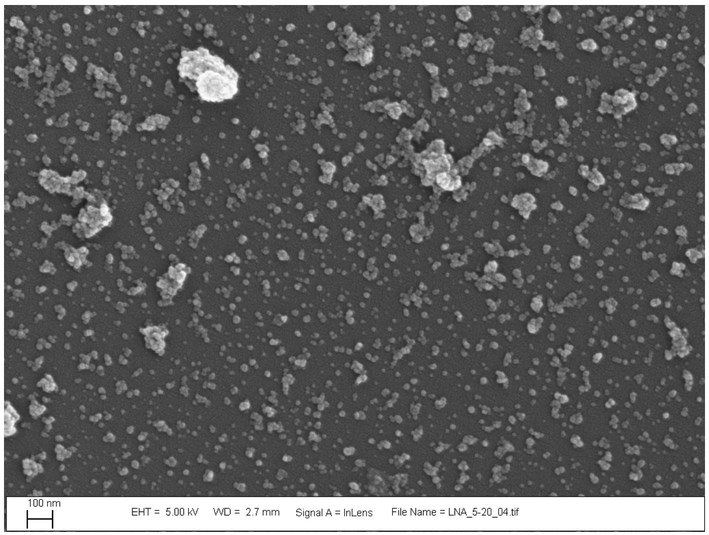


1 μm

DLS (MeOH): XX nm

ZIF-8 Particle Size

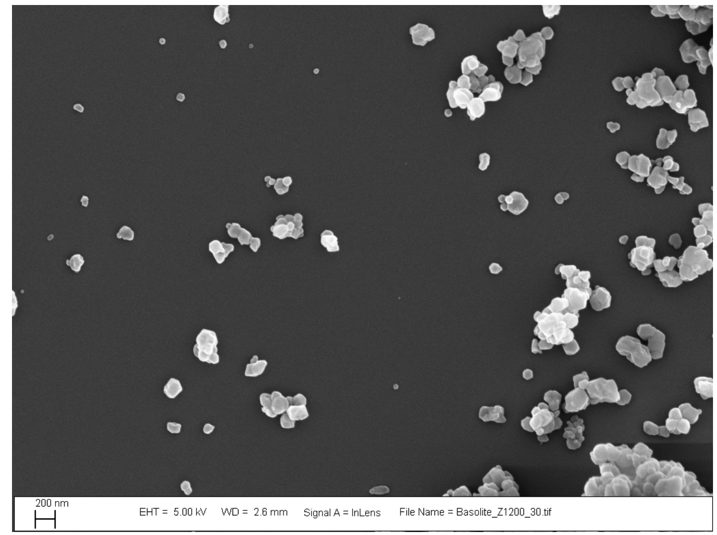
20 nm



20 μm
100 nm

DLS (MeOH): XX nm

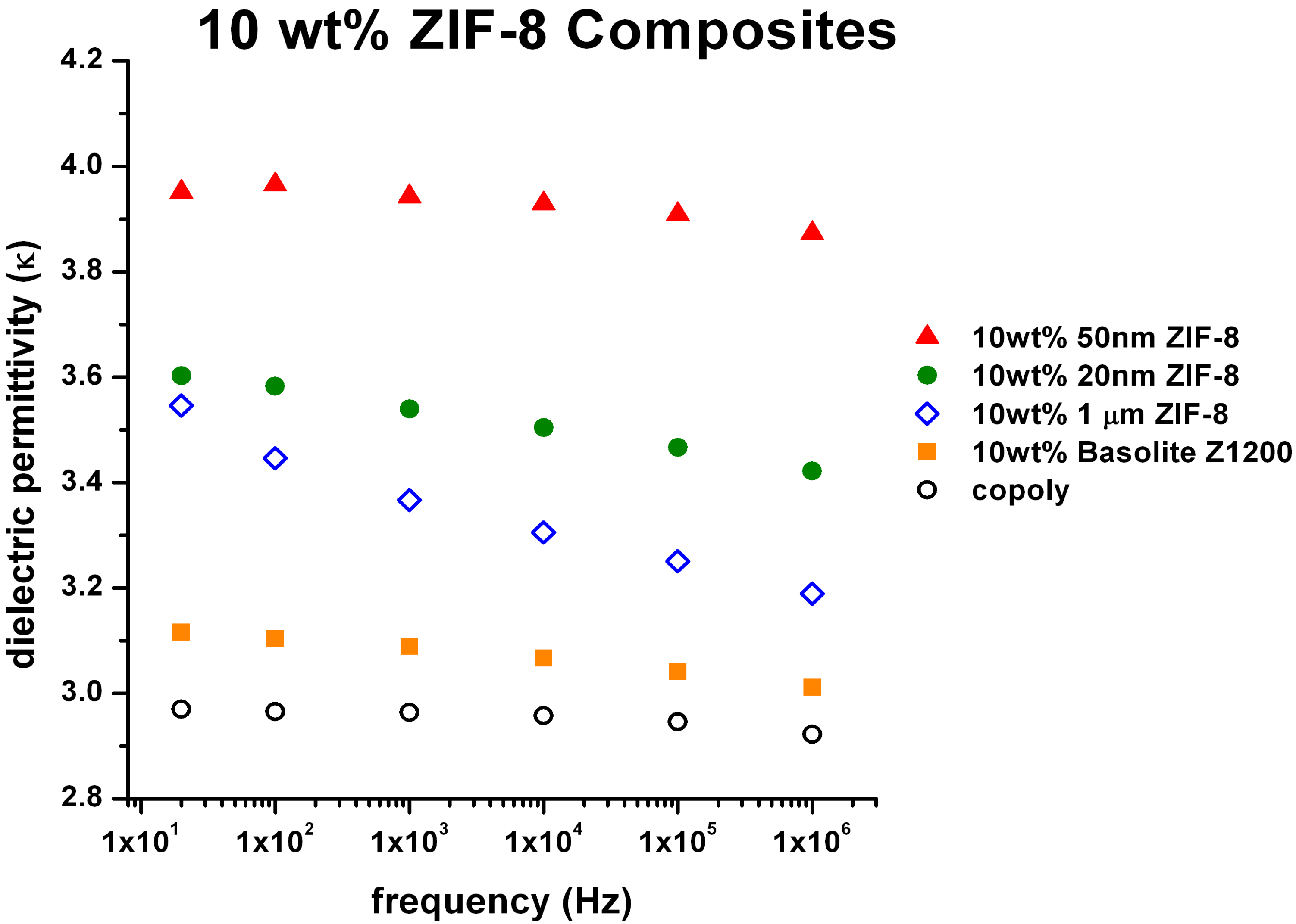
4.9 μm (Basolite Z1200)



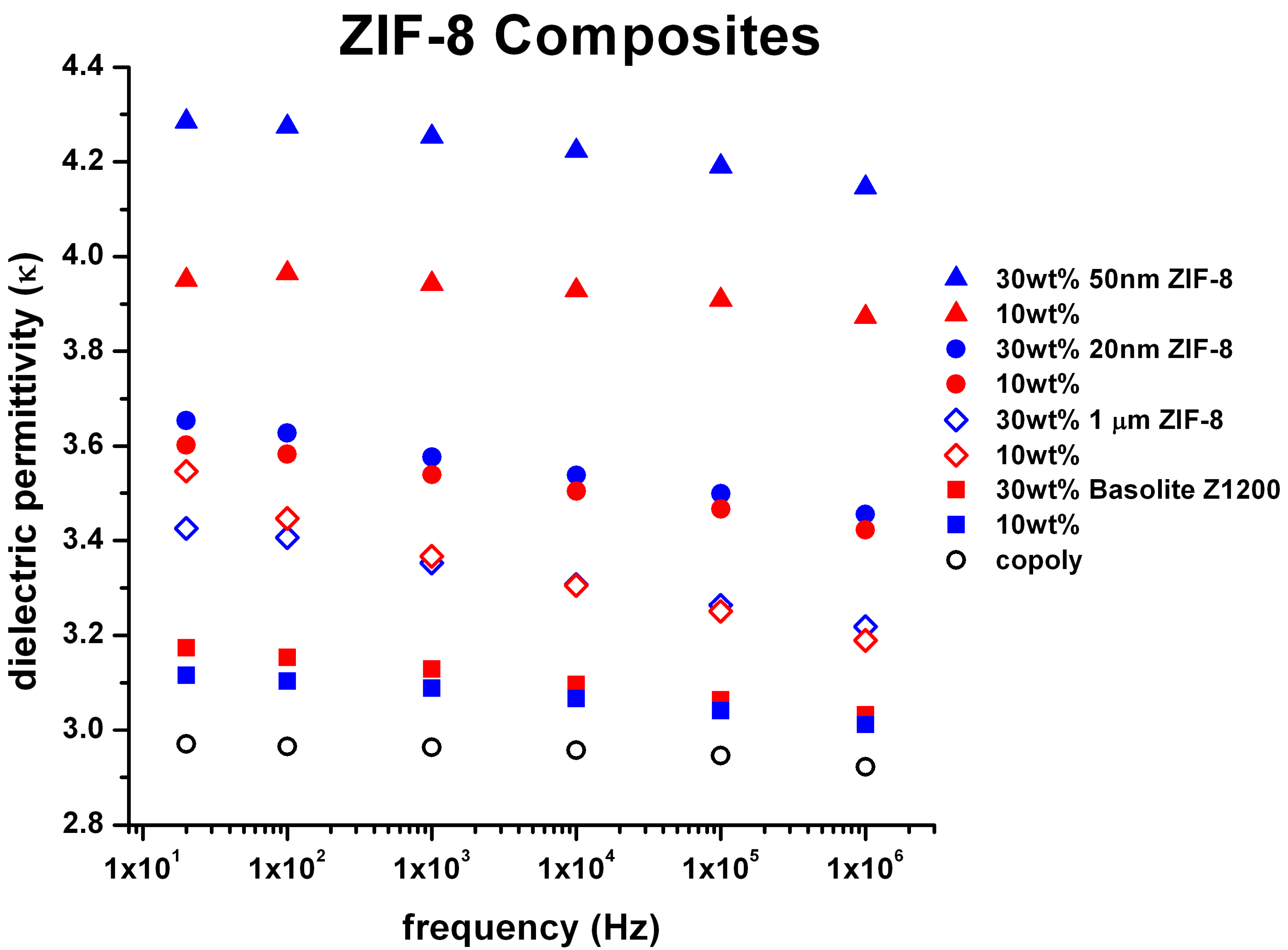
20 μm
200 nm

DLS (MeOH): XX nm

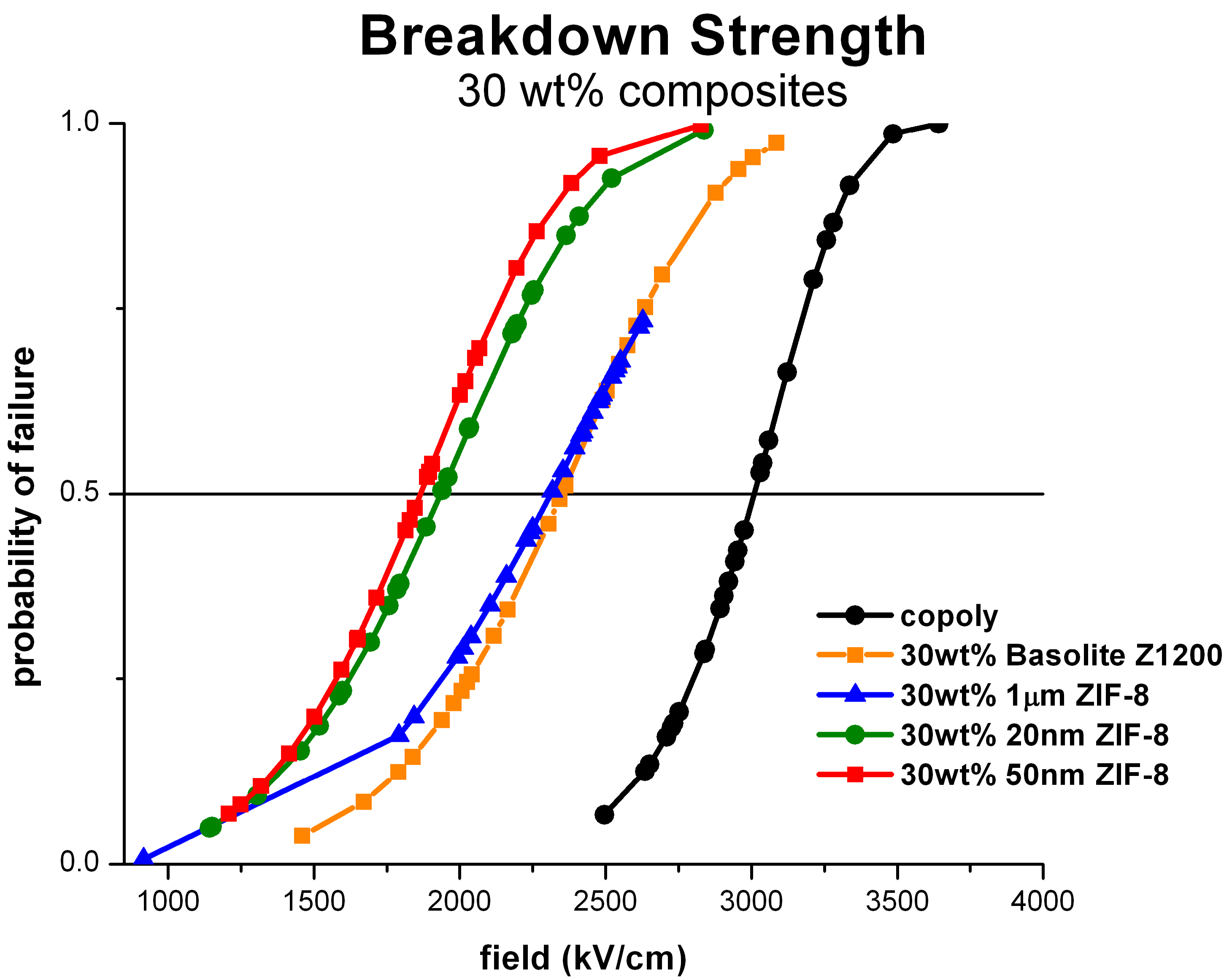
ZIF-8 Particle Size



ZIF-8 Particle Size: Loadings

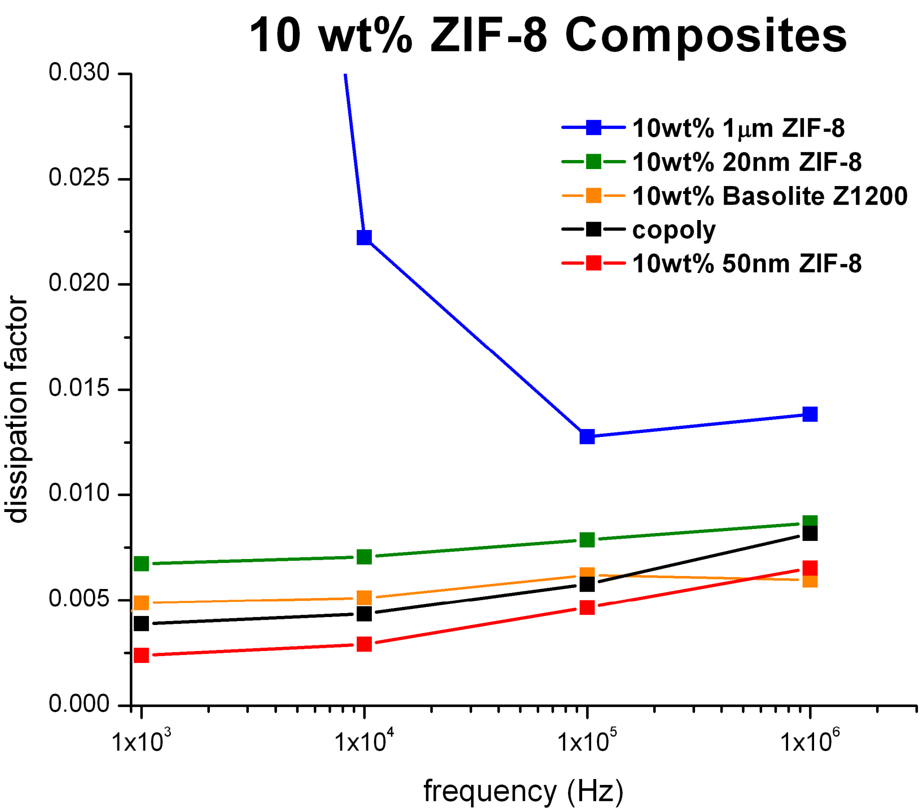


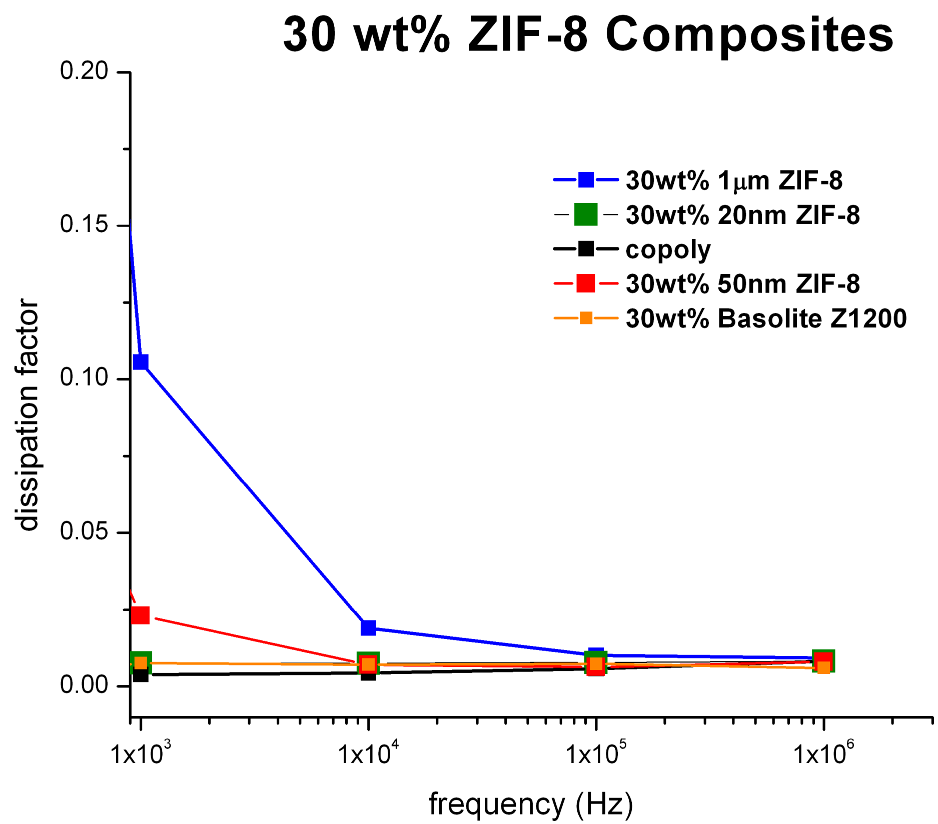
ZIF-8 Particle Size



ZIF-8 Particle Size

Dissipation Factor





ZIF-8 Particle Size

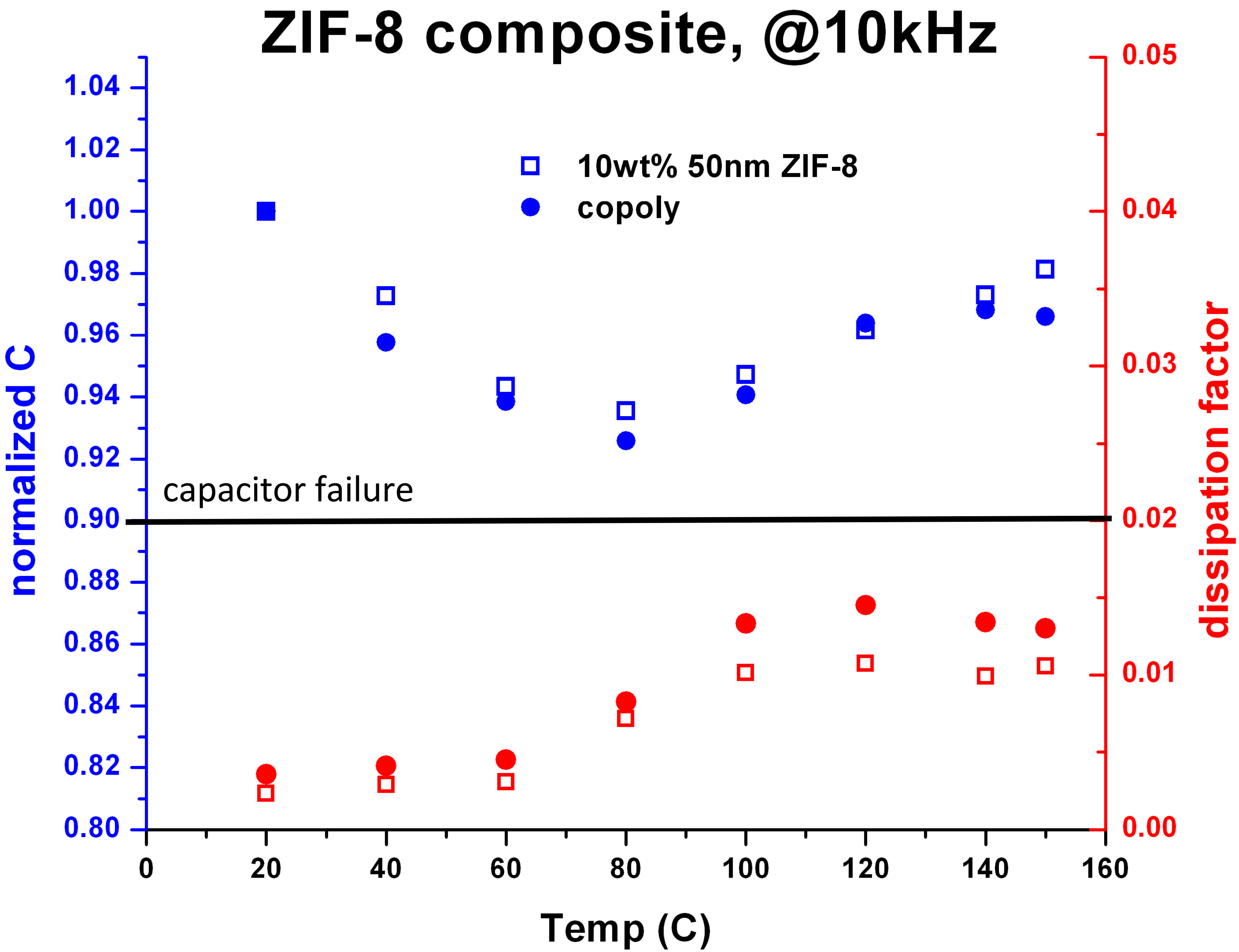
- Both particle size and conglomerate size are key. Smaller better dispersed particles give the best properties at 10wt% loading.

- The increase of relative permittivity with loading is greater for smaller better dispersed particles.

- No clear relationship between particle size/dispersion and breakdown strengths is apparent.

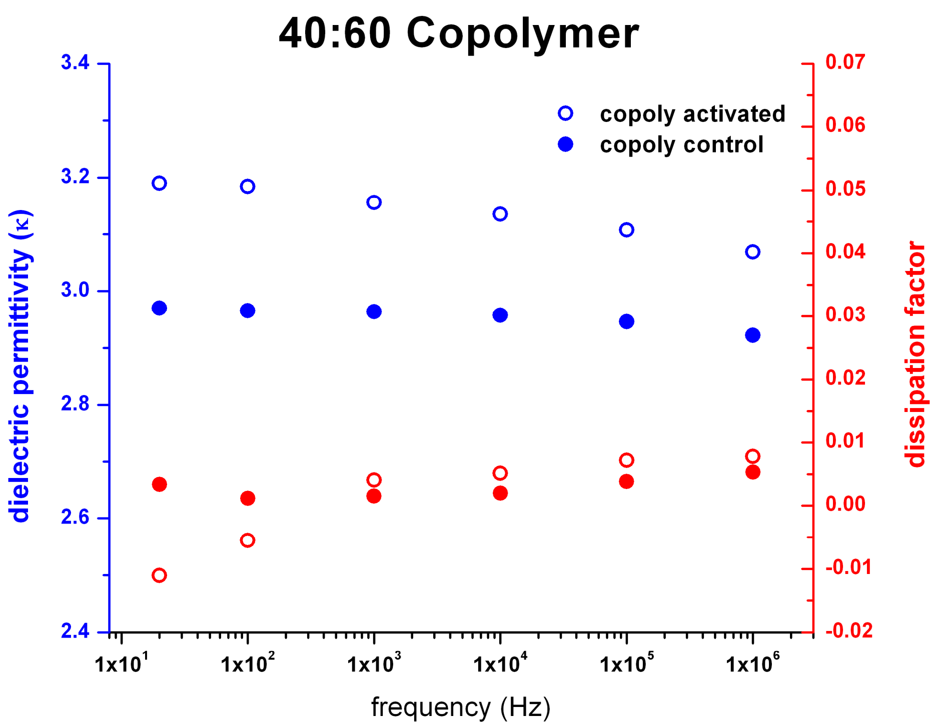
- Dissipation factor is extremely sensitive to the presence of large crystallites (1μm samples).

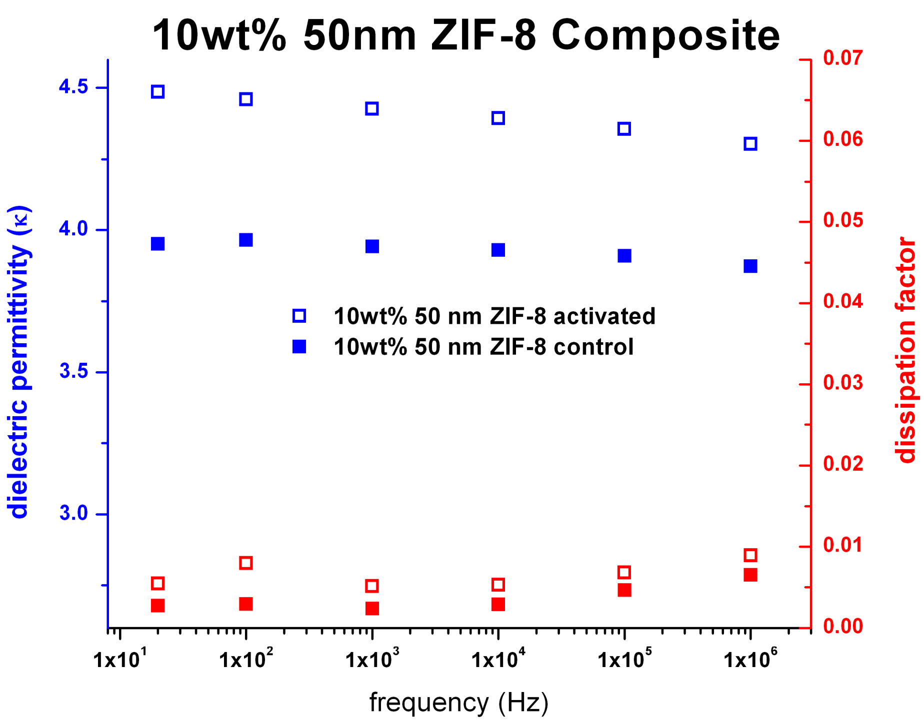
Temperature Stability



'Activation'

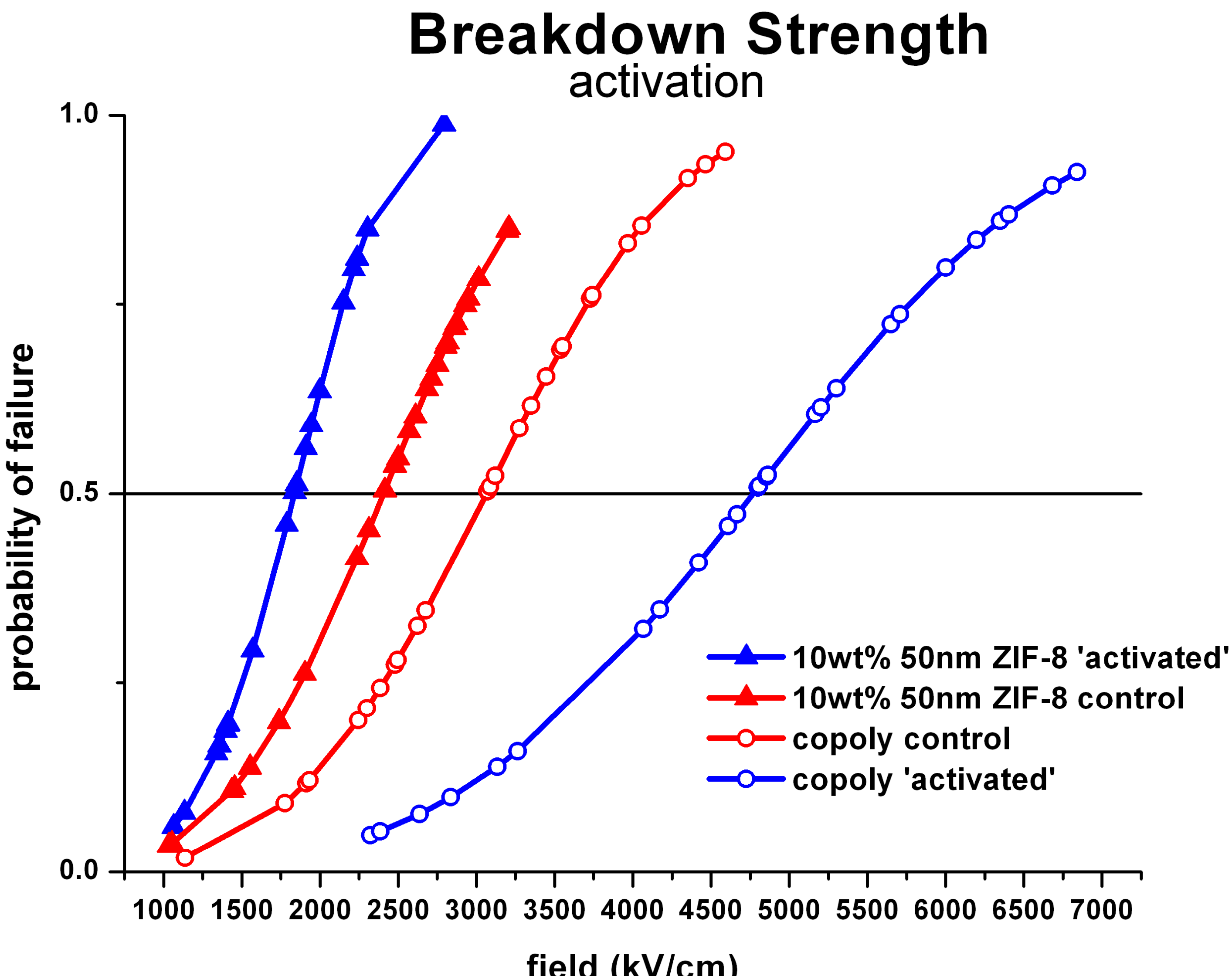
Heat film samples under vacuum at 100 °C for 72hrs





'Activation'

Heat film samples under vacuum at 100 C for 72hrs



Energy Density

Energy density $U_e = ½\, \varepsilon_r \varepsilon_o E_b^2$

~20 μm thick films

sample	breakdown (kV/cm)	ε_r (@10 kV)	U_e (J/cm^3)
30wt% 20 nm ZIF-8	2082	3.54	**0.68**
30wt% 50 nm ZIF-8	2000	4.22	**0.75**
30wt% 5 μm ZIF-8	2496	3.10	**0.85**
30wt% 1 μm ZIF-8	2486	3.31	**0.91**
copolymer	3100	2.99	**1.27**

~13 μm thick films

sample	breakdown (kV/cm)	ε_r (@10 kV)	U_e (J/cm^3)
10wt% TiO2	2565	3.40	**0.99**
10wt% 1 um ZIF-8	2741	3.31	**1.10**
10wt% 5 um ZIF-8	3296	3.07	**1.48**
10wt% 20 nm ZIF	3117	3.50	**1.51**
10wt% 50 nm ZIF-8	3371	3.93	**1.98**
copolymer	3913	2.99	**2.03**

Summary and Future Work

- ZIF-8 composites have higher permittivities than the copolymer alone, despite ZIF-8 having a lower dielectric constant (interface effects).
- ZIF-8 composites perform better than inorganic composites, but do not improve energy density relative to the polymer alone.
- Dispersibility is more important than particle size, but both play a role in determining electrical properties.

- Lower loadings to improve breakdown strengths (also for low ε_r composites)
- Improve particle dispersion in solution prior to polymer addition.
- Alternative high ε_r MOFs.
- Post-synthetic modification of MOF surface ligands.

Acknowledgements

Shawn Dirk

Mark Allendorf

Erik Spoerke

Nelson Bell

Ina Sava

Bonnie McKenzie

$$$

Sandia National Labs- LDRD