ORGANOPHOSPHORUS-HYDRAZIDES AS POTENTIAL REACTIVE FLAME RETARDANTS FOR EPOXY

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Outline

- Review of Current Solutions for Fire Protection of Epoxy Composites
  - Engineering Solutions (Insulation, Metal Shields)
  - Intumescent Barriers
  - Flame Retardant Additives

- Organophosphorus-Hydrazides
  - Synthesis Details
  - Heat Release Reduction Results

- Conclusions & Acknowledgements

Current Flame Retardant / Fire Protection Solutions for Epoxy Composites

Epoxy Composite Use in Transportation

- Epoxy + Carbon or Glass Fiber Composite Benefits:
  - Light Weight
  - Resistance to Corrosion / Rust
  - Unique shapes and forms due to manufacturing process.
- Drawbacks:
  - Non-electrical conductivity
  - Thermal properties
    - Failure of structural composite well before ignition
  - Flammability
    - Inherently higher heat release when compared to metal
    - Requires different fire fighting measures

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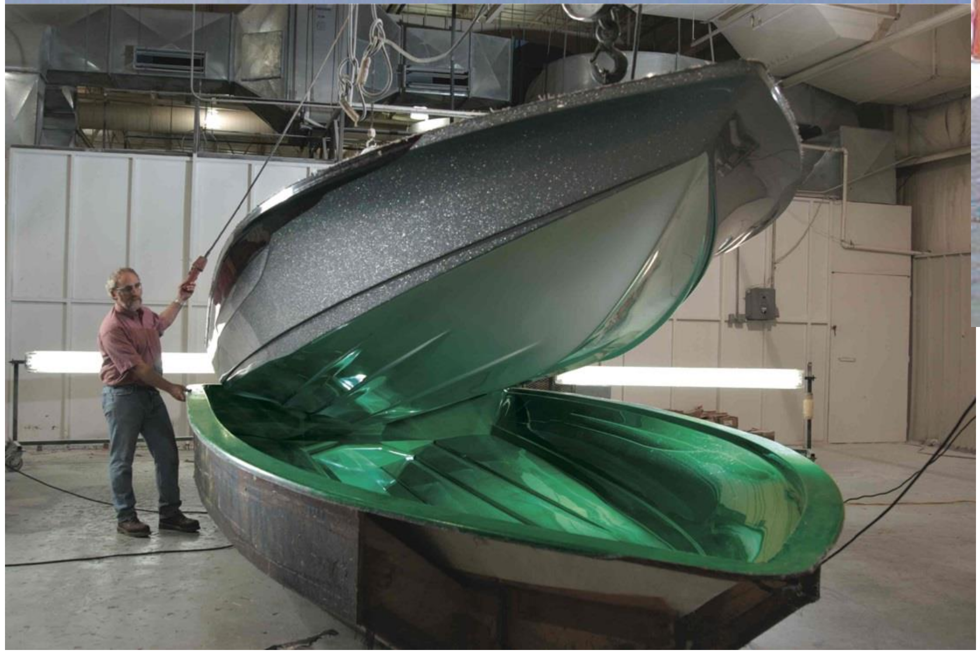
Epoxy Composite Use Examples



Extinguishing Carbon Fiber Composite Fires

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- Due to differences in fire behavior, fire fighting is different for composites vs. metal/fuel pool fires.
  - Fire fighting foam has little to no effect on composite fires, as it does not cool the burning composite – re-ignition common.
  - Water / CO_2 required to put out composite fires.
    - Foam still required to address the fuel pool, as well as tamp down flying ashes from the fire.
  - Cutting into structure to put out fire or release occupants requires diamond saws to cut through carbon fiber.
  - Guidance from Boeing on 787 fire fighting:
  - http://www.boeing.com/assets/pdf/commercial/airports/faqs/787_composite_arff_data.pdf

Other Fire Hazards from Carbon Fiber Composites

- Recent studies have shown that carbon particulates are released when carbon fiber composites burn.
  - More than just soot – parts of the carbon fibers themselves are released.
  - "Dangers relating to fires in carbon-fibre based composite material" Hertzberg, T. *Fire and Materials* **2005**, *29*, 231-248.
  - "Potential for the formation of respirable fibers in carbon fiber reinforced plastic materials after combustion" Eibl, S. *Fire Mater.* **2017**, *41*, 808-816.
- All fires hazardous, but additional care / SCBA equipment and post-fire cleanup may be required with carbon fiber composite fires.

Engineering Solutions

- Engineering approaches focus not on changing polymer chemistry, but on protection of flammable materials from ignition source/heat.
  - Fire protection barriers
    - Mineral Wool Batting / Insulation Packages
    - Metal decorative / structural panels

- Easy to implement, but, they are also easy to defeat.
  - Cut/break in barrier is weak point for fire damage/flame propagation to occur.
  - Barrier falling off/debonding can lead to rapid fire growth or mechanical failure

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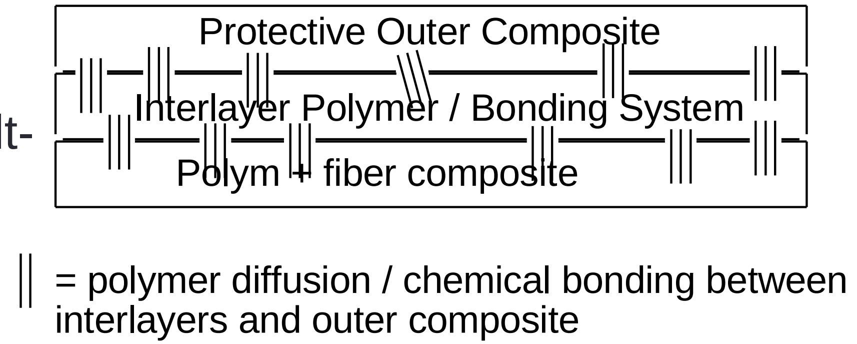
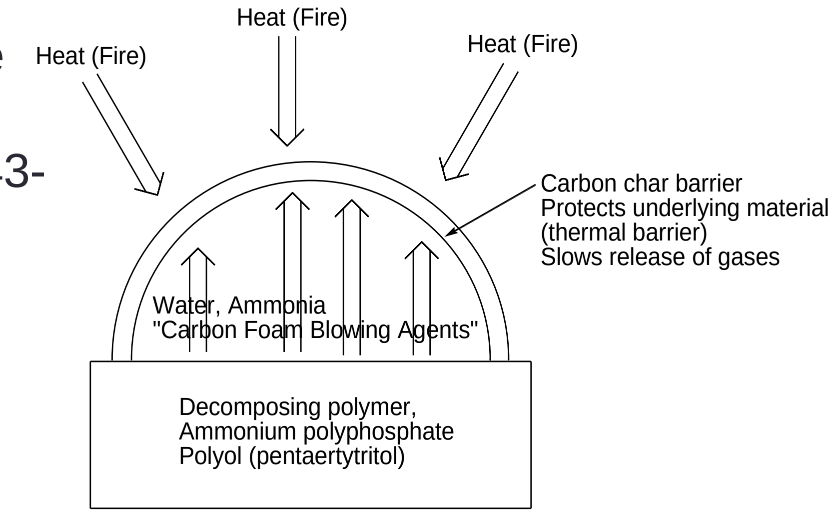
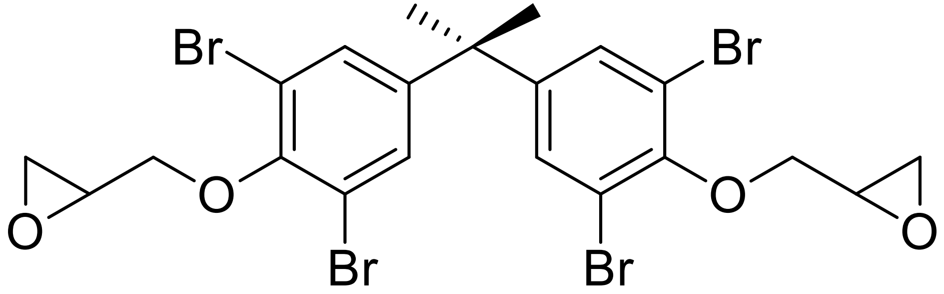
Protective Integrated Coatings/Barriers for Composites

- Coating/Barrier can be misnomer.
  - The material is not for a paint, but an integrated outer layer to protect the composite part
- If successful, the "coating" will not crack/pop-off due to thermal stresses or damage since the coating is actually part of the entire component, not a bolt-on or glued on substrate.
- Some Co-cured Intumescent examples:
  - "Enhancement of Passive Fire Protection Ability of Inorganic Fire Retardants in Vinyl Ester Resin Using Glass Frit Synergists" Kandola, B. K.; Pornwannachai, W. *J. Fire Sci.* **2010**, *28*, 357-381.
  - "The effect of fire-retardant additives and a surface insulative fabric on fire performance and mechanical property retention of polyester composites" Kandare, E.; Chukwunonso, A. K.; Kandola, B. K. *Fire Mater.* **2011**, *35*, 143-155.
  - The use of fire-retardant intumescent mats for fire and heat protection of glass fibre-reinforced polyester composites: Thermal barrier properties" Kandare, E.; Chukwudole, C.; Kandola, B. K. *Fire and Materials* **2010**, *34*, 21-38.

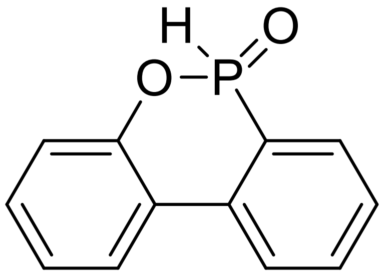




Flame Retardant Additives



Tetrabromobisphenol A
Bis Epoxide



9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)

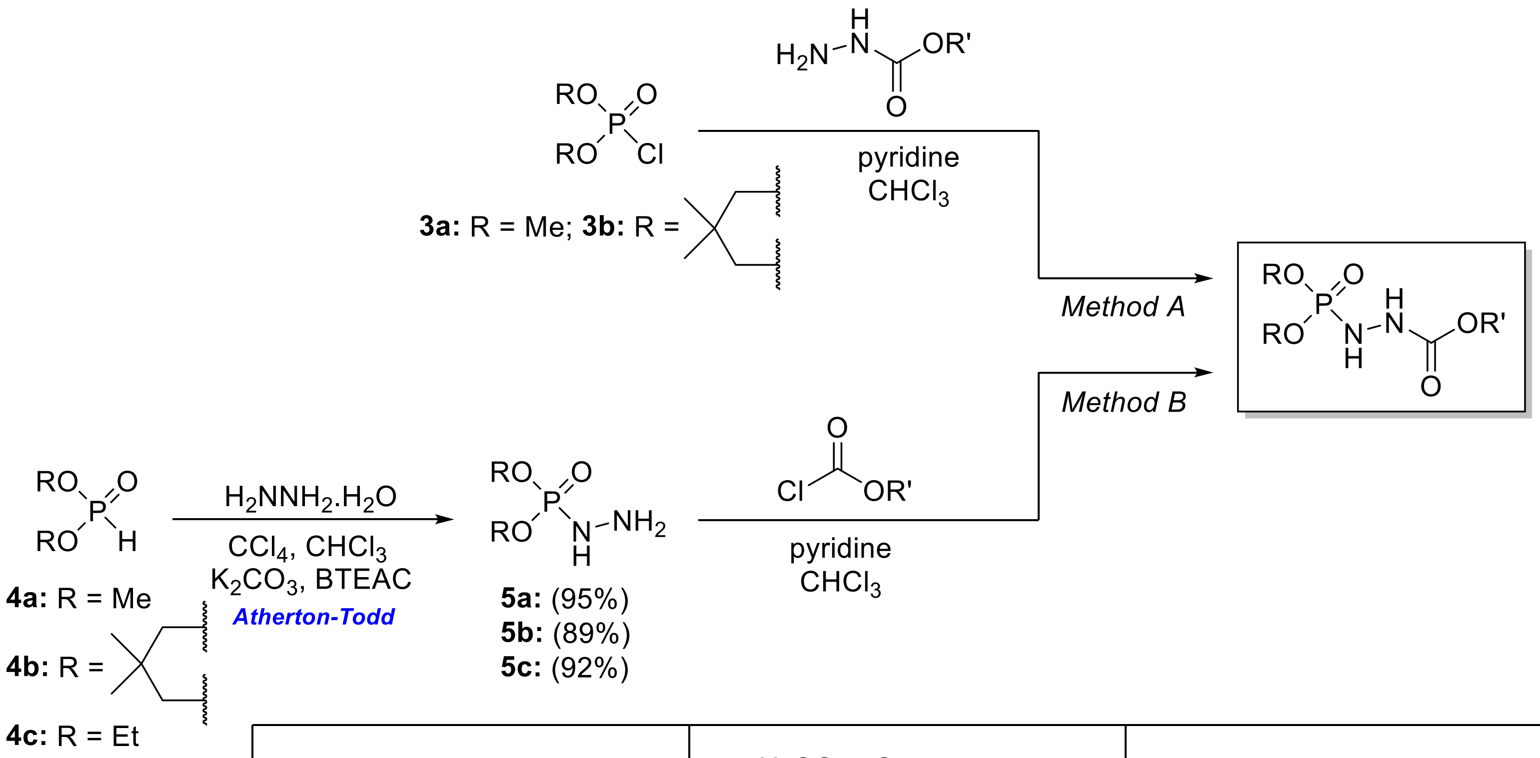
- Common flame retardant additives (FRs) for epoxy include both brominated and phosphorus based additives.
- Reactives are preferred from a durability / prevention of migration perspective.
    - Reactives are FRs which can react into / with the epoxy during composite manufacture, epoxy + curing agent mixing.

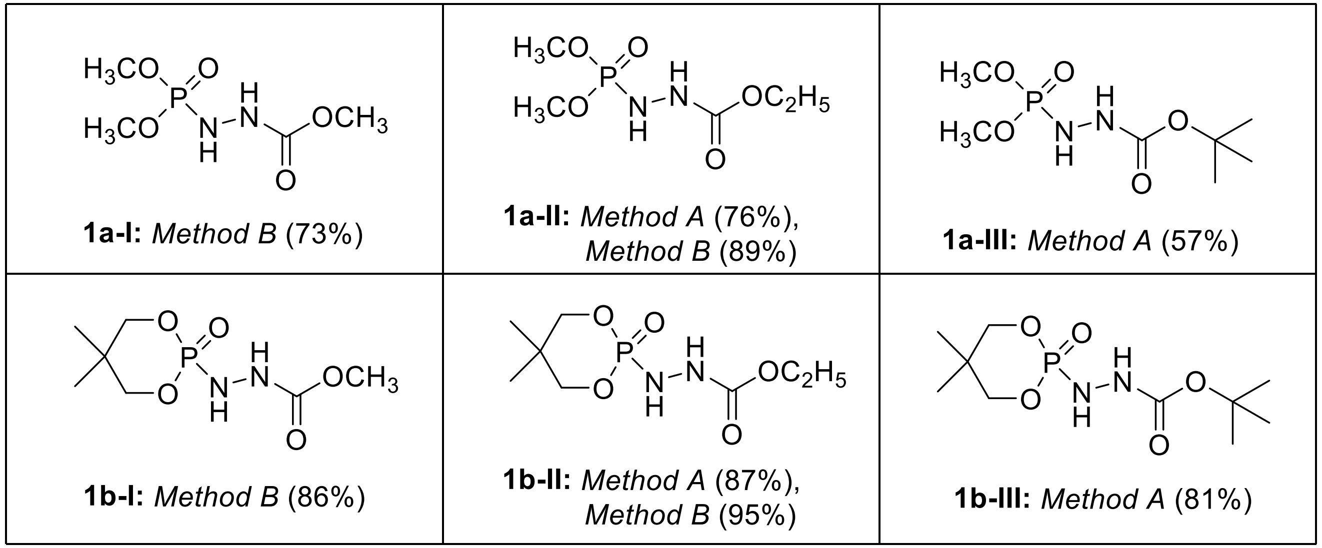
Need for New Epoxy Reactive FRs

- TBBPA based epoxy proven and works, but is incompatible with non-Pb based solder.
  - TBBPA thermally decomposes when exposed to high melt temp solder.
- DOPO based epoxy proven and works for epoxy circuit boards, and likely will continue to gain in use.
  - Currently has no major issues, but may not be appropriate for large scale structural composites
- Very few reactive FRs available for epoxy materials.
  - Mixed vapor phase and condensed phase FR to allow for self extinguishment and reduction in heat release is desirable.

Organophosphorus-Hydrazides

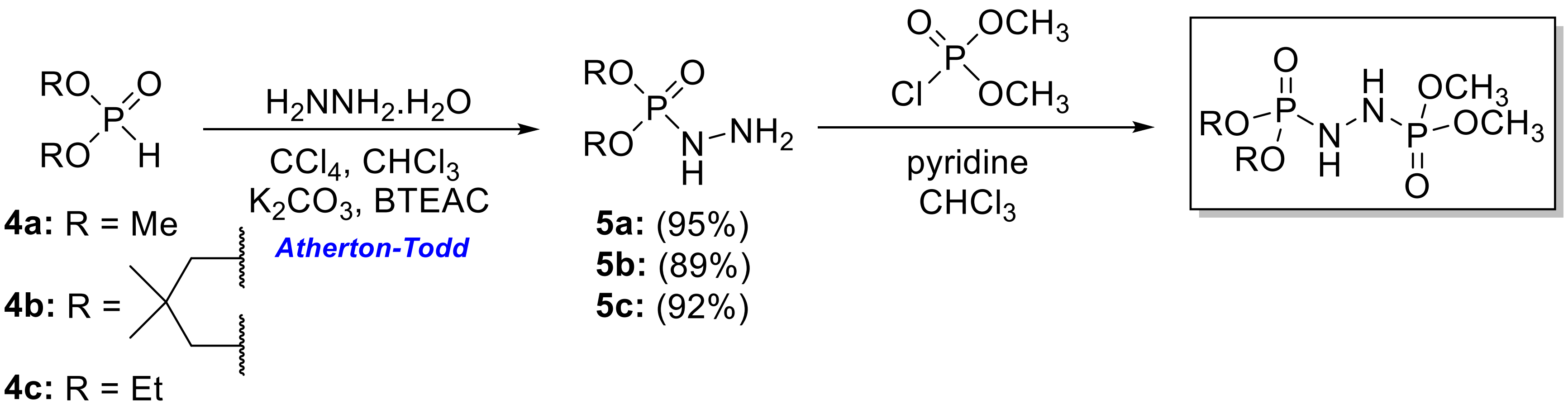
Preparation of the Target Compounds: Hydrazine Monophosphonates

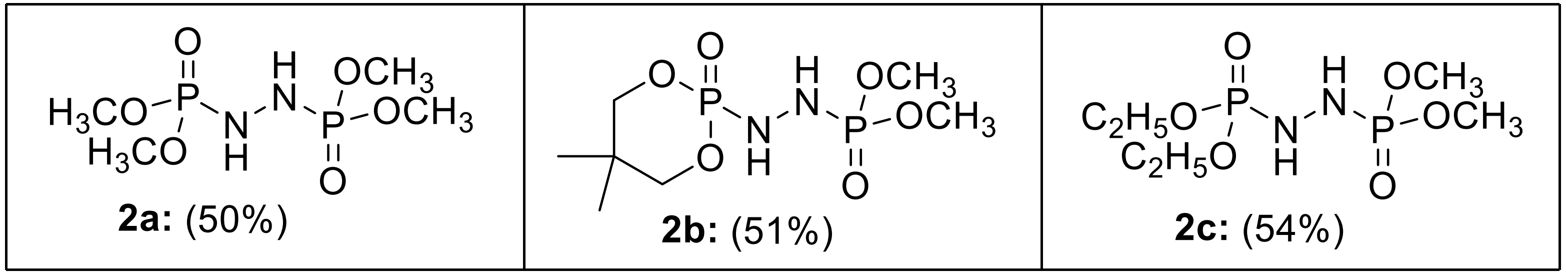




5a = P_Me_H
5b = P_Cyc_H
5c = P_Et_H
1a-I = 1P_Me_Me
1b-I = 1P_Cyc_Me

Preparation of the Target Compounds: Hydrazine Diphosphonates





Not Yet Tested
[2P_me_Me]

2P_cyc_Me

2P_Et_Me

Heat Release Reduction Results

- Epoxy functionalized flame retardants added to Bisphenol F (Epon 862) epoxy
  - Epoxy cured with aliphatic amine
    - Epikure 3274: 50-70% polyoxypropylene diamine, balance 4-nonylphenol
  - Small 2.5 to 3 gram batches for MCC testing
  - Larger batches for cone calorimeter testing.
  - All formulations targeted to have 2.5wt% Phosphorus

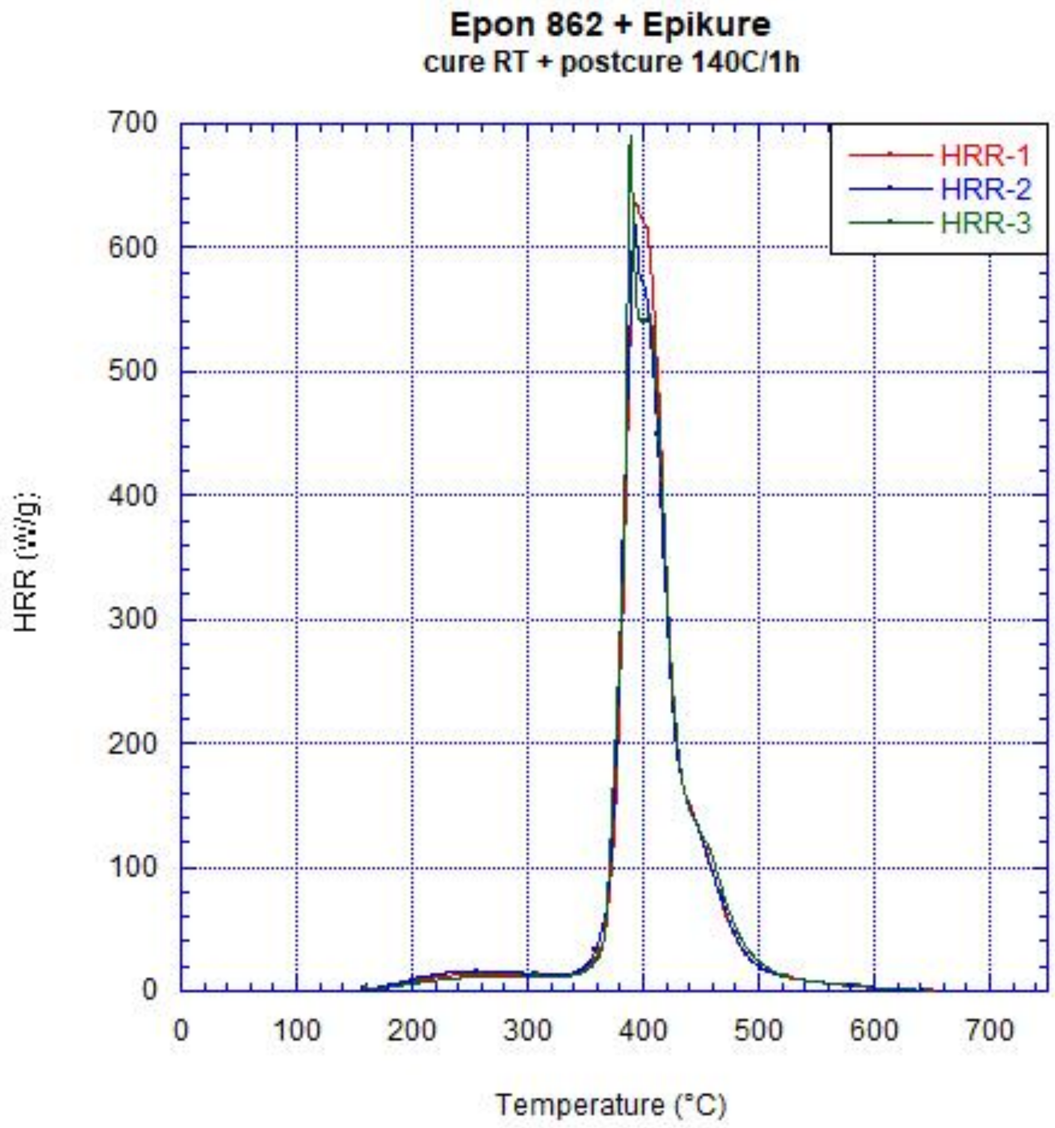
- Materials tested by micro combustion calorimeter (ASTM D7309-13) and cone calorimeter (ASTM E1354-18).

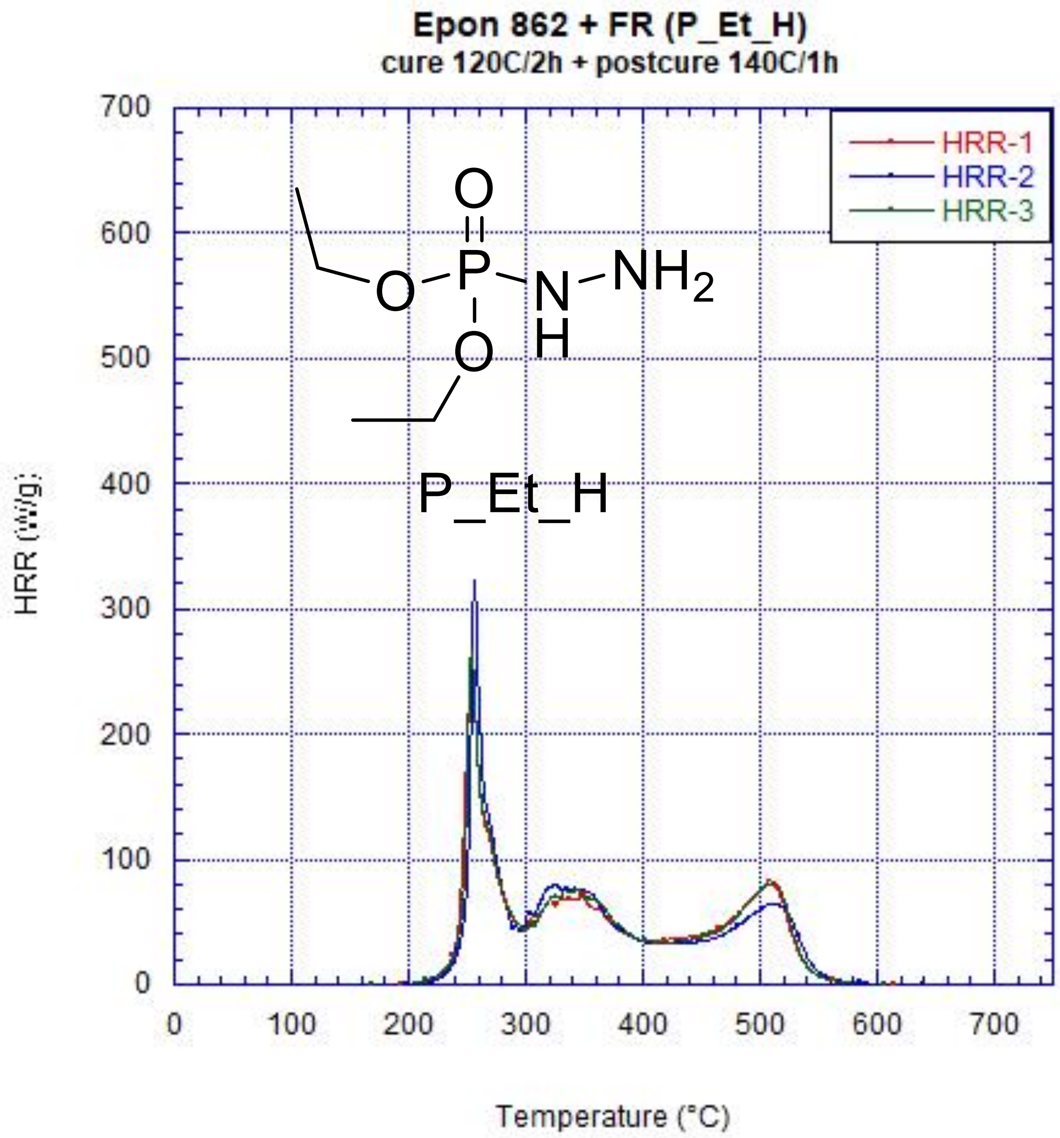
Heat Release Data

- All samples show increased char yield, decreased total HR, decreased peak HRR values.
- Additional peaks of HRR found indicating a change in thermal decomposition chemistry for the epoxies.
- Additional studies needed to determine exact chemistry, but, mechanism of flame retardancy is likely condensed phase char formation

Sample	Char Yield (%)	HRR Peak(s) Value (W/g)	HRR Peak(s) Temp(s) (°C)	Total HR (kJ/g)
Epon 862/Epikure Control	9.21	633, 132	394, 512	23.7
RT + 140C/1 hr	9.36	621, 132	392, 516	23.5
	9.01	684, 124	389, 516	23.8
Epon 862/Epikure/P-Et-H	27.77	205, 207, 31	286, 337, 530	16.6
RT + 140C/1 hr	28.04	270, 193, 34	285, 339, 534	16.9
	27.85	290, 184, 33	284, 334, 528	16.7
Epon 862/Epikure/1P-Me-Me	18.52	292, 110, 22	331, 377, 514	20.3
RT + 140C/1 hr	19.43	294, 106, 19	334, 374, 508	20.3
	17.77	291, 110, 24	334, 390, 520	20.6
Epon 862/Epikure/2P-Et-Me	22.46	260, 196, 14	336, 354, 526	20.0
RT + 140C/1 hr	23.18	265, 185, 16	336, 356, 526	19.7
	22.57	280, 197, 15	337, 355, 539	19.9
Epon 862/Epikure/2P-cyc-Me	19.44	311, 190, 15	336, 353, 523	21.0
RT + 140C/1 hr	21.82	293, 192, 14	334, 354, 530	20.5
	20.71	298, 164, 16	336, 361, 526	20.6
Epon 862/Epikure/P-Me-H	27.13	25, 183, 19	254, 359, 530	17.6
RT + 140C/1 hr	27.59	27, 192, 19	254, 355, 540	17.4
	26.54	31, 171, 14	253, 359, 539	16.9
Epon 862/Epikure/1P-cyc-Me	25.59	38, 166, 22	287, 338, 529	17.5
RT + 140C/1 hr	24.92	36, 168, 22	282, 338, 499	17.9
	25.69	35, 164, 17	280, 348, 534	17.0
Epon 862/Epikure/P-cyc-H	15.21	35, 296	284, 351	22.1
RT + 140C/1 hr	15.55	37, 251	280, 357	21.9
	15.51	34, 275	277, 360	21.7
PS std 6 2018	0.03	1246	447	36.2
	0.05	1268	444	36.3
	0.00	1295	446	36.4

Heat Release Curves – MCC Testing





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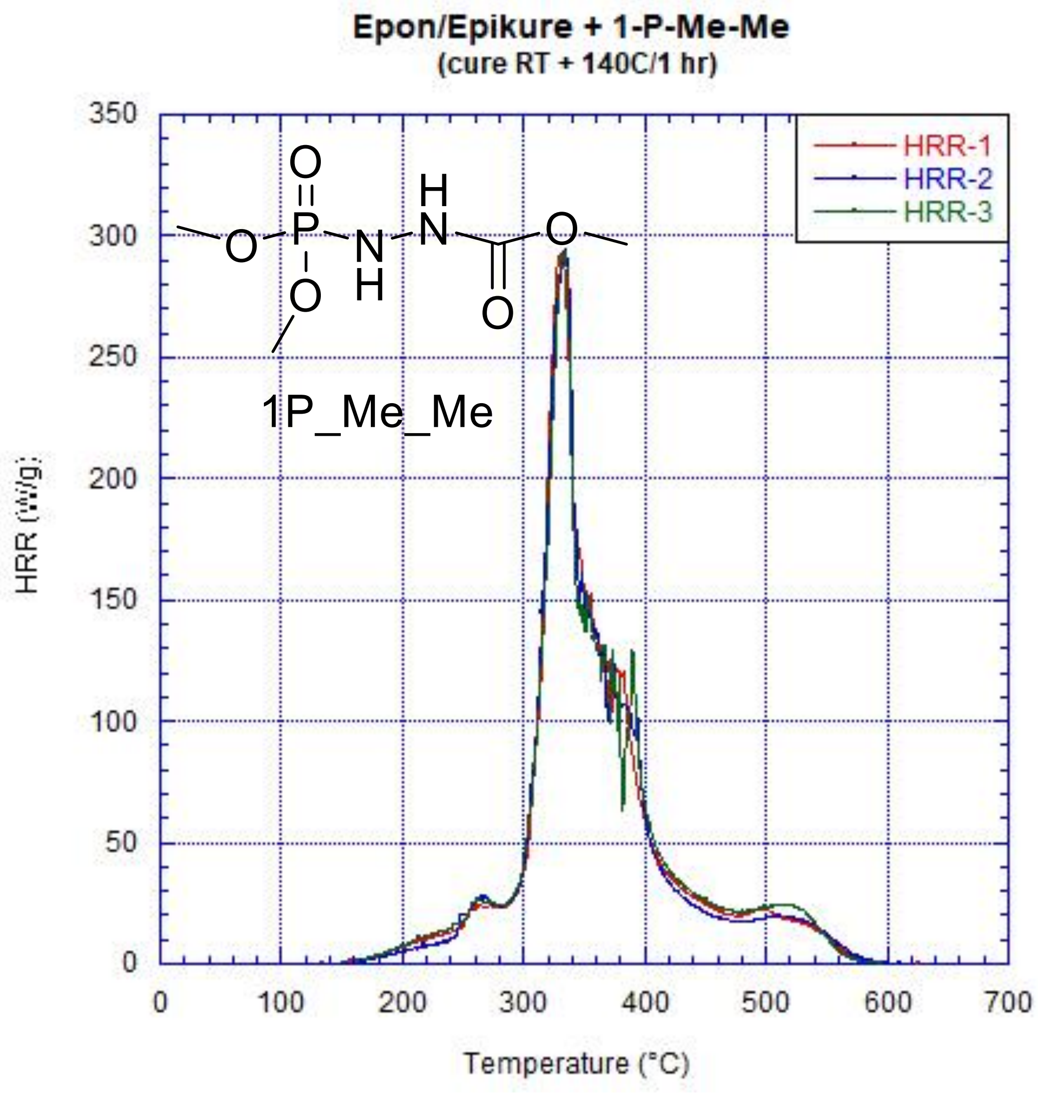

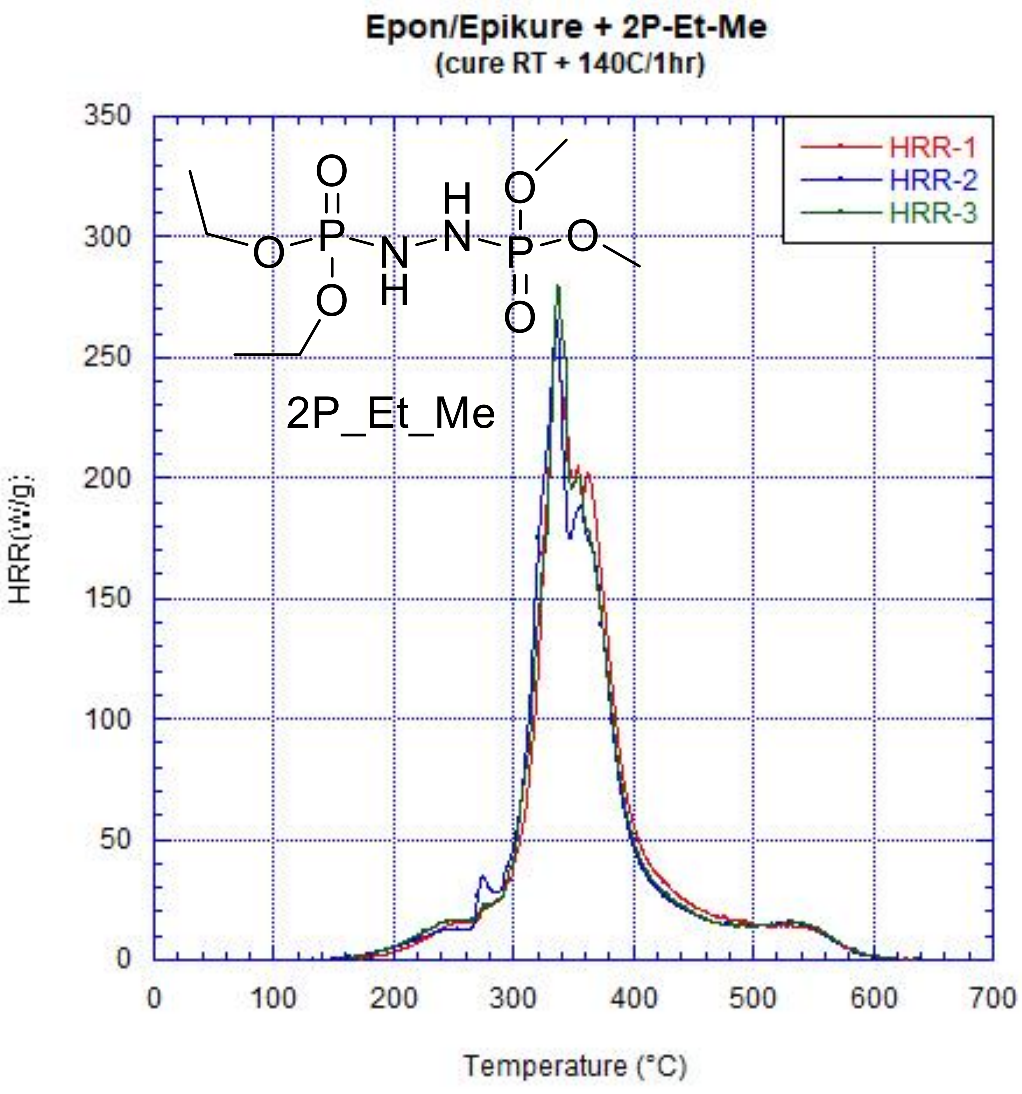

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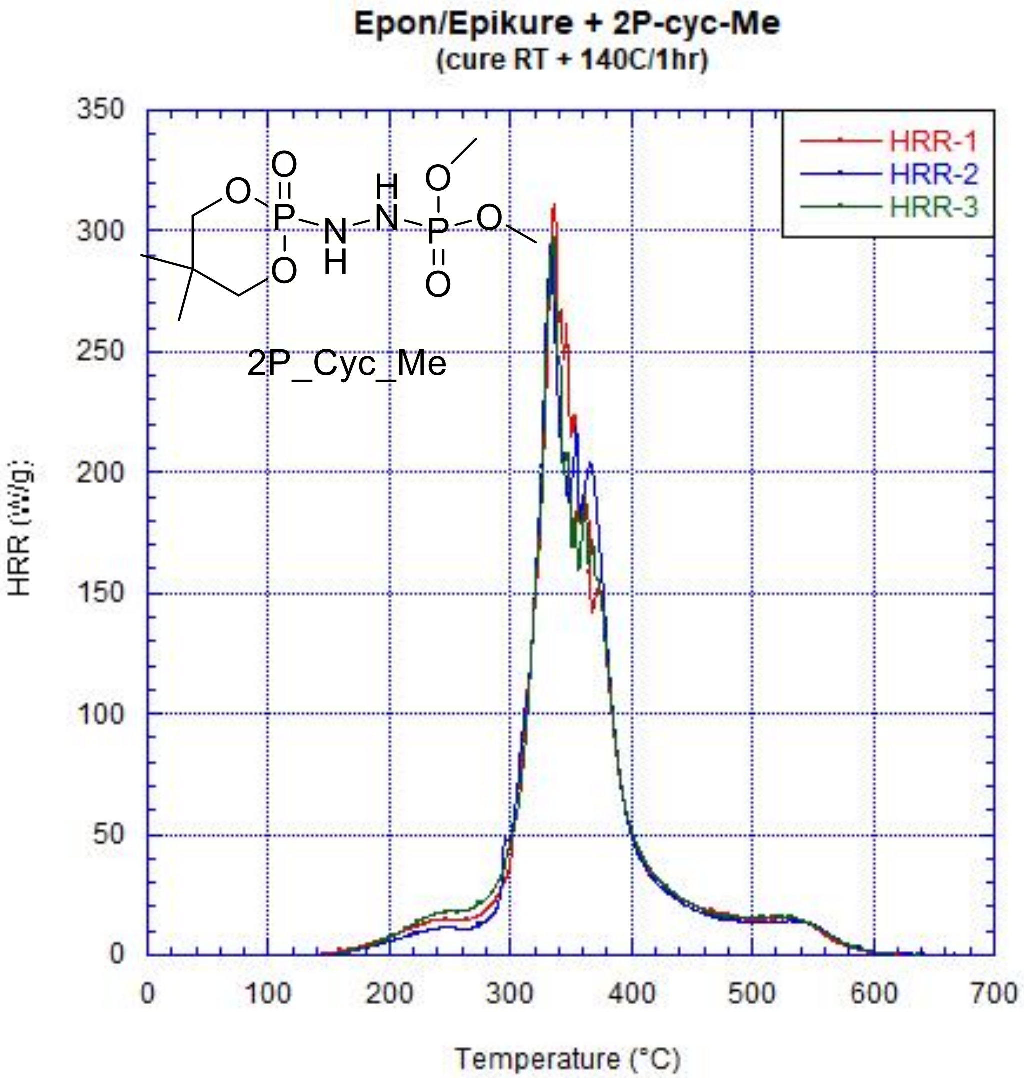

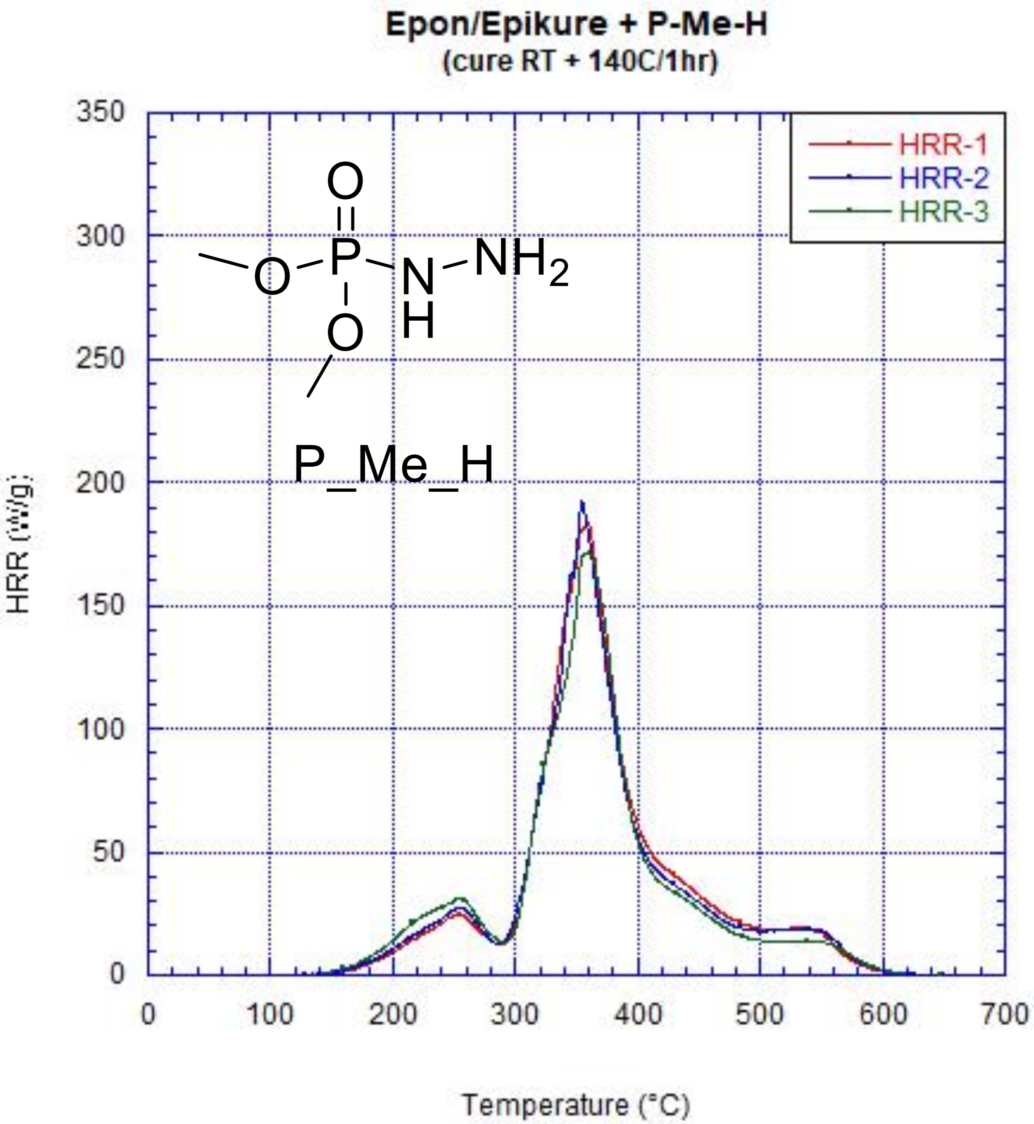

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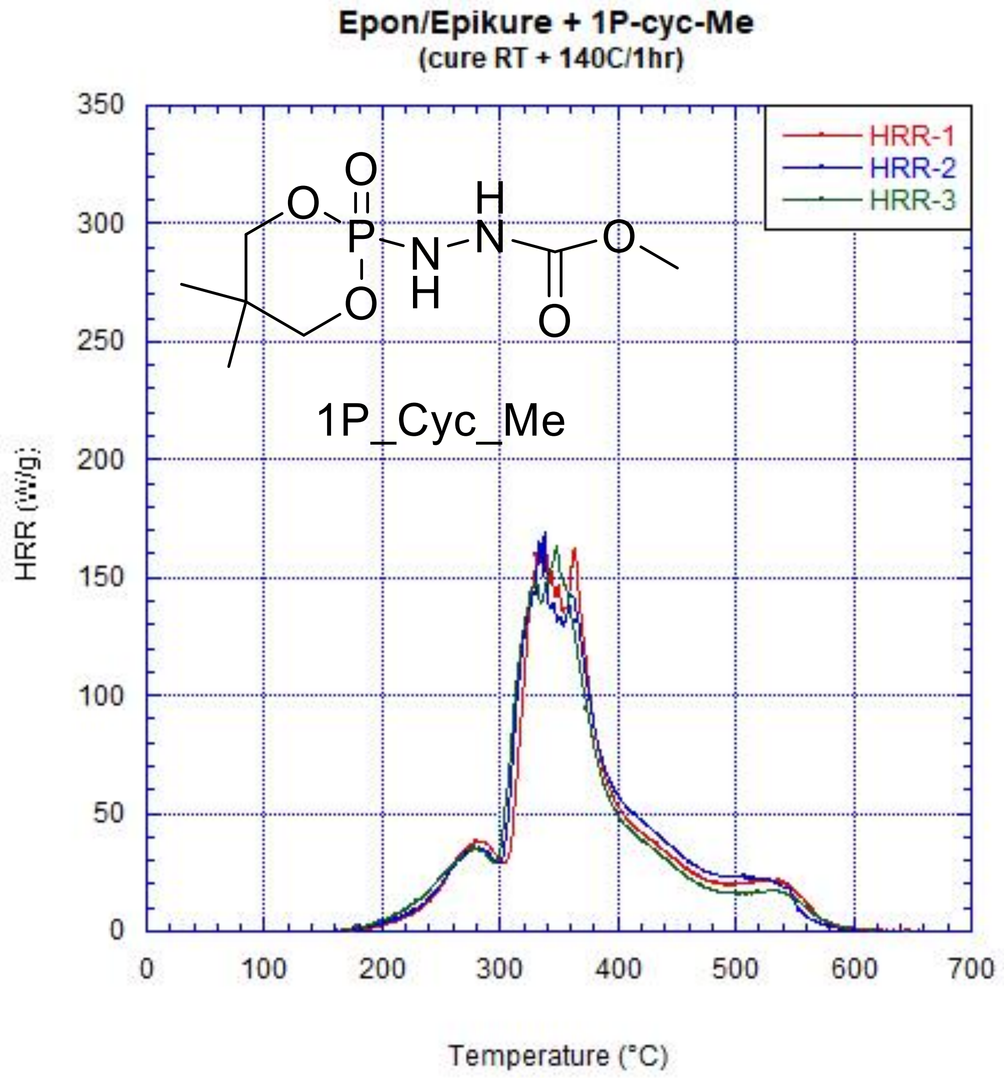
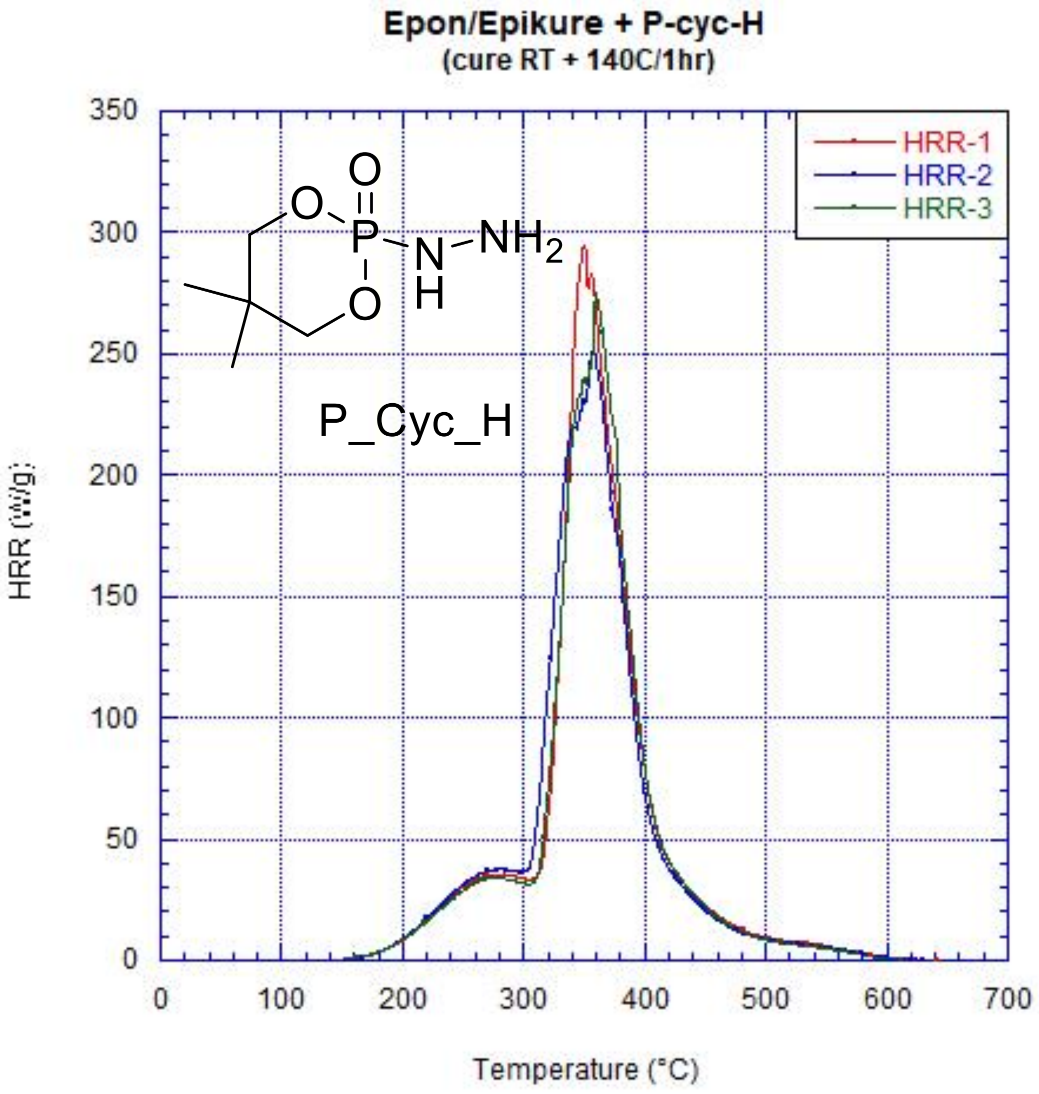
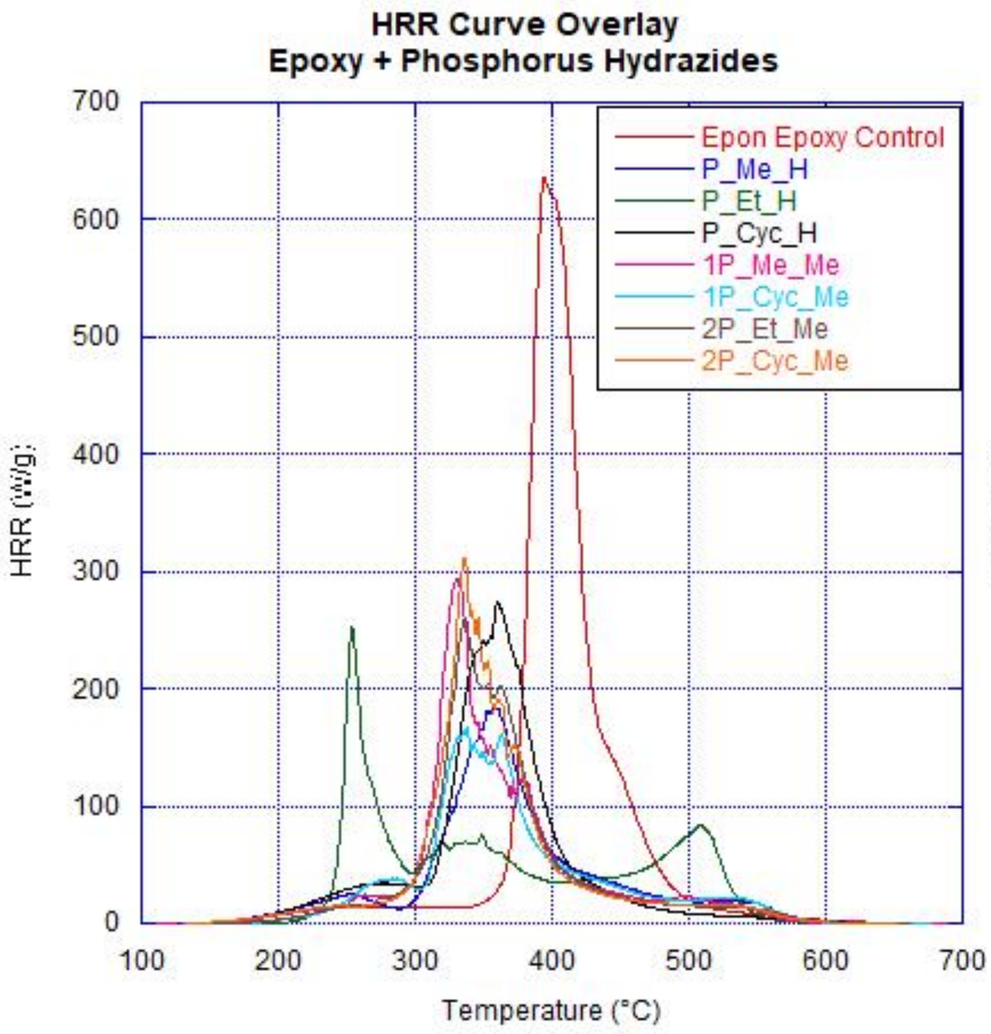
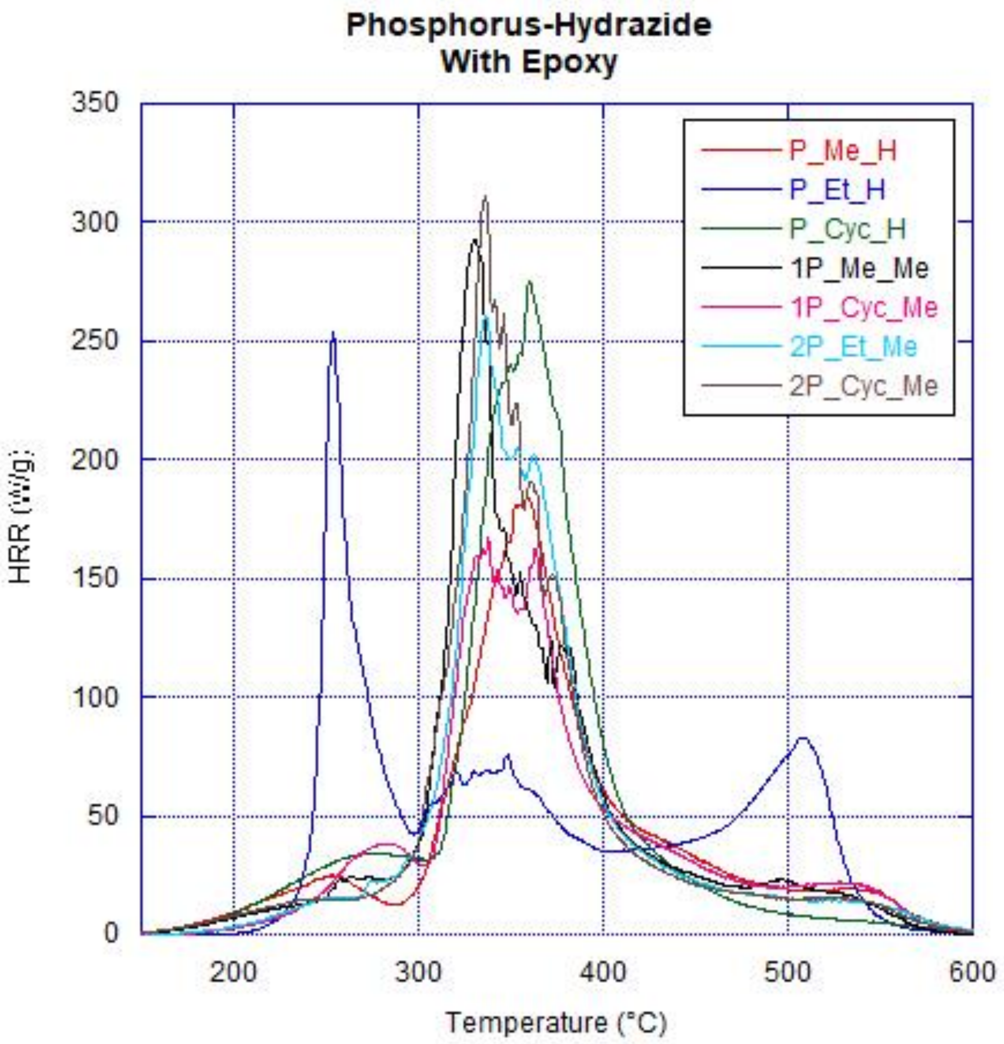




MCC Summary of Results

- Phosphorus -Hydrazides show reductions in HRR
- Greatest reductions in HRR selected for scale-up for cone calorimeter testing





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Cone Calorimeter Testing

- Best candidates from MCC testing scaled up and tested via cone calorimeter.
  - P-Et-H, P-Me-H easily scaled up, but P-Me-H interfered with epoxy curing – too reactive.
  - 1P-Cyc-Me could not be scaled up
  - 2P-Et-Me could be scaled up and was tested, even though MCC did not show superior performance.
- P-Et-H, 2P-Et-Me blended into Epon 862 with Epikure 3274
- Cone calorimeter testing at 35 kW/m^2 heat flux, 3mm thick, with and without frame and grid.
  - Samples showed some deformation during burning – used frame and grid to force them to lay flat during testing.

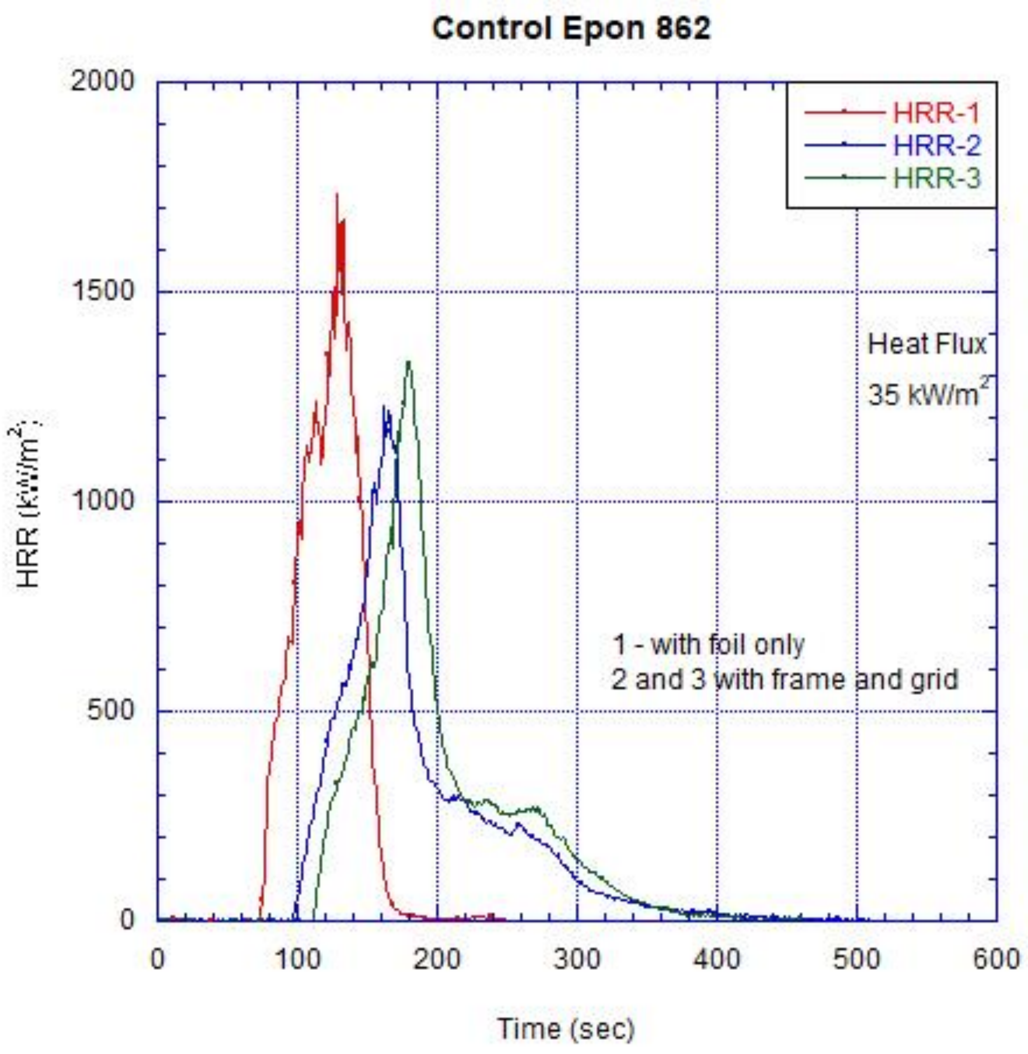
Cone Calorimeter Testing

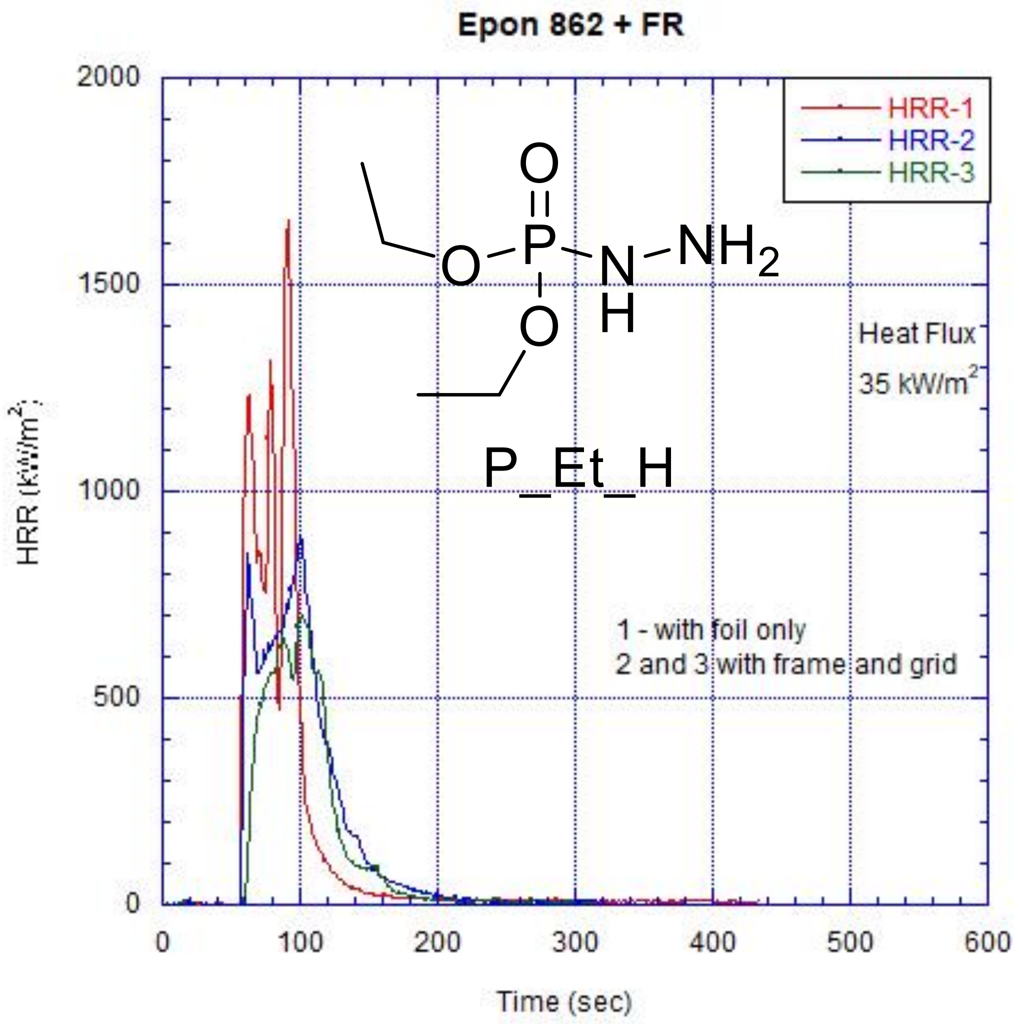
Sample Description	Time to ignition (s)	Peak HRR (kW/m2)	Time to Peak HRR (s)	Average HRR (kW/m2)	Weight % Lost (%)	Total Heat Release (MJ/m2)	Total smoke Release (m2/m2)	Avg. Effective Heat of Comb. (MJ/kg)	MARHE (kW/m2)
Epoxy Control	69	1735	129	718	93.6	78.3	2054	24.63	494
	89	1227	162	250	92.2	87.6	2690	24.33	304
	105	1334	178	297	91.1	91.0	2681	24.98	300
Average Data	88	1432	156	422	92.3	85.6	2475	24.65	366
Epoxy +	50	1654	91	152	79.9	51.3	1623	17.99	432
FR (P-Et-H)	49	889	100	260	68.8	50.1	1713	19.26	340
	53	700	101	220	55.0	38.6	1330	17.68	268
Average Data	51	1081	97	211	67.9	46.7	1555	18.31	347
Epoxy +	57	987	120	183	73.0	71.7	2169	20.48	355
FR (2P-Et-Me)	54	772	131	251	68.9	63.5	2060	20.45	315
	55	826	111	209	72.0	63.1	2149	21.03	330
Average Data	55	862	121	214	71.3	66.1	2126	20.65	334

- No strong reduction in peak HRR, MARHE
- Notable reductions in total HR, total smoke, average effective heat of combustion

Cone Calorimeter Results

- Erratic results due to strong physical effects of burning





Cone Calorimeter Results

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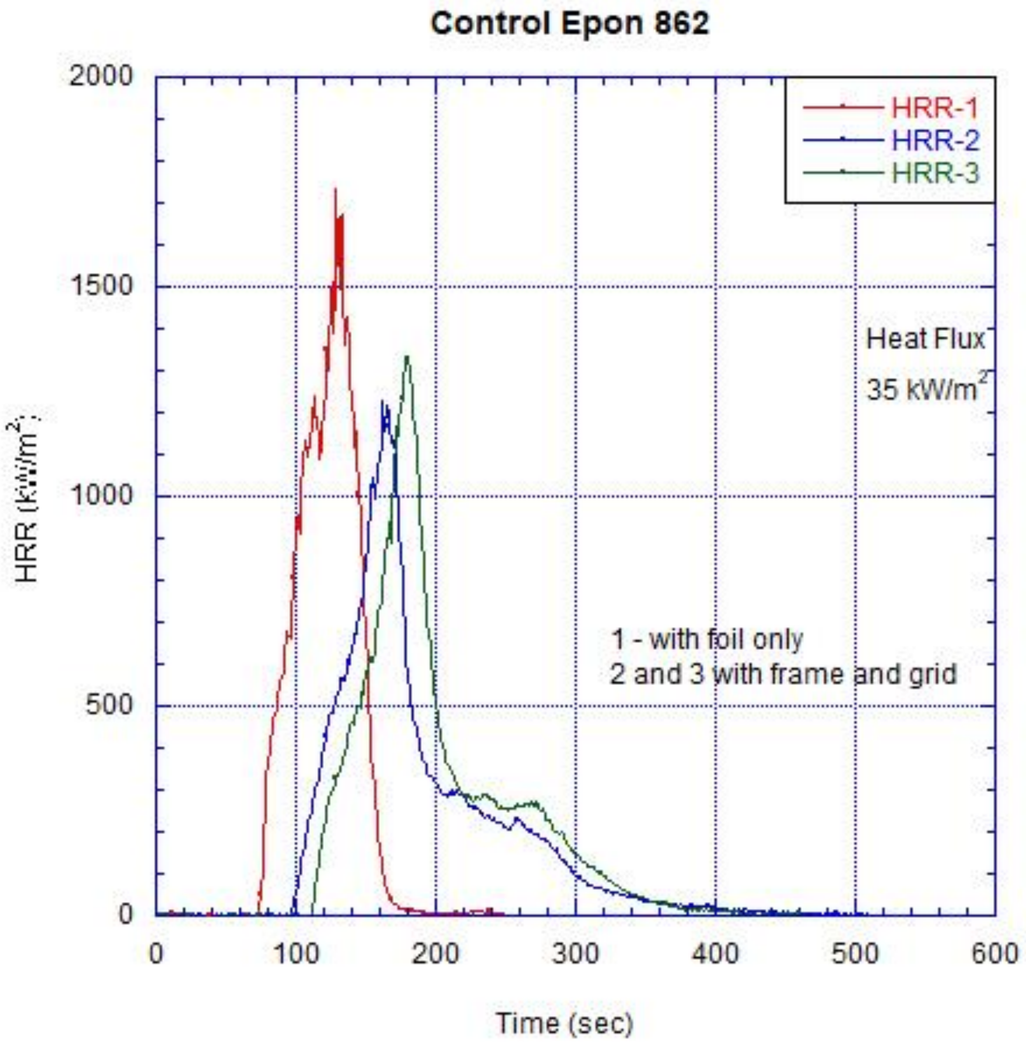
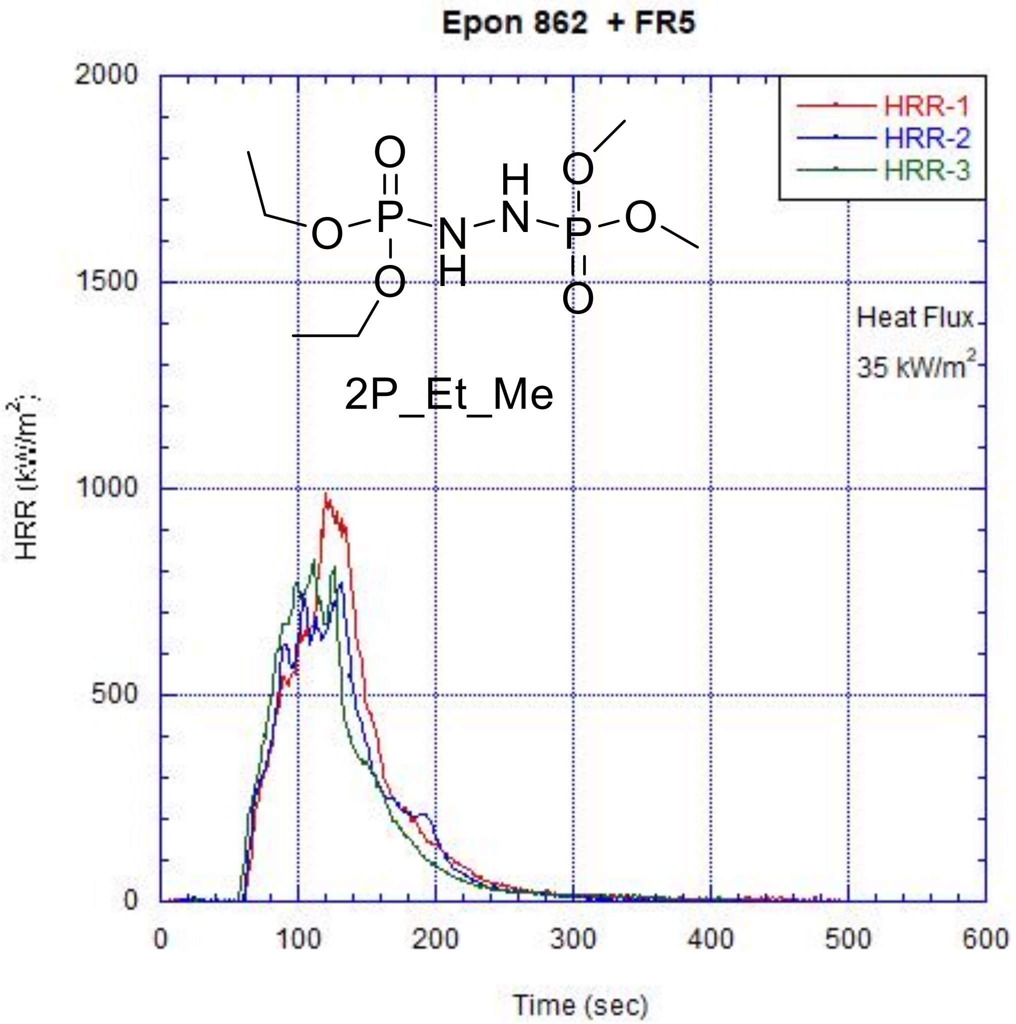




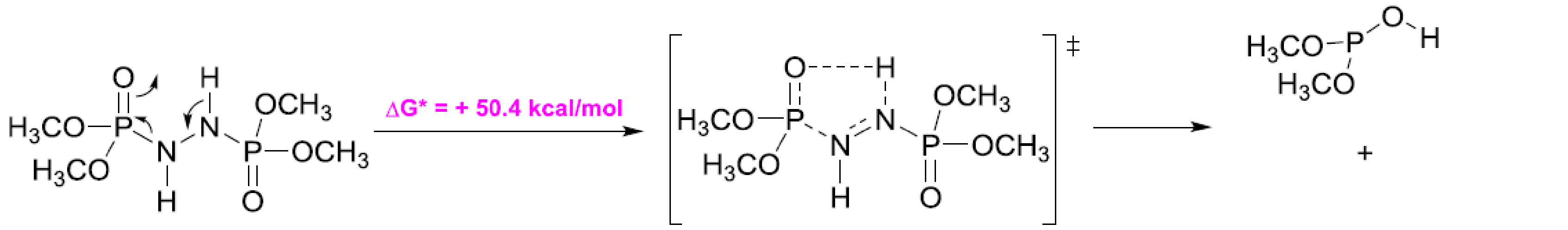
Cone Calorimeter Chars

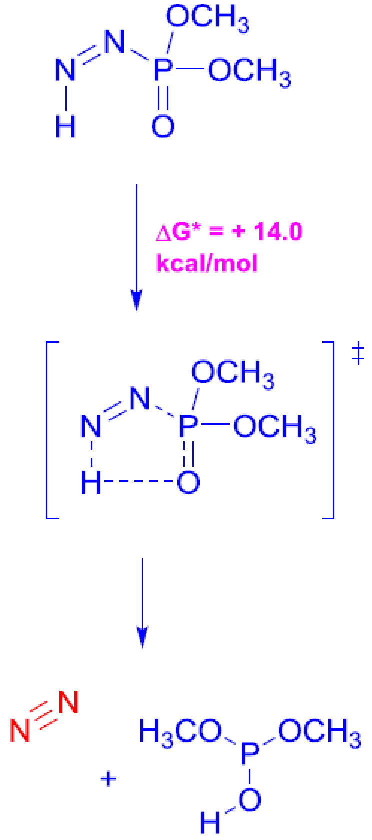
Control Sample

Epoxy + P-Et-H

Epoxy + 2P-Et-Me

Conclusions





- Organophosphorus Hydrazides show both vapor phase and condensed phase flame retardancy:
  - Reduced effective heat of combustion.
  - Increased char yield, decreased total HR.
  - Mechanism likely a combination of nitrogen release and vapor phase phosphorus, along with phosphorus / epoxy interactions in the condensed phase.
    - Thermodynamic modeling of chemical structure shows a pathway to this potential flame retardant release.

Conclusions

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- Peak HRR, MARHE not reduced as much as desired.
  - Unexpected benefit: reduction in smoke release

- Chemistry may be useful to combine with other flame retardants.

- Further study needed to verify utility, effect on epoxy Tg, and reactivity into epoxy matrix.
  - Epoxy reactivity assumed based upon known chemical interactions between epoxy, aliphatic amines, and phosphorus esters at elevated temperatures.

Acknowledgements

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  - Abdhulhamid bin Sulayman (graduated Master’s Student)

Questions?