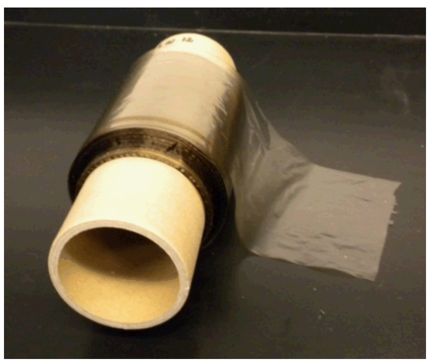
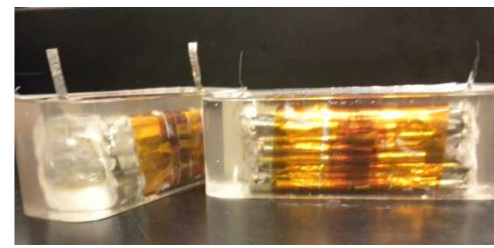
DEPARTMENT of CHEMICAL & NUCLEAR ENGINEERING

SAND2013-9963P

High Temperature Polymer Dielectrics for Electric Vehicle Capacitor Applications





Kylen Shanel Johns

Masters Defense

Department of Chemical and Nuclear Engineering

Advisor: Plamen Atanassov

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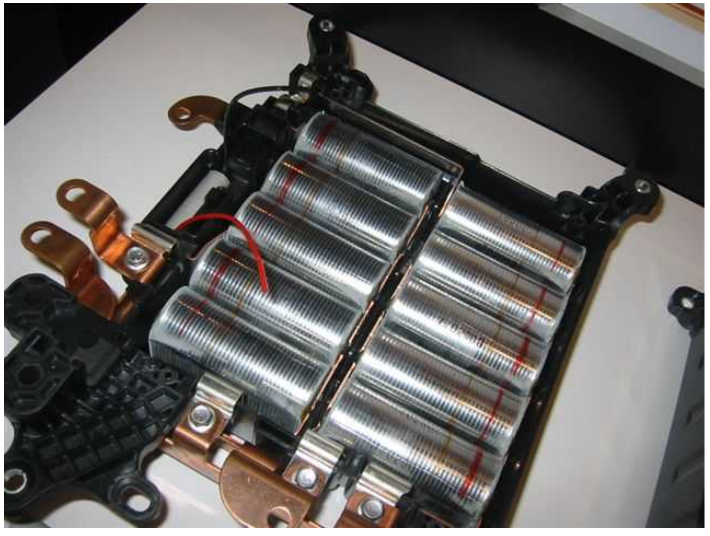
Outline

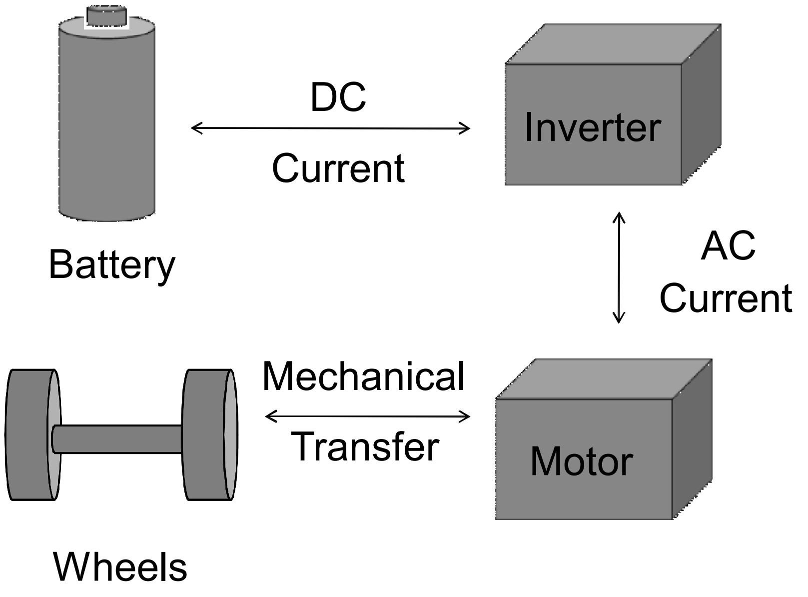
- Chapter 1: Background and Introduction
- Chapter 2: Materials and Methods
- Chapter 3: Evaluation and Characterization of Additives Incorporated in S-POW
- Chapter 4: Electrochemical Study of Polymer/Additive Composites
- Chapter 5: Evaluation and Characterization of Poly(PhNDI) and Poly(PhNDI)/Polynorbornene Copolymers
- Chapter 6: Conclusions and Future Work

Problem

- Inverters are used in HEVs to absorb ripple current and prevent damage to battery
- Current DC bus capacitors prevent significant barriers for meeting DOE specifications for cost, weight, volume and reliability



Bank of 138 μF polymer film capacitors in 2004 Prius Inverter



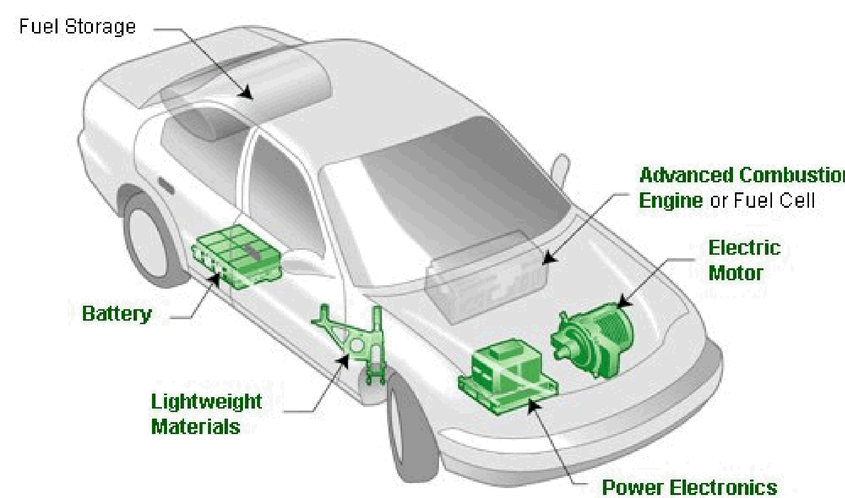
- Contributes up to 23% of cost and weight of an inverter and 30% of the inverter volume
- Thin film capacitors limited by a ceiling operational temperature of 105 °C

Qualities of a Good Capacitor for HEV Applications

- Larger Energy Density
  - Smaller capacitors
- High Operating Temperature
  - Capacitors function without additional cooling device
- Low Dissipation Factor
  - Capacitor can store charge longer
- Large Dielectric Breakdown Strength
  - Thinner films can be used, decreasing amount of material required and overall capacitor size
- Low cost (major incentive for auto industry)

2015 DOE OVT Requirements

- 140°C Ceiling operating temperature
- 450 V Operation
- 0.6 L Target volume



Current Options

- Biaxially oriented polypropylene (BOPP) is "dielectric of choice" for current automotive manufacturers
  - Inexpensive at $10/lb
  - Superior breakdown strength
- Problem with BOPP:
  - Poor performance at temperatures >105 °C
  - Low dielectric constant

UNM

Sandia National Laboratories

Why high temperature polymer?

- High temperature allows inverters to handle larger ripple currents and reduces need of cooling system
  - Reduction in cost and weight
- Polymer allows high temperature operation of 150 °C while still delivering graceful failure
- Potential to develop inexpensive high temperature polymer capacitors with increased energy densities
  - Price <$0.015/μF

Electronic Concepts, Inc.

Objectives

- Develop novel inexpensive high temperature polymer dielectric materials to be used in next generation DC bus capacitors for hybrid electric vehicles (HEVs)
- Engineer and improve energy density of polymer material using organic additives
- Produce polymer films with increased energy densities as well as improved mechanical properties

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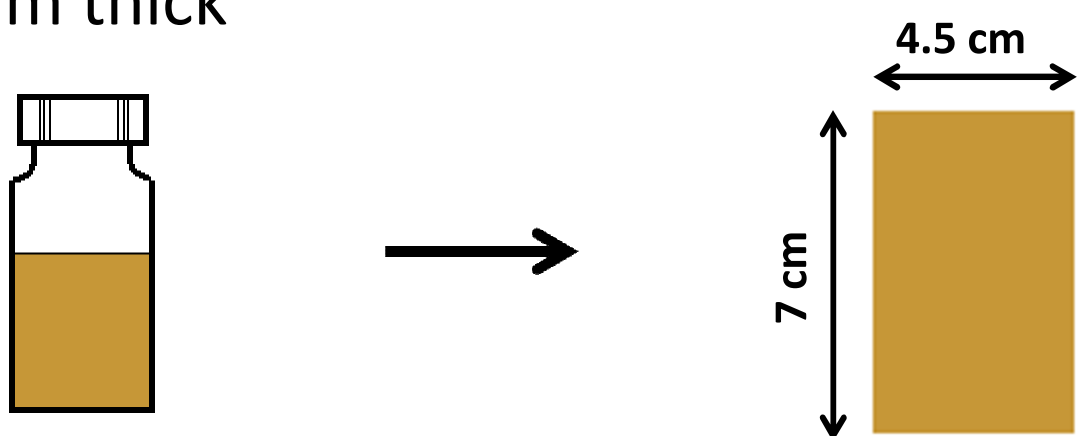
Polymer Film Preparation

- Polymers dissolved in $CHCl_3$ (S-POW and PhNDI copoly) or xylenes (TOPAS®)
- Solvent cast on drawdown
- Films metallized using sputtering
  - 50 nm thick



Polymer solution in 20 mL glass scintillation vial

Cut polymer film after drying

Polymer Film Preparation

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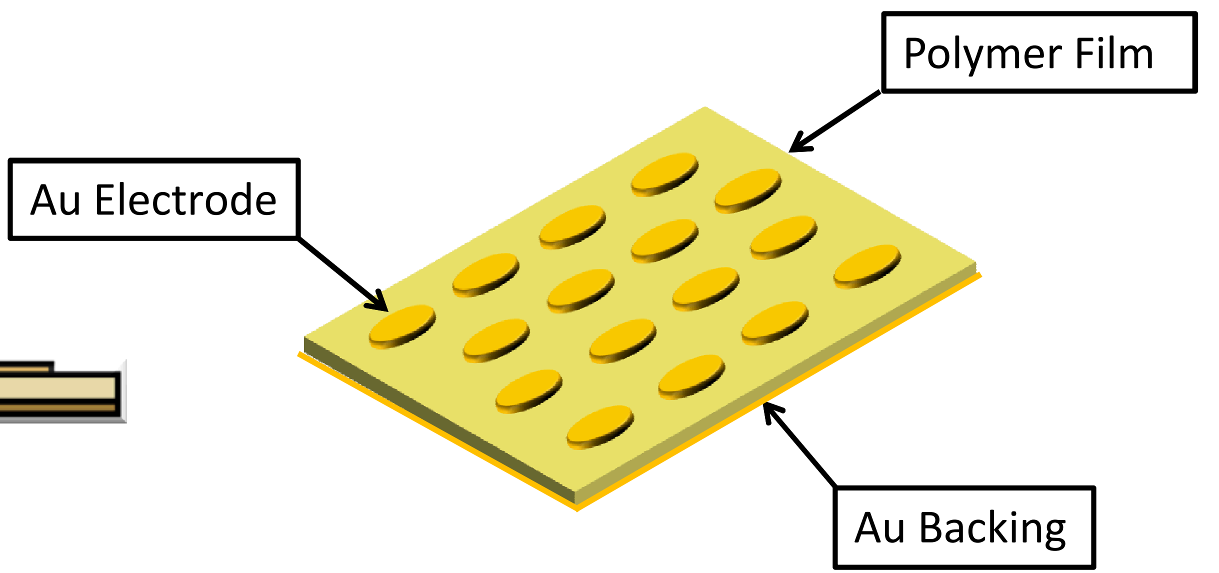
  - 50 nm

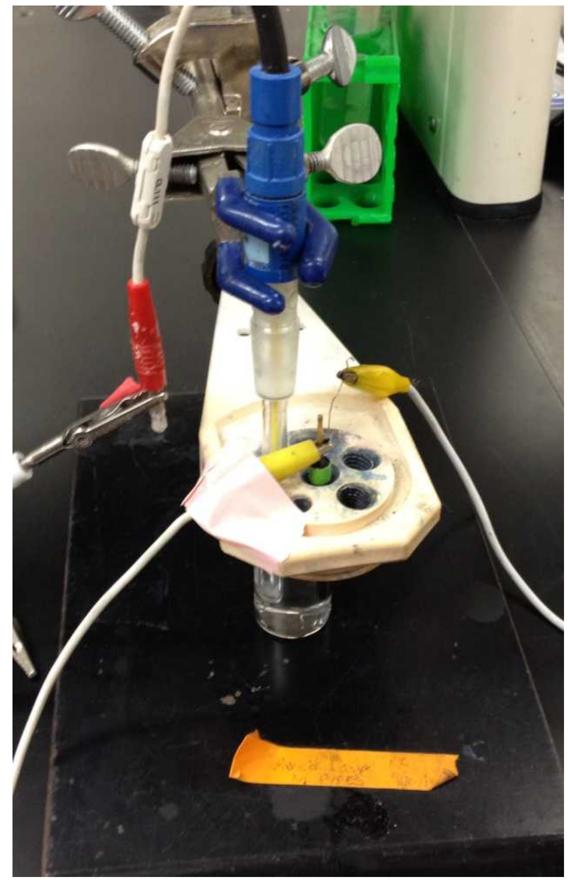


Chronoamperometry Measurements

- A Gamry Reference 600 Potentiostat/Galvanostat/ZRA was utilized
- Glassy carbon electrode with a surface area of 0.03 cm^2 was polished and sonicated in EtOH for 15 minutes prior to each measurement
- 5 µL of polymer solution dropped onto the electrode and allowed to air dry

Chronoamperometry Measurements

- Electrode placed in a 0.1M KOH with 0.1M KCl electrolyte solutions
  - pH 9.5 and 11.5.
- Potential was applied starting from -1.0 to1.0 V (step of 0.1 V) vs. an Ag/AgCl reference electrode and a Pt wire counter electrode



Characterization

- Thermal
  - TA Instruments Q200 DSC and Q500 TGA
    - DSC run from 20 °C to 250 °C under nitrogen and repeated for three cycles
    - RCS 90 cooling unit
- Mechanical
  - TA Instruments Q800 DMA was used to measure the stress versus strain of the polymer films with a film/fiber tension clamp fixture
  - Ramp force of 3 N/min to 18 N/min

Electrical Evaluation

- Hewlett Packard 4284A Precision LCR meter was used to measure the dielectric permittivity at 10 kHz and 5 kV
- DC breakdown strength was found using a Trek 30/20A with an amplified voltage ramp at 500 V/s
- Breakdown measurements taken with metallized films on a Cu plate submerged in Fluorinert® FC-40

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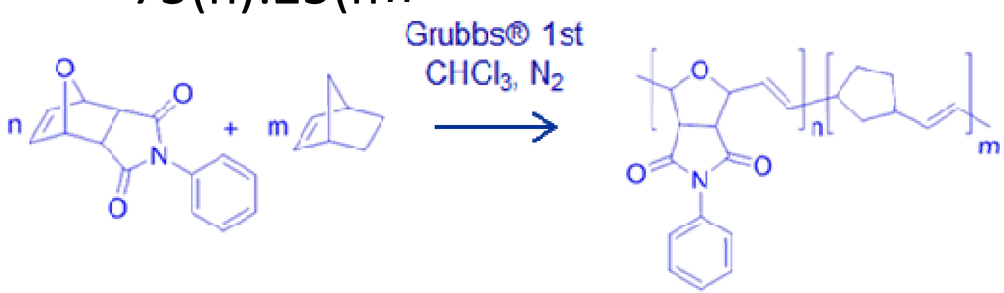
Development of S-POW

- An inexpensive high temperature dielectric was developed using ring opening metathesis polymerization (ROMP)
- Poly(PhONDI) homopolymer films brittle
- A copolymer of norbornene (NBE) and N-phenyl-7-oxanorbornene-5,6-dicarboximide (PhONDI)
  - Stoichiometry was varied and a 75(n):25(m)

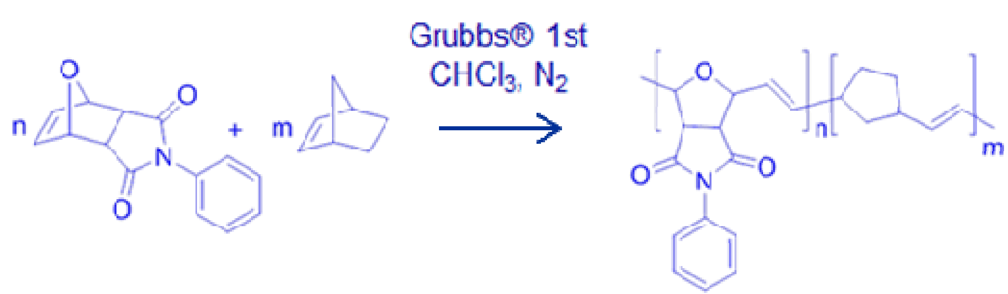
% ONDI (n)	% NBE (m)
0	100
25	75
50	50
75	25



Dirk, S.M., et al., *High temperature polynorbornene copolymer dielectric materials.* Abstracts of Papers of the American Chemical Society, 2009. 237.

Development of S-POW

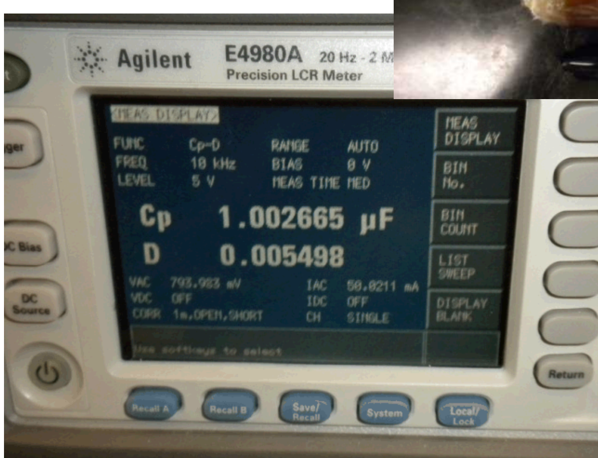
- Polymer precipitating out when solution left over 48 hours
  - – Consistent with free-radical induced crosslinking
- Hydrogenating olefin in polymer used to increase lifetime/improve processability
- Hydrogenated 75:25 copoly = S-POW



Denton, M.L.B., et al., *High Temperature Polymer Dielectrics from the ROMP reaction.* Journal of Applied Polymer Science, in prep.

Stacked Capacitor Prototype

- Several stacked capacitors fabricated
- Pressed & potted "in-house" from solvent cast films (~20 µm)



Rolled Capacitor Prototype

layered

rolled
C = 41 nF

pressed
C = 85 nF

- Layers of solvent cast films and discrete (6 μm) Al foil
  - Leads placed off each layer of Al
  - Layers rolled and pressed
- Packaged in parallel to form capacitor banks

Stacked vs. Rolled

~1 μF rolled pressed capacitor

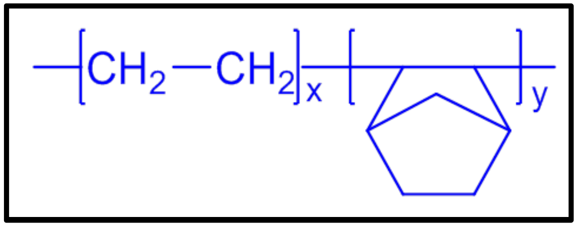
~1 μF stacked pressed capacitor

- Significant reduction in volume when using rolled technique
- Thinner/more uniform films will improve energy density
  - Extruded films reduce size defects

Commercial Alternative

- An inexpensive polymer identified with similar characteristics to S-POW
- Used in a variety of applications
  - high temperature packaging, optical, electronics, and healthcare
- Similar price point to BOPP

TOPAS® COC



TOPAS®	BOPP
$8/lb	$10/lb

Additive Studies

- Dielectric permittivity and breakdown testing performed on four organic additives in TOPAS®
  - 2-nitrodiphenylamine (NDPA)
  - 4-NDPA
  - 4-nitrophenol
  - 2-nitroaniline
- Higher energy density allows less material
- Breakdown strength (V) important due to large effect on energy density

breakdown (voltage) strength

$$U_e = \frac{1}{2}(\varepsilon_r \varepsilon_0 V^2)$$

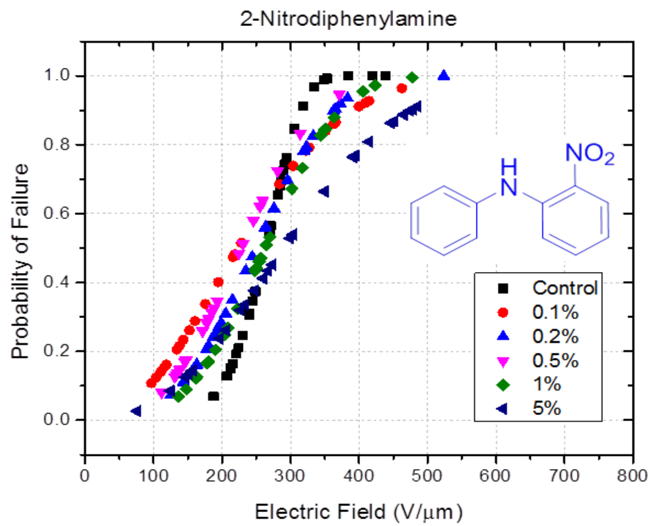
dielectric permittivity (constant)

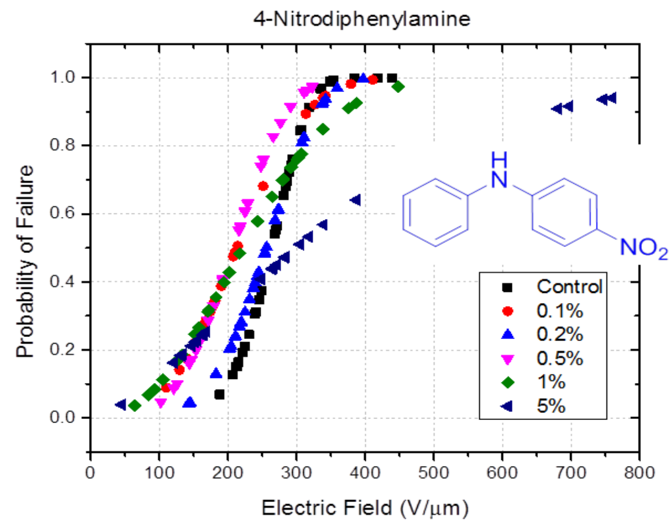
vacuum permittivity

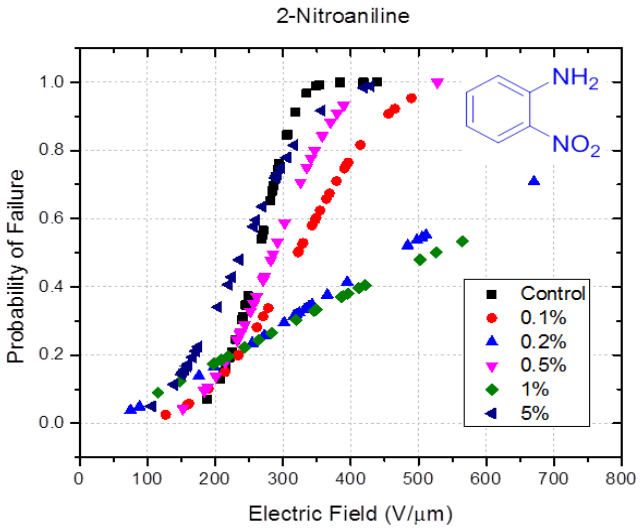
Additive Studies

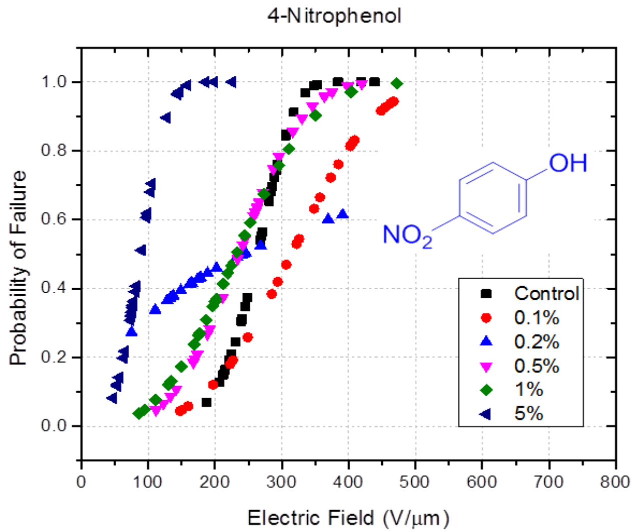
- Films cast on drawdown machine and metallized using 0.1%, 0.2%, 0.5%, 1%, 5% (w/w) of additives
- Electrical characterization performed to determine which additive will have the greatest increase on breakdown strength
- Weibull distribution used to analyze breakdown results
  - Probability of failure: $$P = 1 - e^{\left(\frac{E}{E_0}\right)^{\beta}}$$
- E_0 is a scale parameter which represents the probability of failure at 62.3%.

Breakdown Evaluation: Additives in TOPAS®

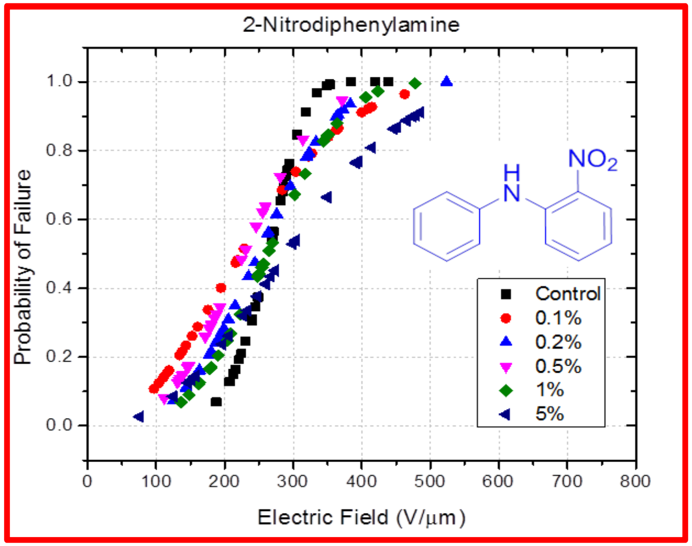


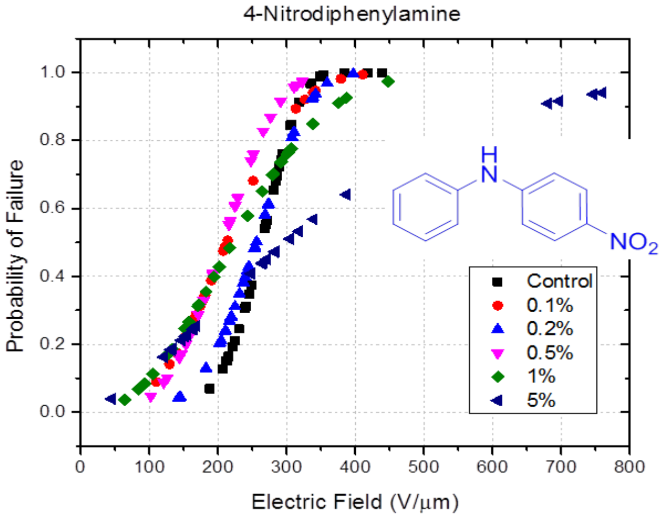


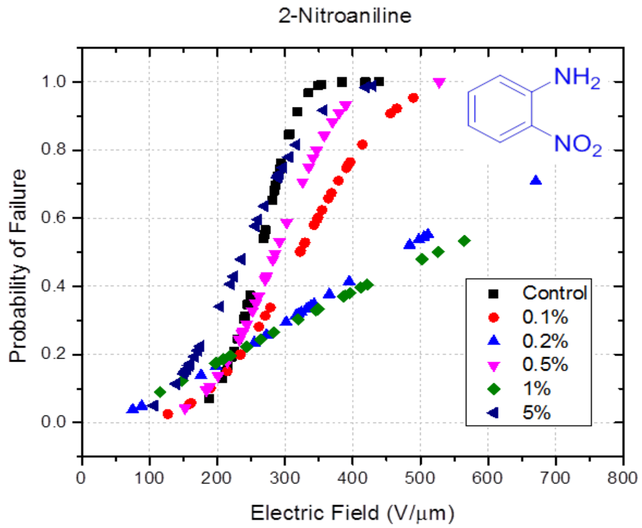


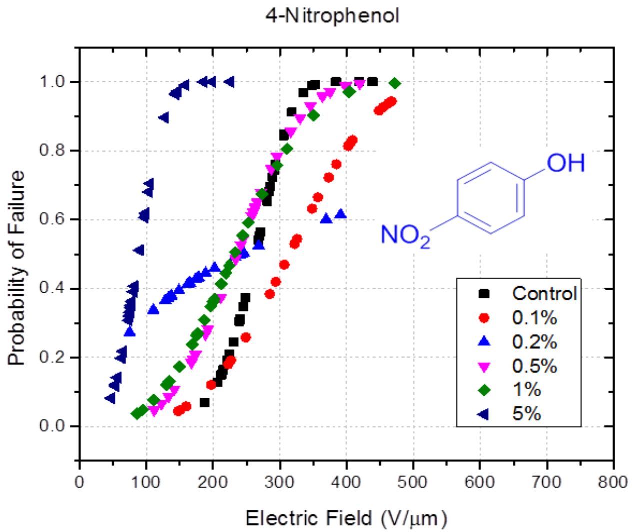


Breakdown Evaluation: Additives in TOPAS®

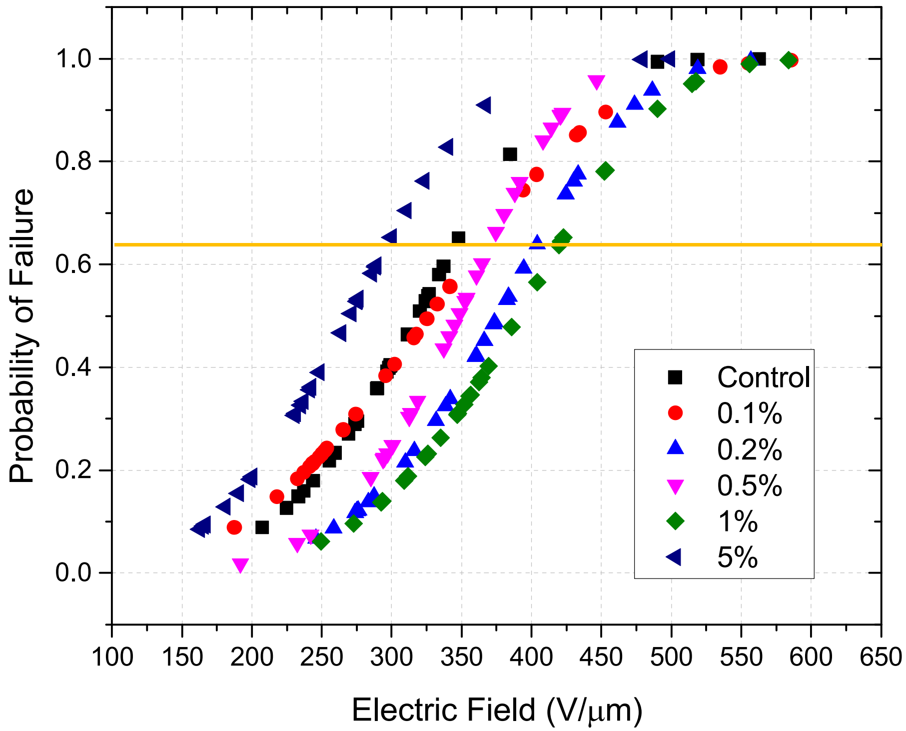






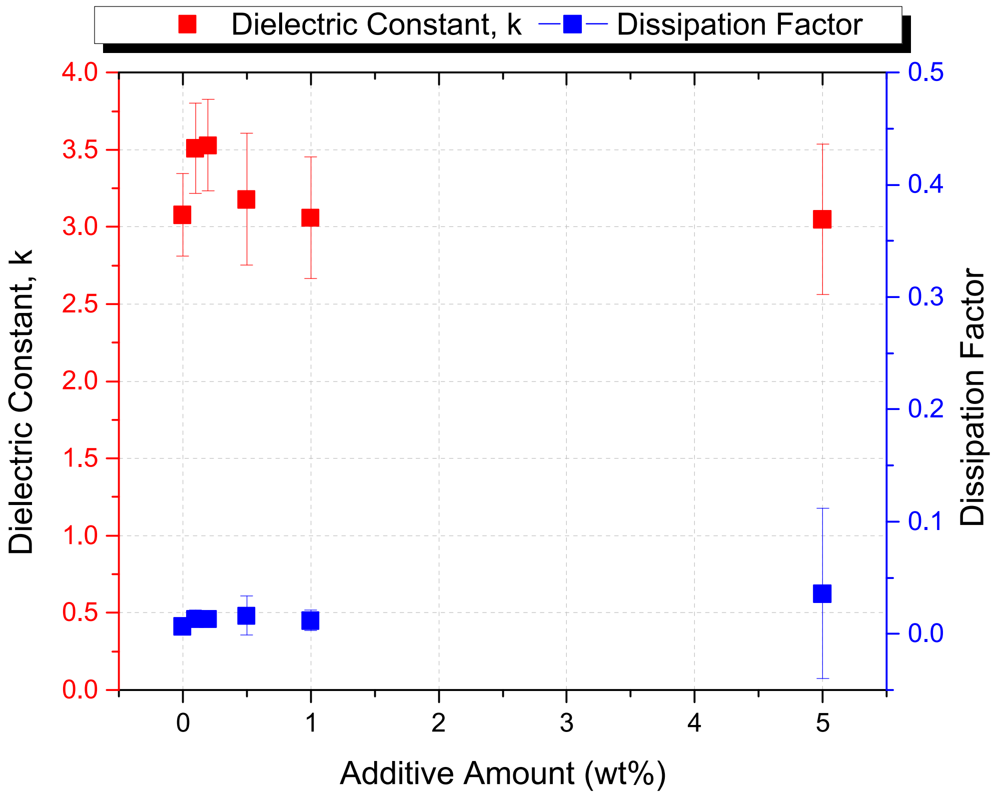


2-NDPA in S-POW



- Increase in breakdown strength > 50 V/µm at 0.2% and 1.0% (w/w)
- Increase of 25 V/µm at 0.5% from the control S-POW film

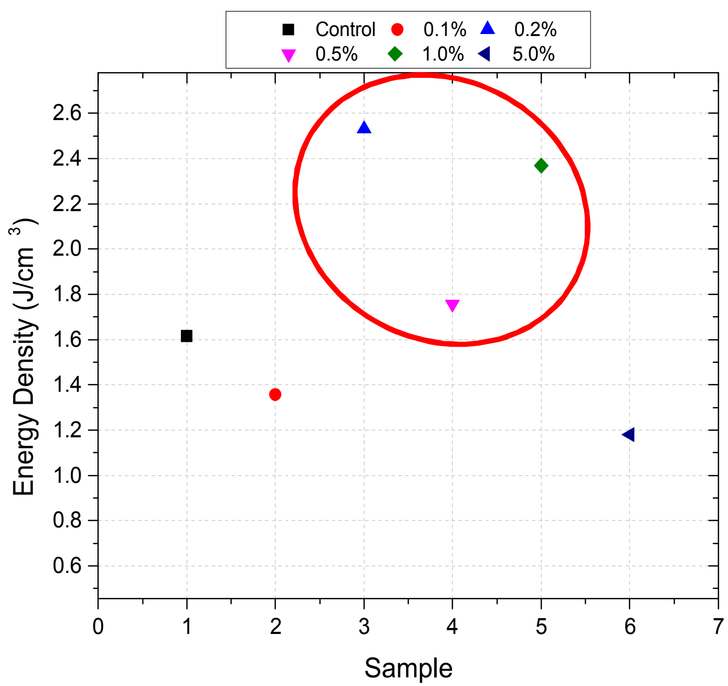
2-NDPA in S-POW



- Slight increase in k observed at 0.1% and 0.2%
- No negative effect on dissipation factor

2-NDPA Effect on Energy Density

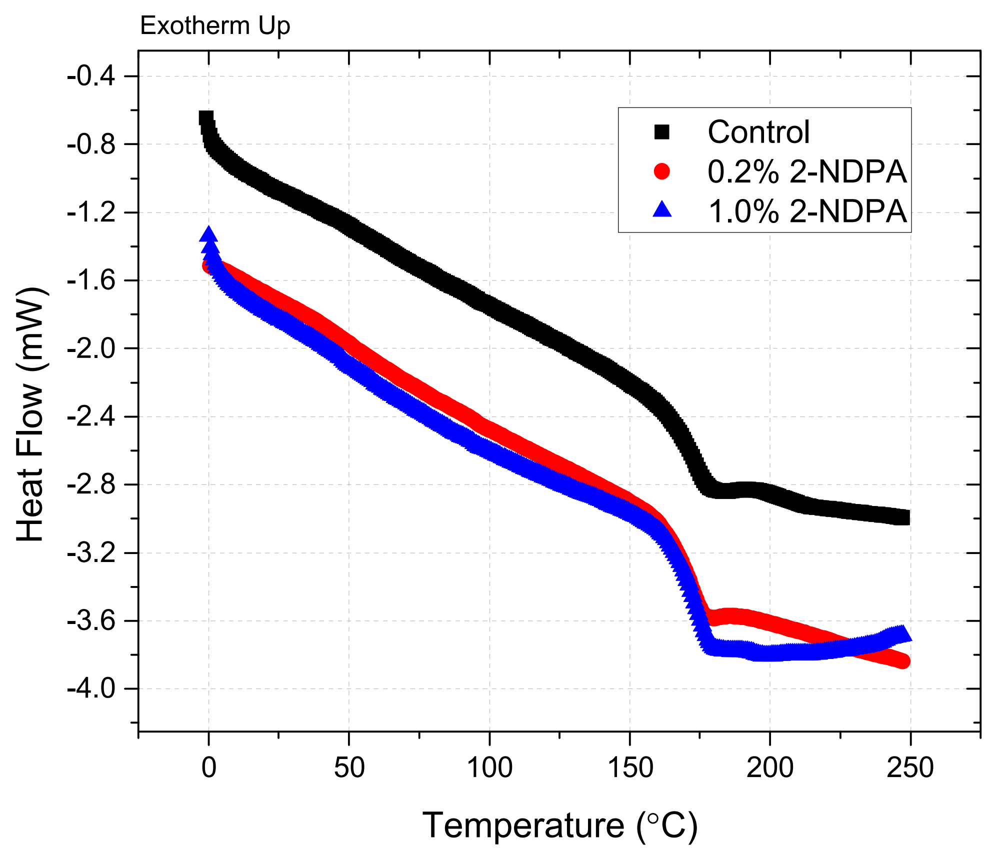
2-NDPA Concentration (w/w)	Breakdown (V/µm)	Energy Density (J/cm^3)
0	345	1.62
0.1	365	1.36
0.2	405	2.53
0.5	370	1.76
1.0	415	2.37
5.0	290	1.18



- Significant increase in energy density due to increase in breakdown strength of 1% and 0.2%

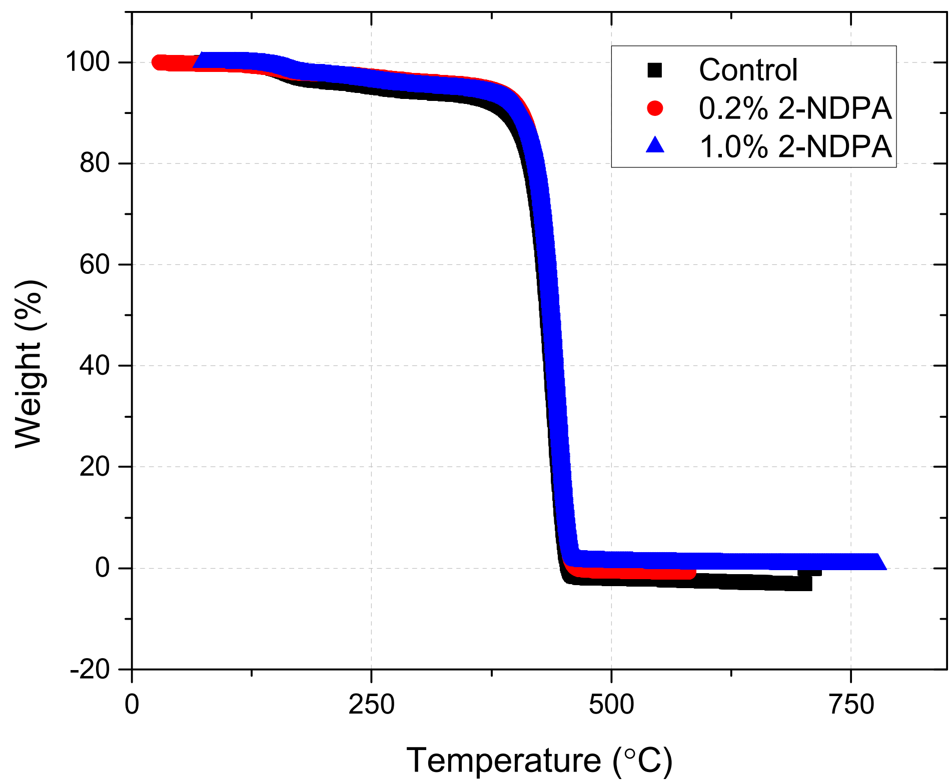
Effect of 2-NDPA: T_g

- Differential scanning calorimetry (DSC) used to determine effect of additive on glass transition temperature (T_g)
- No negative impact observed

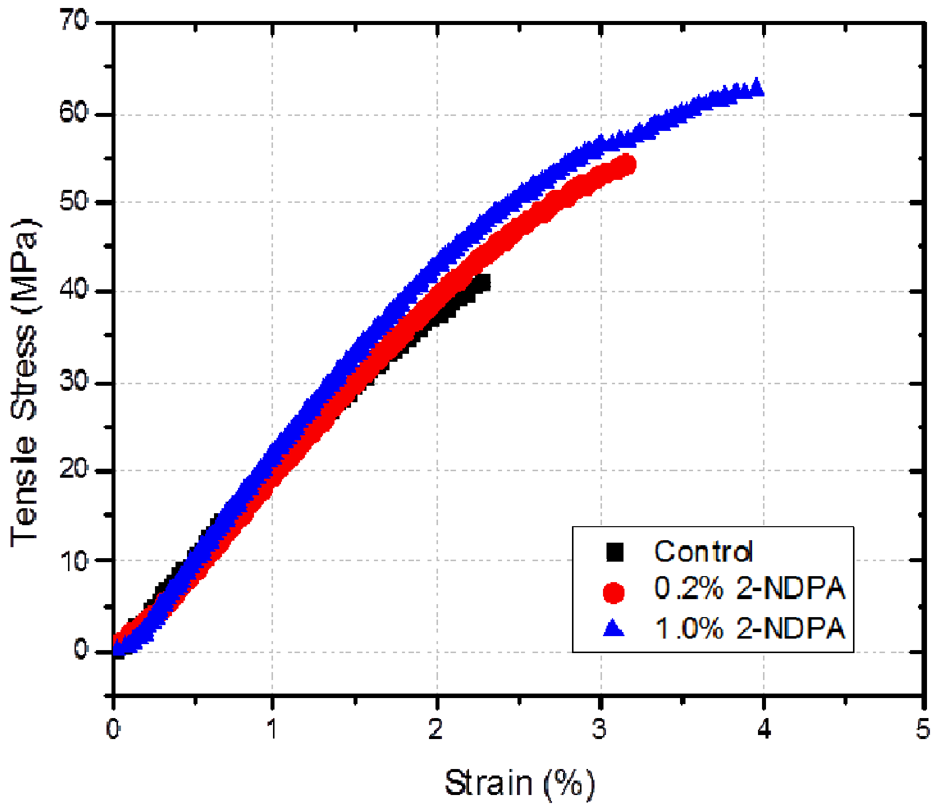


Effect of 2-NDPA: T_d

- Thermogravimetric analysis (TGA) performed to determine decomposition temperature (T_d) of polymer and polymer/additive films
- Confirmed additive had no effect



Effect of 2-NDPA: Mechanical Properties



- Stress-strain curve was developed using dynamic mechanical analysis (DMA) for the S-POW additive films
- Slight improvements in modulus observed with additive and no negative consequences were observed

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Electrochemical Study

- Chronoamperometry used to determine redox potential
  - S-POW
  - Influence of the additive amount
  - Solutions of the same concentrations of 2-NDPA in 9.7% (w/w) S-POW in chloroform analyzed

2-NDPA Mass Fraction	Polymer Mass Fraction
0%	9.7% S-POW
0.10%	9.7% S-POW
0.20%	9.7% S-POW
0.50%	9.7% S-POW
1.00%	9.7% S-POW
2.50%	9.7% S-POW
5.00%	9.7% S-POW
1.00%	no S-POW

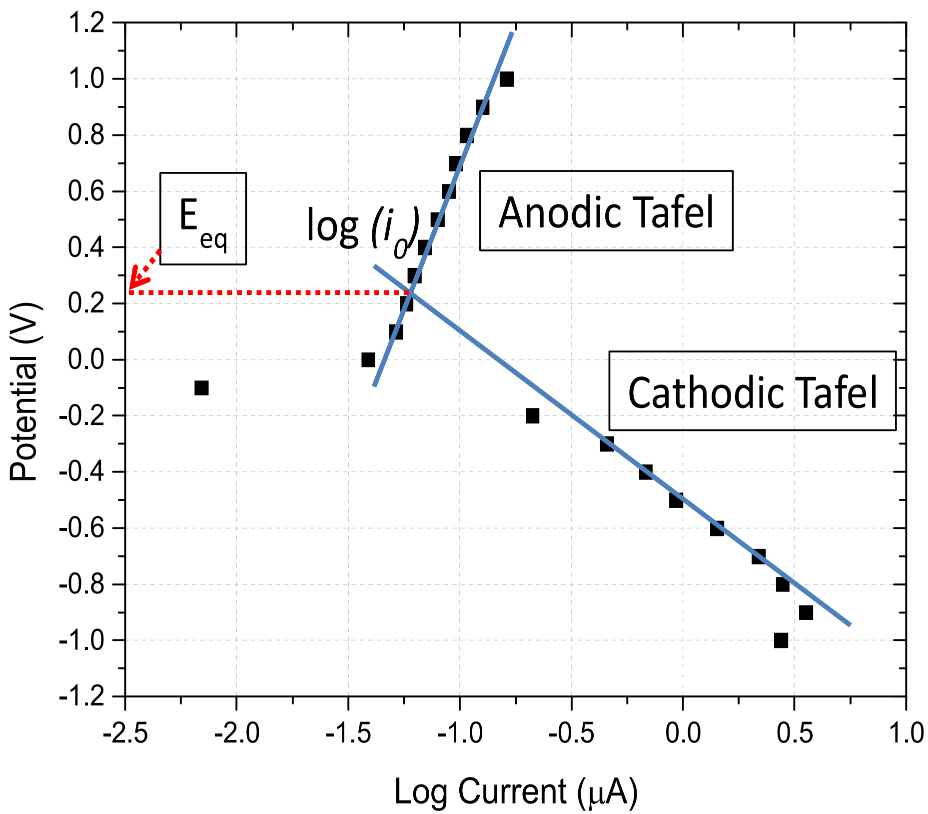
Goal: find a correlation between the shifts in the polymer redox potential with the changes in the breakdown strength

Redox Potentials

2-NDPA Mass Fraction	Redox potential (V) at pH 9.5	Redox potential (V) at pH 11.5
0%	-0.025	-0.025
0.10%	0.1	0
0.20%	0.15	0
0.50%	0.175	0.05
1.00%	0.25	0.1
2.50%	0.4	0.25
5.00%	0.4	0.25
100%	-0.1 and -0.35	-0.1 and -0.35

- Significant difference in the redox potentials of the additive and the polymer
- Oxidation/reduction of the additive and polymer obtained separately

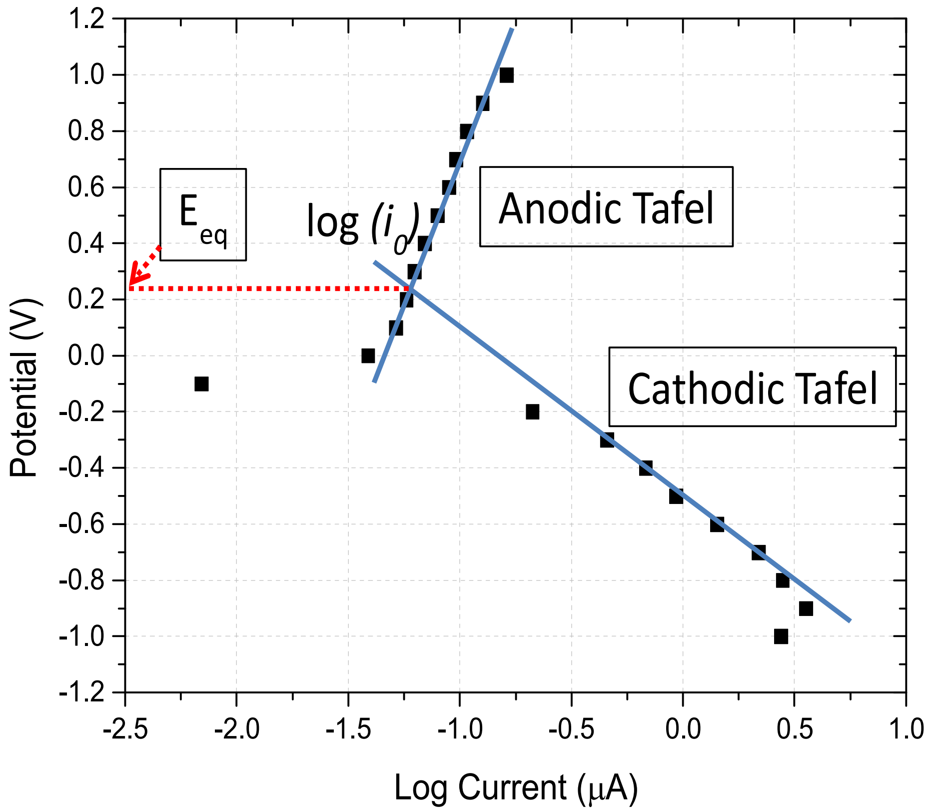
Tafel Plot



- Tafel plot used to determine redox potential
- Tafel plots applicable at high overpotentials:
  - (> 0.05V)
- Redox potentials of the polymer/additive mixtures determined for all concentrations at
  - pH 9.5
  - pH 11.5

**Tafel plot for 1.0% (w/w) 2-NDPA in S-POW at pH 9.5*

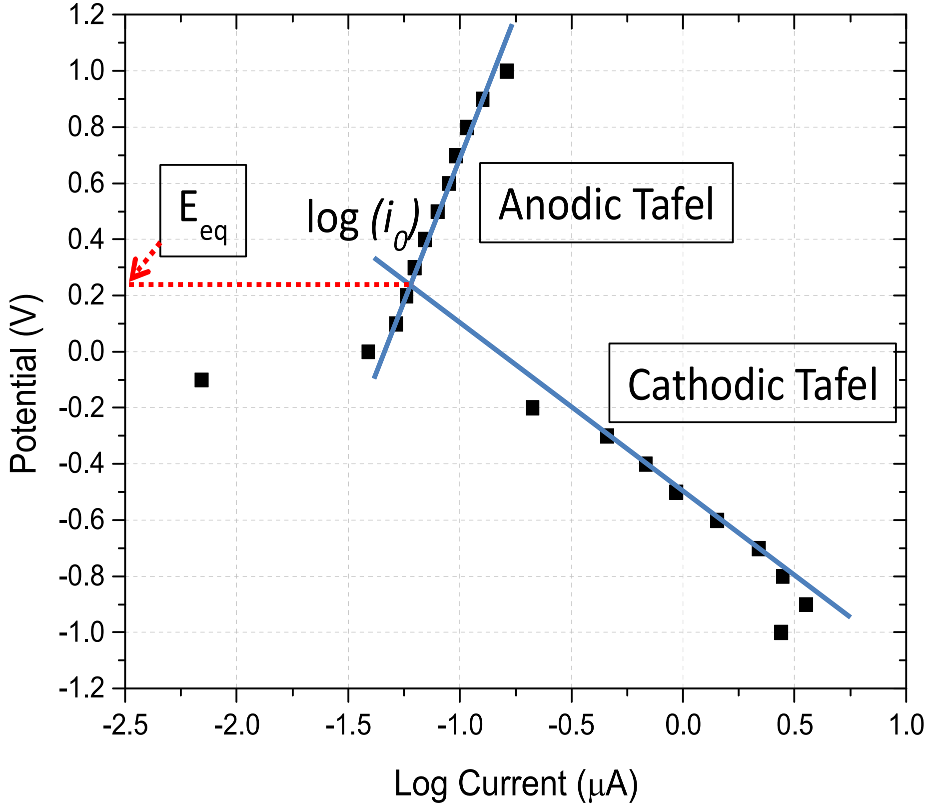
Tafel Plot



The shape of the Tafel plots of the polymer/additive composites suggests:

i. **non reversible electrochemical reaction**
   i. different number of electrons involved in the oxidation and the reduction processes

Tafel Plot

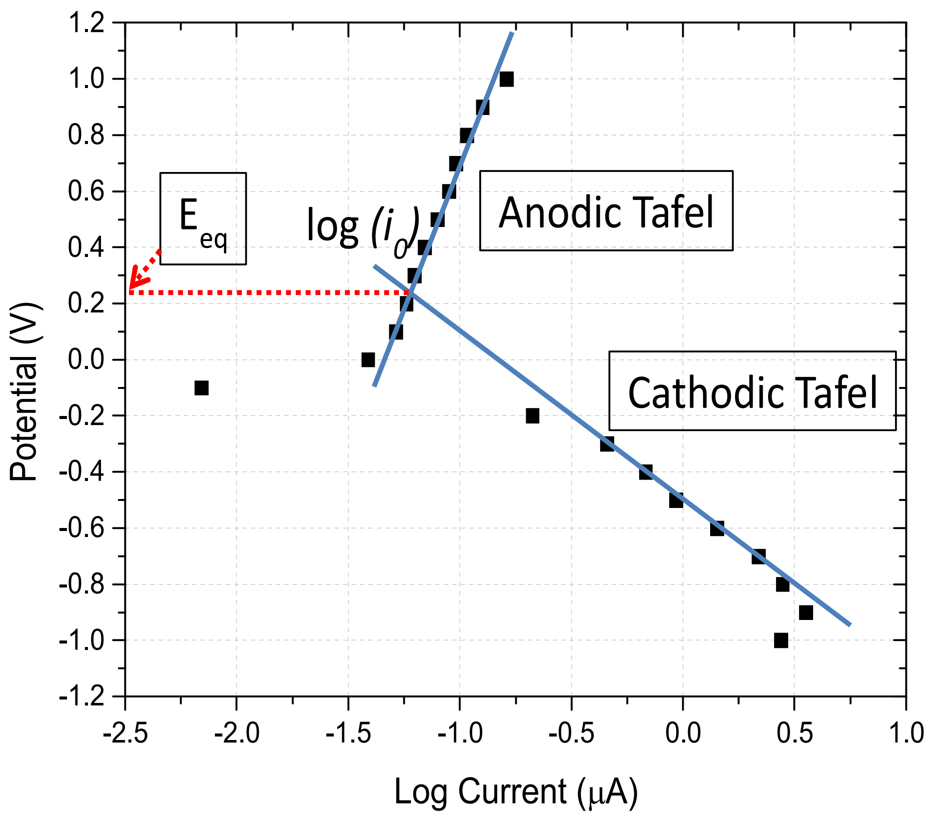


The shape of the Tafel plots of the polymer/additive composites suggests:

ii. a small difference in the redox potentials of the polymer and the additive separately

i. only one redox potential can be seen on the plots

Tafel Plot

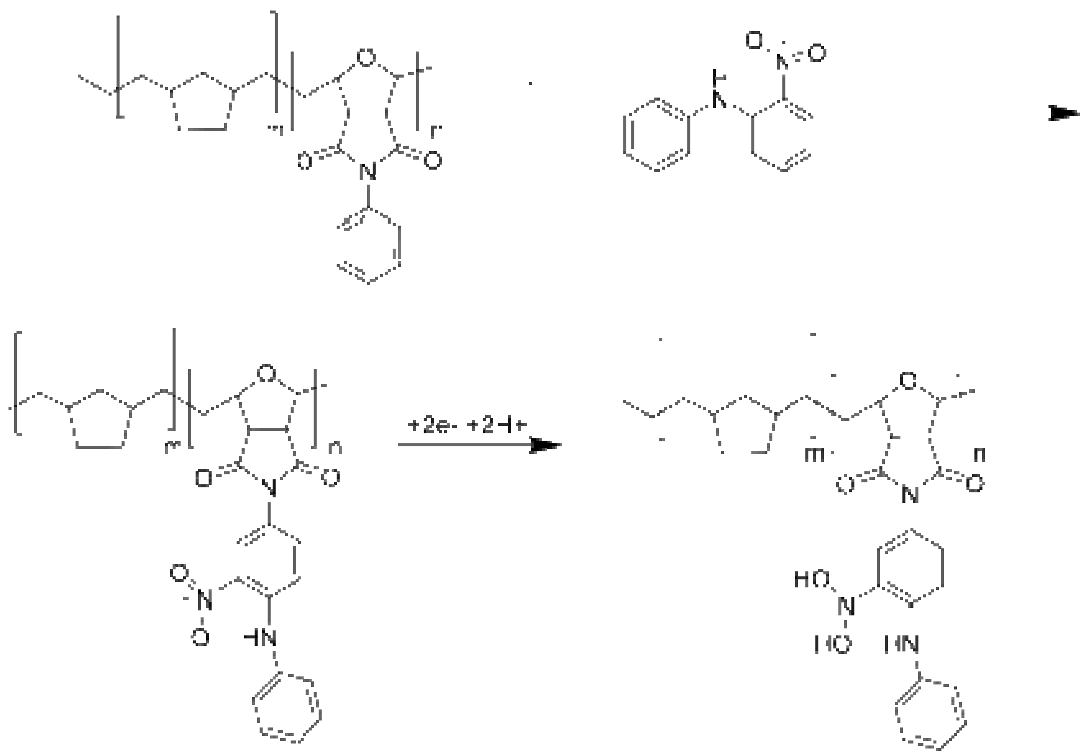


The shape of the Tafel plots of the polymer/additive composites suggests:

iii. polymer chemically interacts with the additive

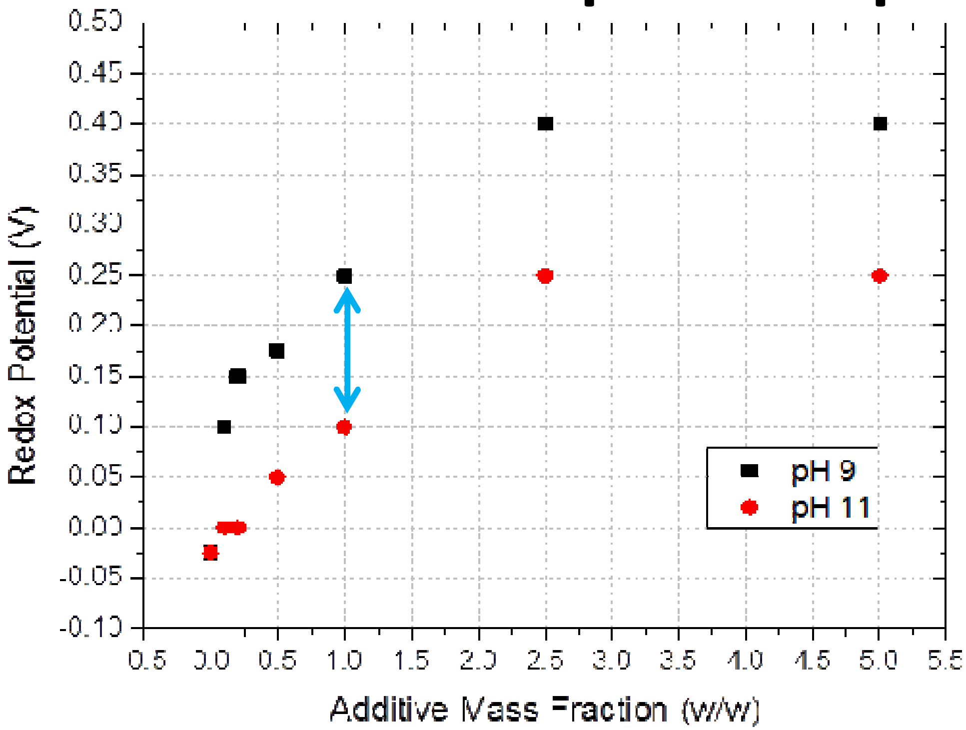
Hypothesis: iii. polymer chemically interacts with the additive, forming one "new" polymer

Proposed Mechanism



- Phenyl ring in polymer replaced by the additive, creating a covalent bond at the meta-position in the additive benzene ring

Redox pH Dependence

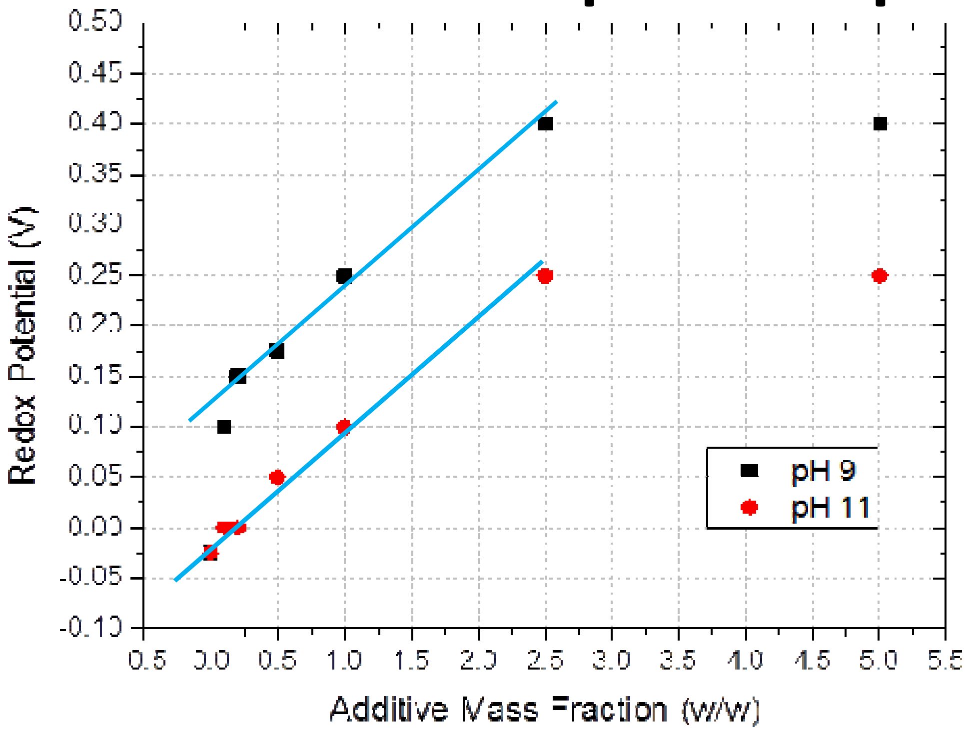


$$\Delta E = E_{pH\ 9.5} - E_{pH\ 11.5}$$

- ΔE approximately 120 mV for most polymer/additive composites
- 2 protons/2 electrons

- Redox potentials plotted against amount of additive introduced
- Difference in the recorded redox potential at the two pHs indicates protons involved in the electrochemical reaction

Redox pH Dependence



- Linear increase of redox potential with increase in additive amount
  - Saturation point observed
- Increased potential led to enhanced oxidative stability

- Redox potentials plotted against amount of additive introduced
- Difference in the recorded redox potential at the two pHs indicates protons involved in the electrochemical reaction

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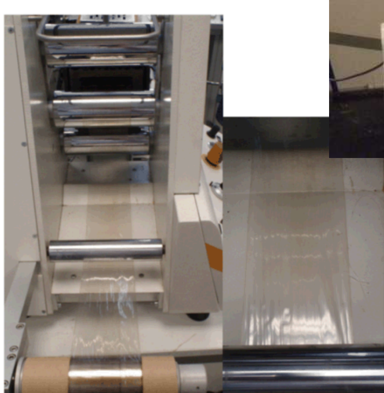
Extruded S-POW

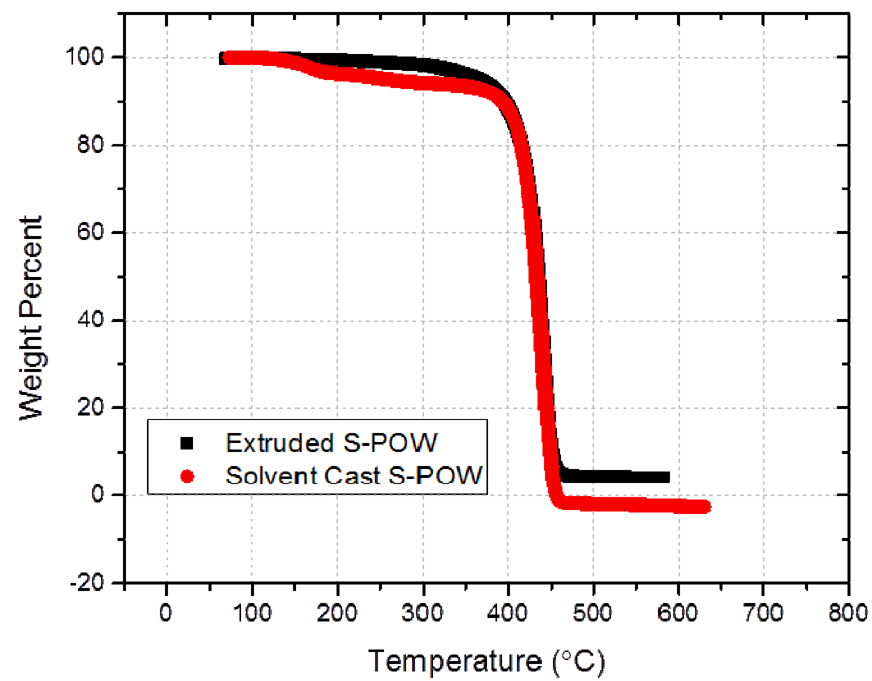
- Solvent casting of films cost-prohibitive on large scale
- More defects compared to extruded films



- Extrusion demonstrated in-house at Sandia extruder purchased from Dr. Collin® Co.
- Initial films brittle and striations observed

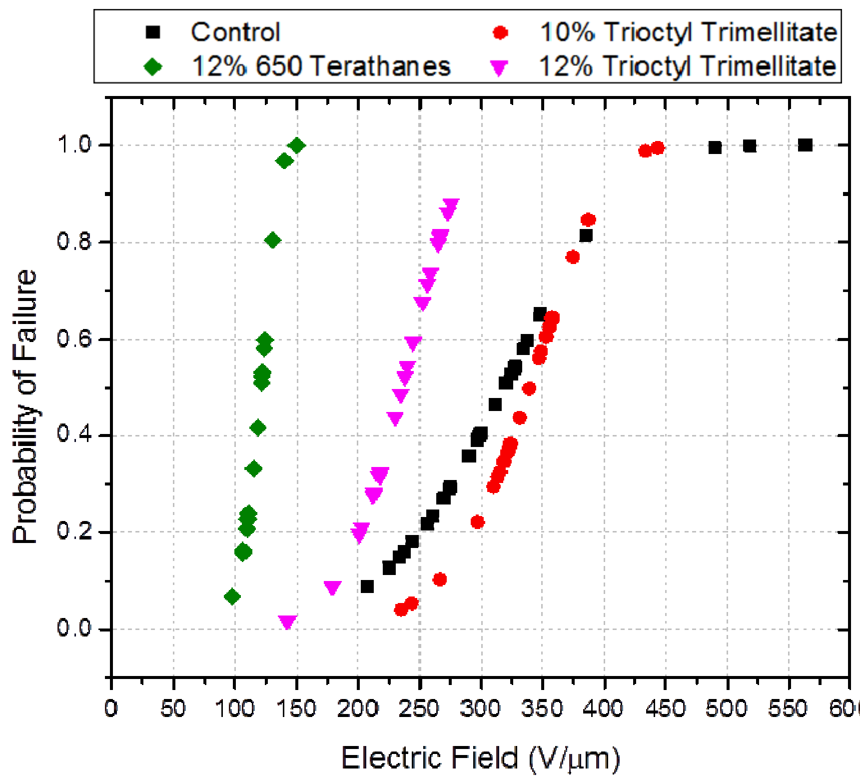
Solvent vs. Extruded: TGA

- Physical defects/color change initially observed when compared to solvent cast S-POW
- T_d not affected by extrusion



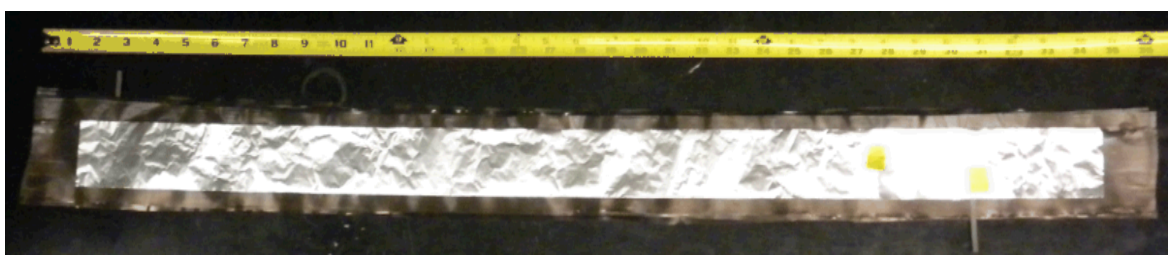
Plasticizer Breakdown Evaluation

- Several plasticizers screened for use in extrusion
  (performed by Kirsten Cicotte)
- Ultimately 650 terathanes and trioctyl trimellitate chosen for studies
  - 12% (w/w) of both plasticizers demonstrated severely diminished breakdown
  - 10% TT did not show negative impact



Extruded Film Capacitor Fabrication

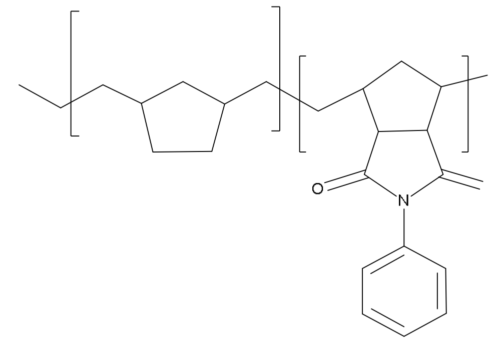
- 3 ft capacitor of extruded 10% (w/w) trioctyl trimellitate in S-POW
- Capacitance of 9.5nF/DF of 0.004
- Thermal sprayed (Babbitt)
- SnCu leads and potted in high Tg epoxy



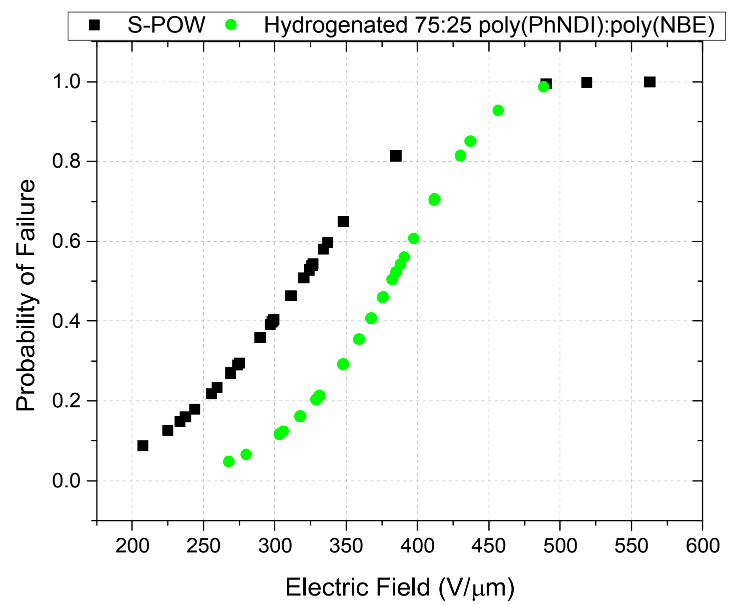
Synthesis of PhNDI

- Yoon *et al*. demonstrated a greater thermal stability and T_g of carbon analog (PhNDI) to poly(PhONDI)
  - oxygen bridge causing degradation
- Synthesis of poly(PhNDI) and PhNDI:NBE copolymers explored for high temperature dielectric
  - 75:25 poly(PhNDI) poly(NBE) copolymer

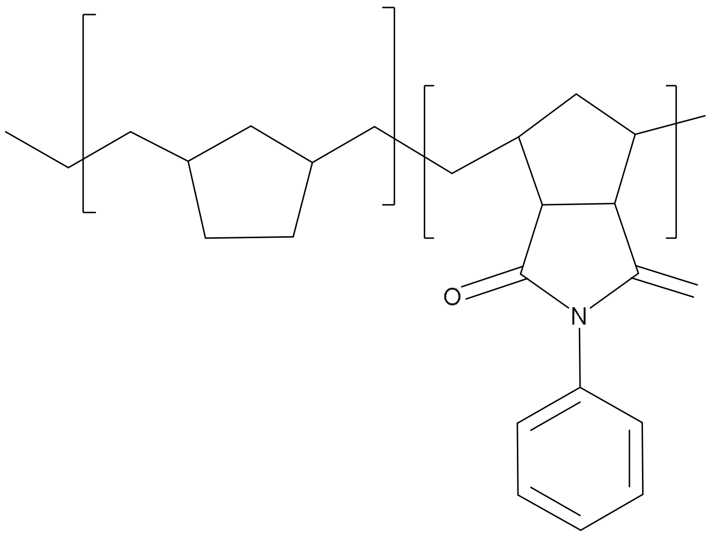
Impressive 400 V/µm observed!



poly(PhNDI) poly(NBE)



Synthesis of PhNDI



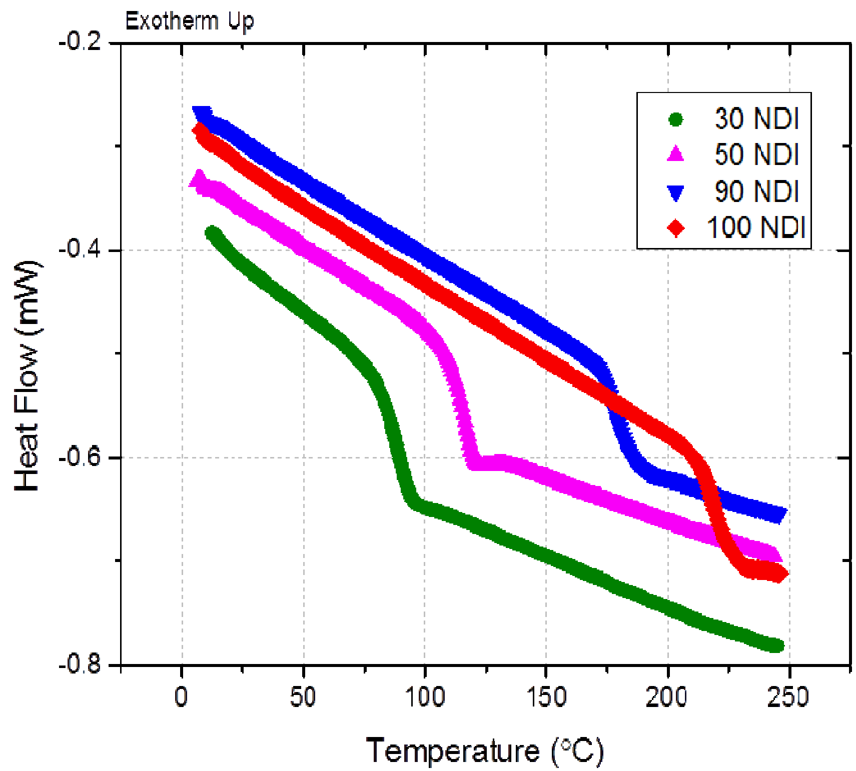
poly(PhNDI) poly(NBE)

% NDI	% NBE
100	0
90	10
50	50
30	70

- Homopolymer of poly(PhNDI) was prepared in addition to three PhNDI:NBE copolymers
- Thermal/mechanical characterization performed

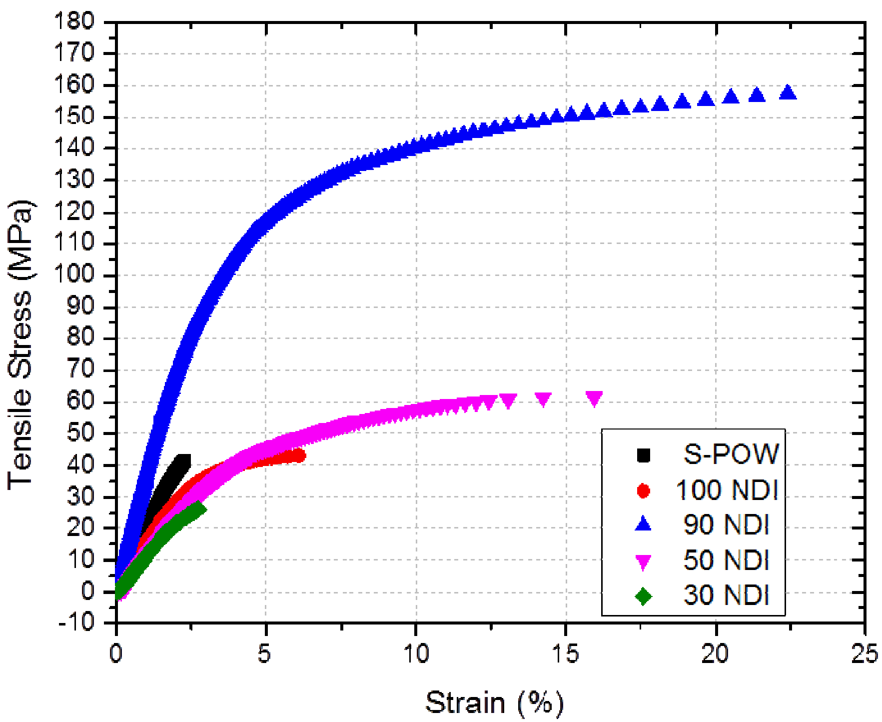
Thermal Characterization

- DSC performed on PhNDI homopolymer and PhNDI:NBE copolymers
- Homopolymer provided the highest T_g (as expected)
  - Films brittle
- 30 and 50 NDI demonstrated an unfavorable T_g
  - ~90 °C and ~125 °C
- 90 NDI matches S-POW T_g



Mechanical Characterization

- DMA used to create stress-strain curve of PhNDI:NBE copolymers vs. S-POW
- 90 NDI displayed impressive tenfold increase in elongation
- Improve processability of dielectric polymer and permit melt extrusion



Outline

- Chapter 1: Background and Introduction
- Chapter 2: Materials and Methods
- Chapter 3: Evaluation and Characterization of Additives Incorporated in S-POW
- Chapter 4: Electrochemical Study of Polymer/Additive Composites
- Chapter 5: Evaluation and Characterization of Poly(PhNDI) and Poly(PhNDI)/Polynorbornene Copolymers
- Chapter 6: Conclusions and Future Work

Conclusions

- Additive (2-NDPA) produced a significant increase in breakdown voltage and ED in S-POW at concentrations of 0.2%, 0.5% and1.0% (w/w)

- Electrochemical evaluation determined correlation between increase in breakdown strength and redox potential (oxidative stability) up to ~1.0% (w/w) additive

- Overwhelming mechanical characteristics of the 90 NDI copolymer should eliminate use of plasticizers and facilitate transition to industry

Future Work

- Working with Electronic Concepts, Inc. (ECI) to develop a solvent casting technique
- Extrusion technique developed at the Natick Soldier Center will allow more than 100 m of thin polymer films to be produced
  - used to fabricate next generation prototype capacitors
- Inexpensive nanoparticle fillers used to further increase dielectric breakdown strength and improve the relative permittivity of the high temperature polymer dielectrics

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