REACTIVE FLAME RETARDANTS FOR AEROSPACE GRADE EPOXY + CARBON FIBER COMPOSITES

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Outline

- Review of Epoxy + Carbon Fiber Systems in Aircraft and Fire Hazards
  - Fire Hazards & Emissions from Epoxy + Carbon Fiber Composites
  - Commercially available reactive flame retardants for epoxy

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

- Phosphine Oxide “Bisphenol A” Epoxy
  - Synthesis Details
  - Heat Release Reduction Results

- Conclusions & Acknowledgements

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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

Epoxy+ Carbon Fiber Aerospace Composite Examples

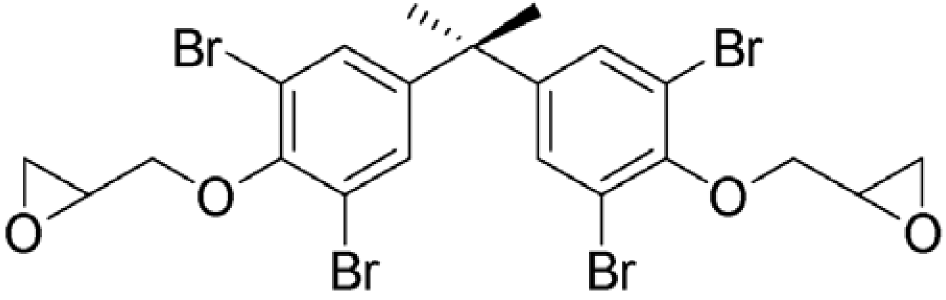
Extinguishing Carbon Fiber Composite Fires

- 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

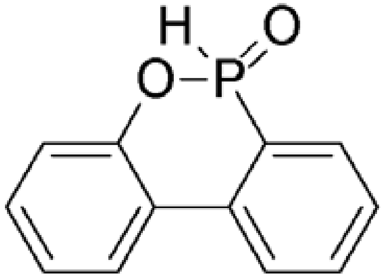
Other Fire Hazards from Carbon Fiber Composites

- 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.
  - “Smolder Behavior and Emissions Byproducts of Aircraft Composite Coupons” Hatch, J.; Wardall, A.; Jackson, J.; McNeilly, R.; Kirsh, J.; Parker, A.; Morgan, A. B.: Duran, C. *Fire Safety Journal* **2021**, *123*, https://doi.org/10.1016/j.firesaf.2021.103366
- All fires hazardous, but additional care / SCBA equipment and post-fire cleanup may be required with carbon fiber composite fires.

Reactive Flame Retardant Additives for Epoxy



Tetrabromobisphenol A
Bis Epoxide



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

- 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.
  - Can change cure chemistry, glass transition temperature, and properties.
  - Commercial examples above – but mostly limited to circuit board applications, no current use in structural aerospace composites.
  - Brominated reactives under regulatory scrutiny.

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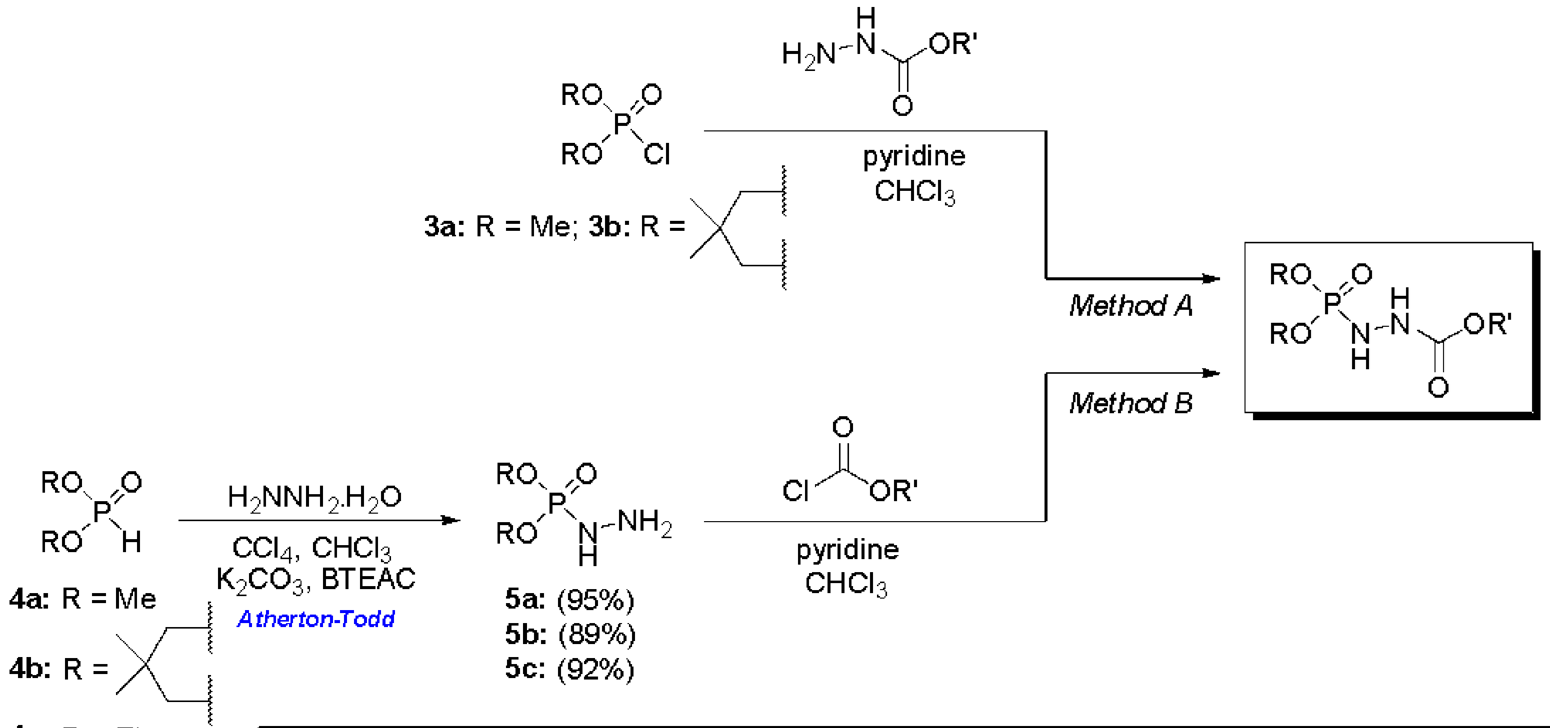
Preparation of the Target Compounds: Hydrazine Monophosphonates



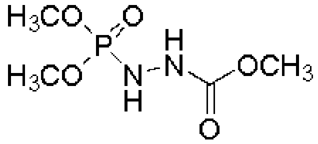
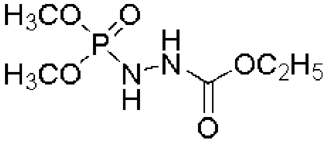
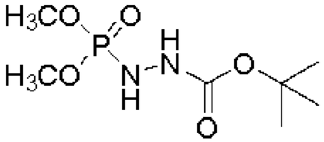
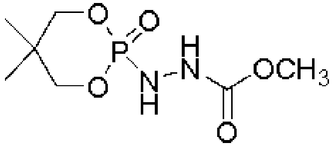
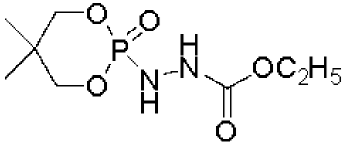
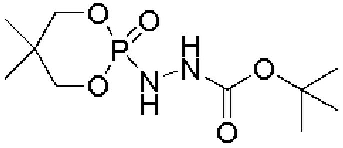
3a: R = Me; **3b:** R =

4a: R = Me

4b: R =

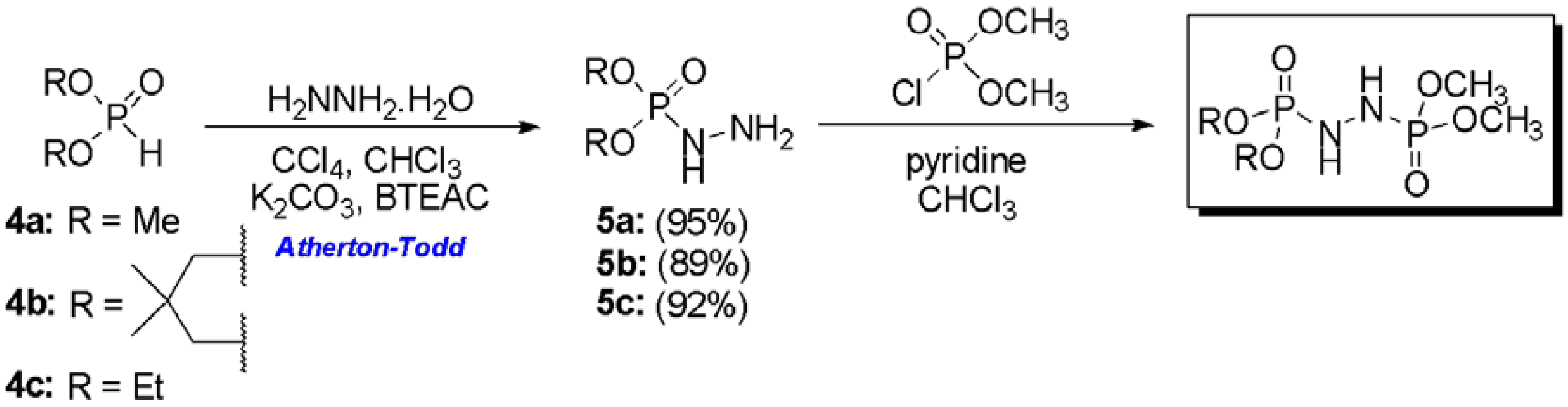
4c: R = Et

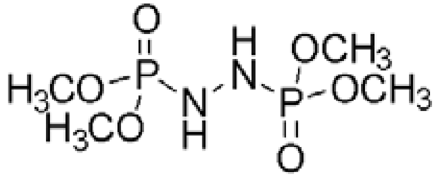
5a: (95%)
5b: (89%)
5c: (92%)

 **1a-I:** *Method B* (73%)	 **1a-II:** *Method A* (76%), *Method B* (89%)	 **1a-III:** *Method A* (57%)
 **1b-I:** *Method B* (86%)	 **1b-II:** *Method A* (87%), *Method B* (95%)	 **1b-III:** *Method A* (81%)

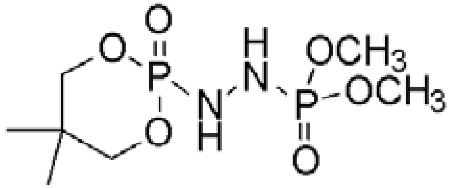
5a = P_Me_H
5b = P_Cyc_H
5c = P_Et_H
1a-I = 1P_Me_Me
1b-I = 1P_Cyc_Me

Preparation of the Target Compounds: Hydrazine Diphosphonates

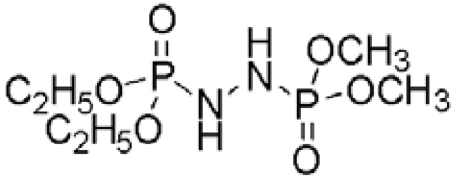




2a: (50%)



2b: (51%)



2c: (54%)

Not Yet
Tested
[2P_me_Me]

2P_cyc_Me

2P_Et_Me

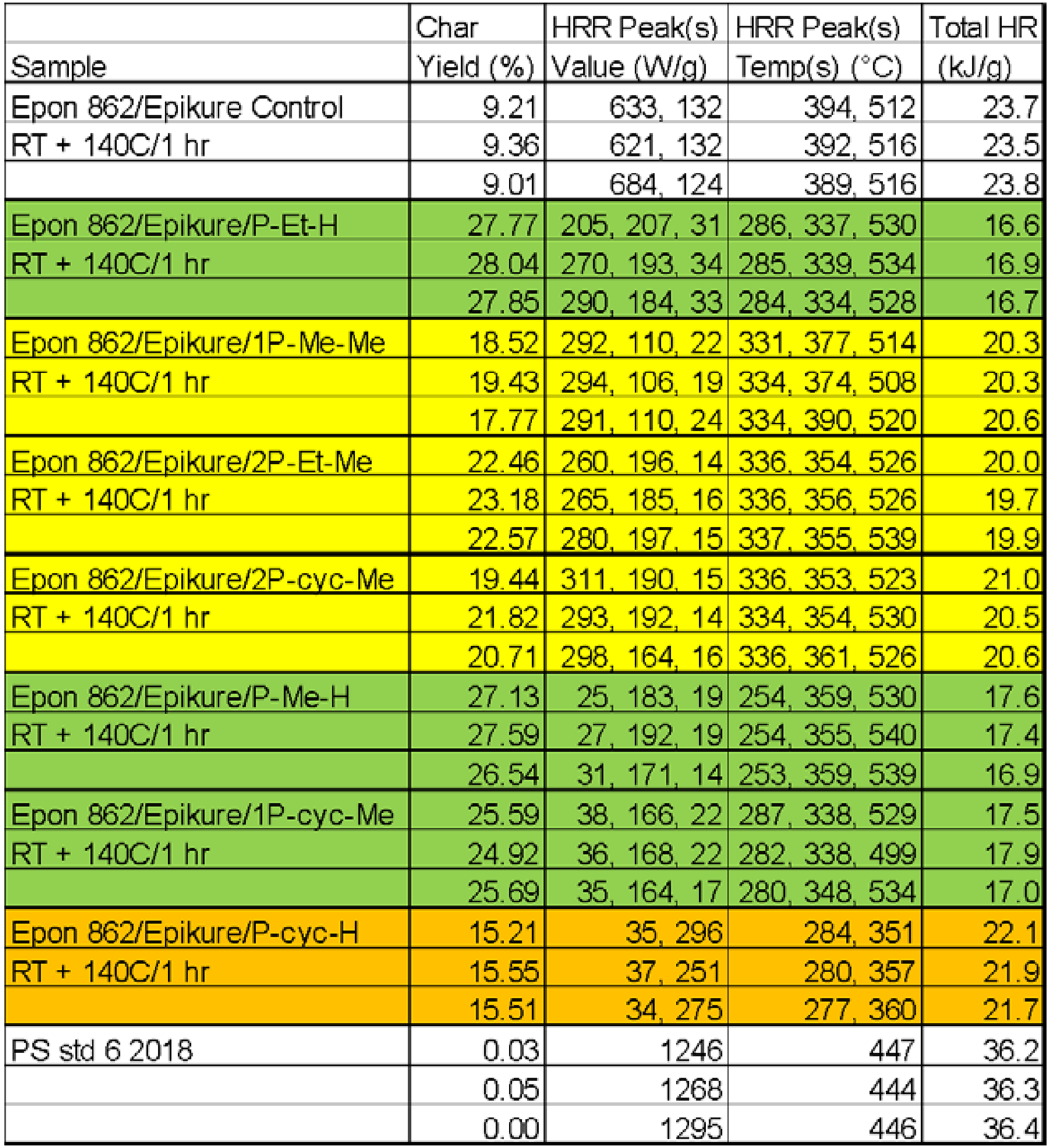
Heat Release Reduction Results

- 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).

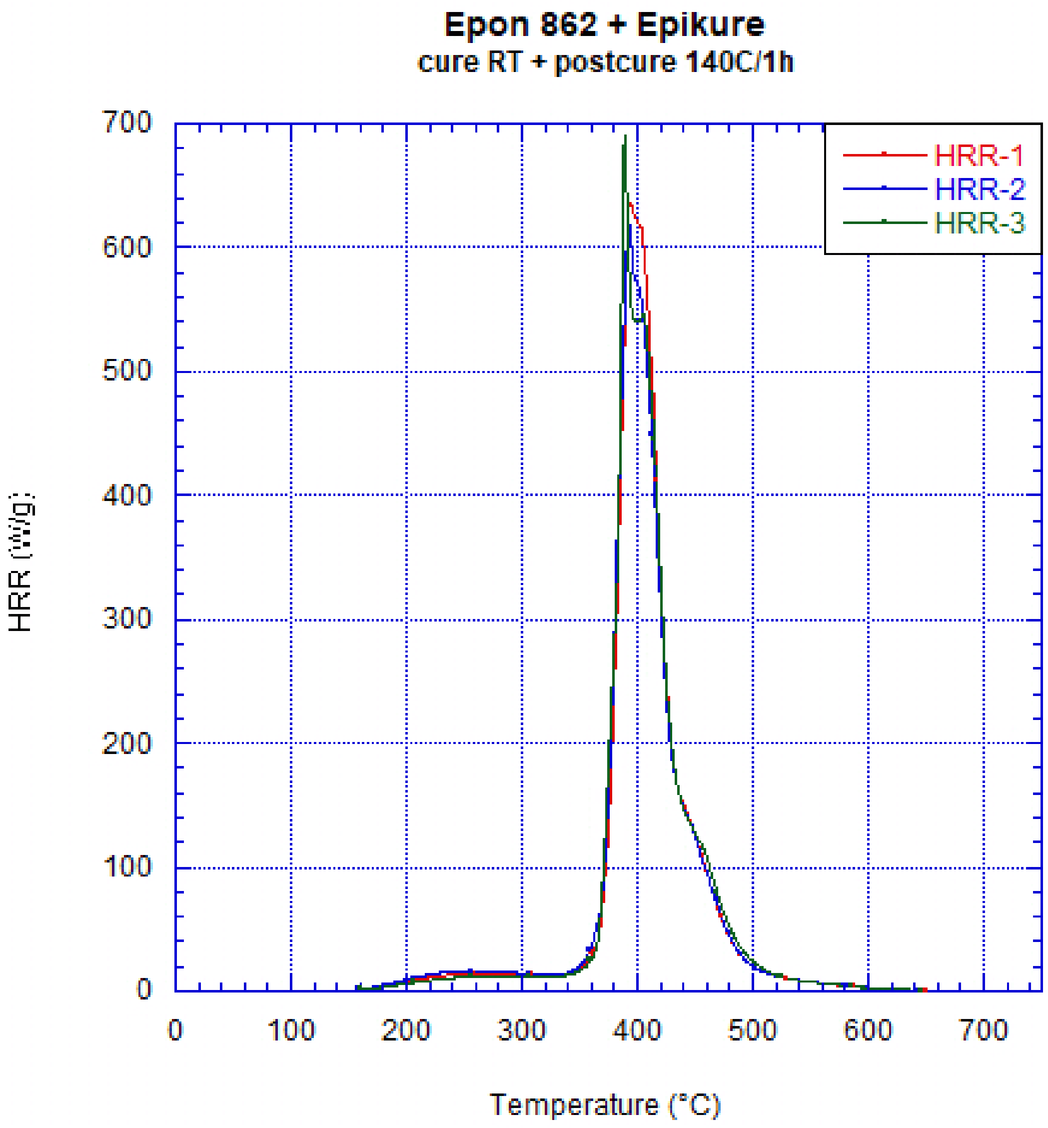
Heat Release Data

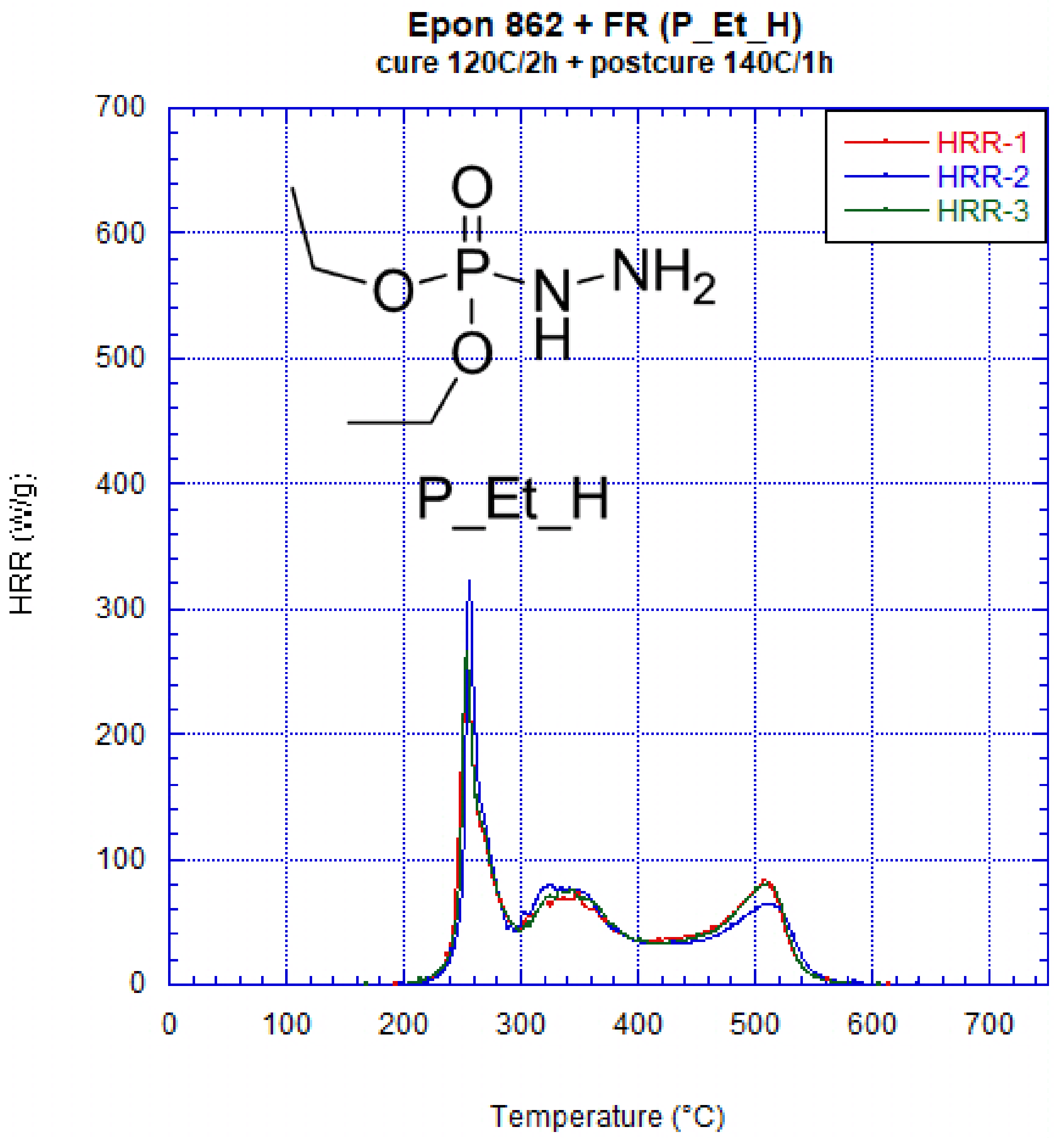
- All samples show increased char yield, decreased total HR, decreased peak HRR values.
- Additional peaks of HRR found indicating a change in thermal decomposition chemistry for the epoxies.
- Additional studies needed to determine exact chemistry, but, mechanism of flame retardancy is likely condensed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



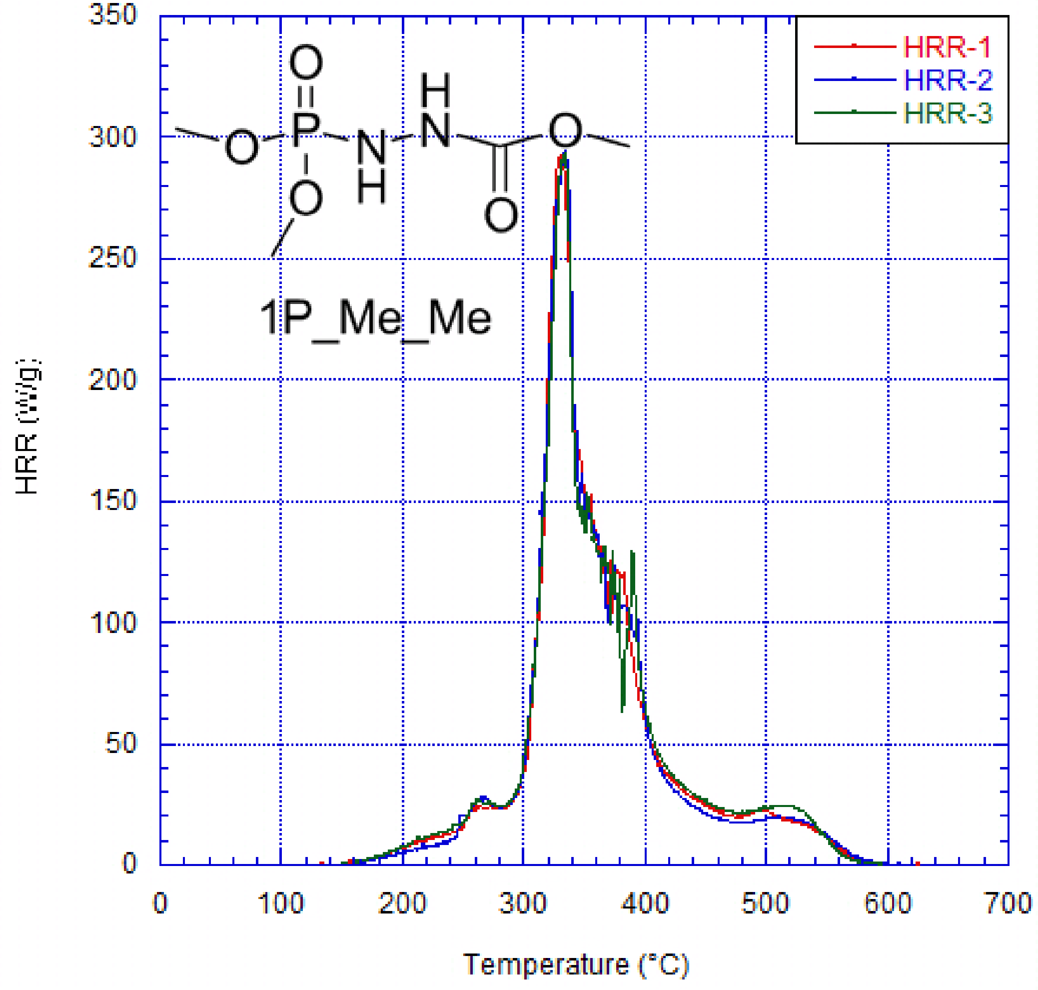
Sample	Char Yield (%)	HRR Peak(s) Value (W/g)	HRR Peak(s) Temp(s) (°C)	Total HR (kJ/g)
Epon 862/Epikure Control	9.21	633, 132	394, 512	23.7
RT + 140C/1 hr	9.36	621, 132	392, 516	23.5
	9.01	684, 124	389, 516	23.8
Epon 862/Epikure/P-Et-H	27.77	205, 207, 31	286, 337, 530	16.6
RT + 140C/1 hr	28.04	270, 193, 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

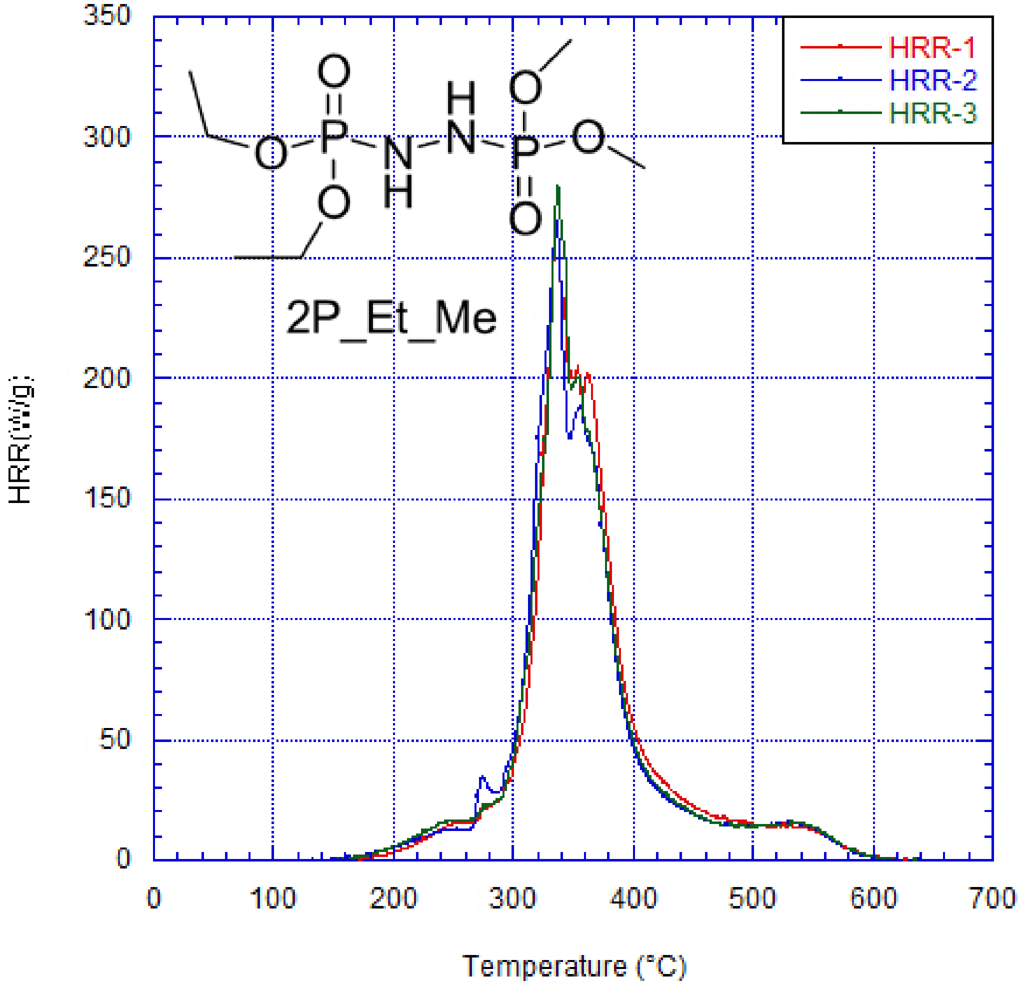

Epon 862 + Epikure
cure RT + postcure 140C/1h


Epon 862 + FR (P_Et_H)
cure 120C/2h + postcure 140C/1h

Heat Release Curves – MCC Testing

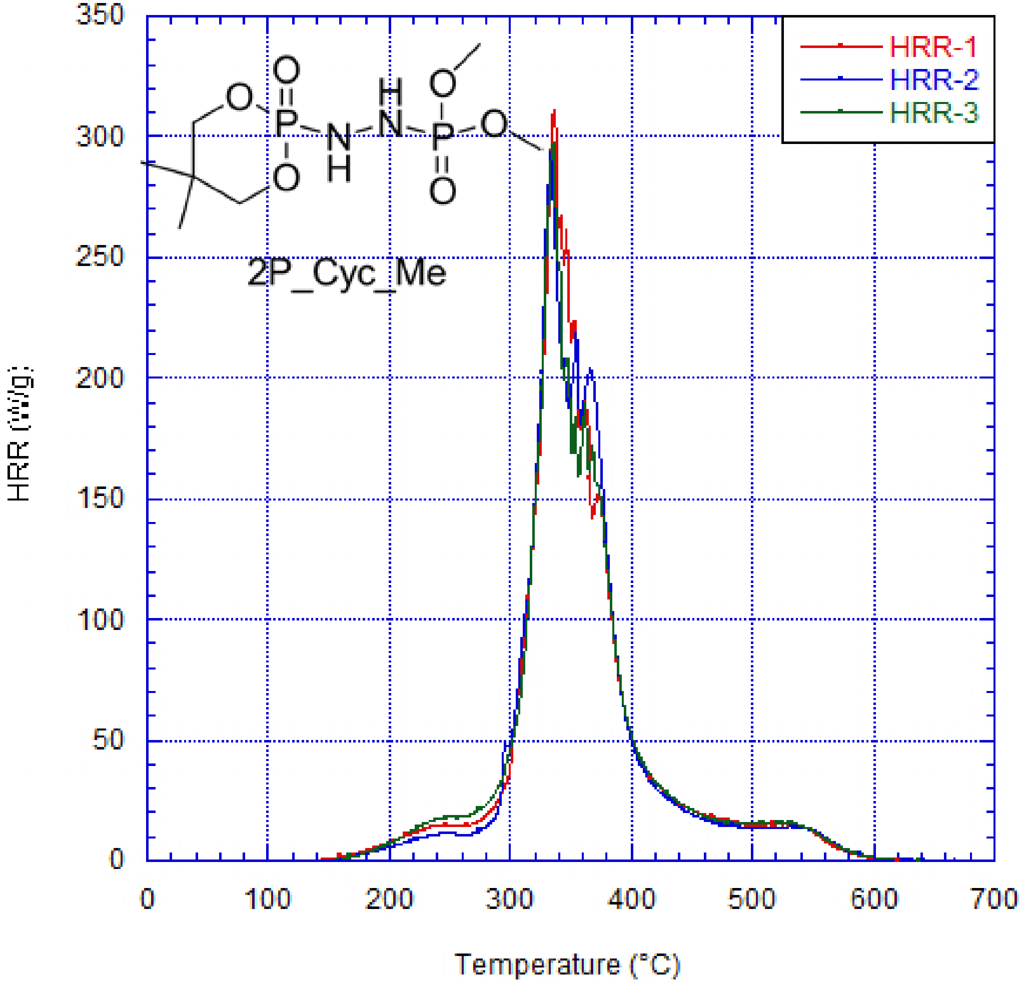


Epon/Epikure + 1-P-Me-Me
(cure RT + 140C/1 hr)

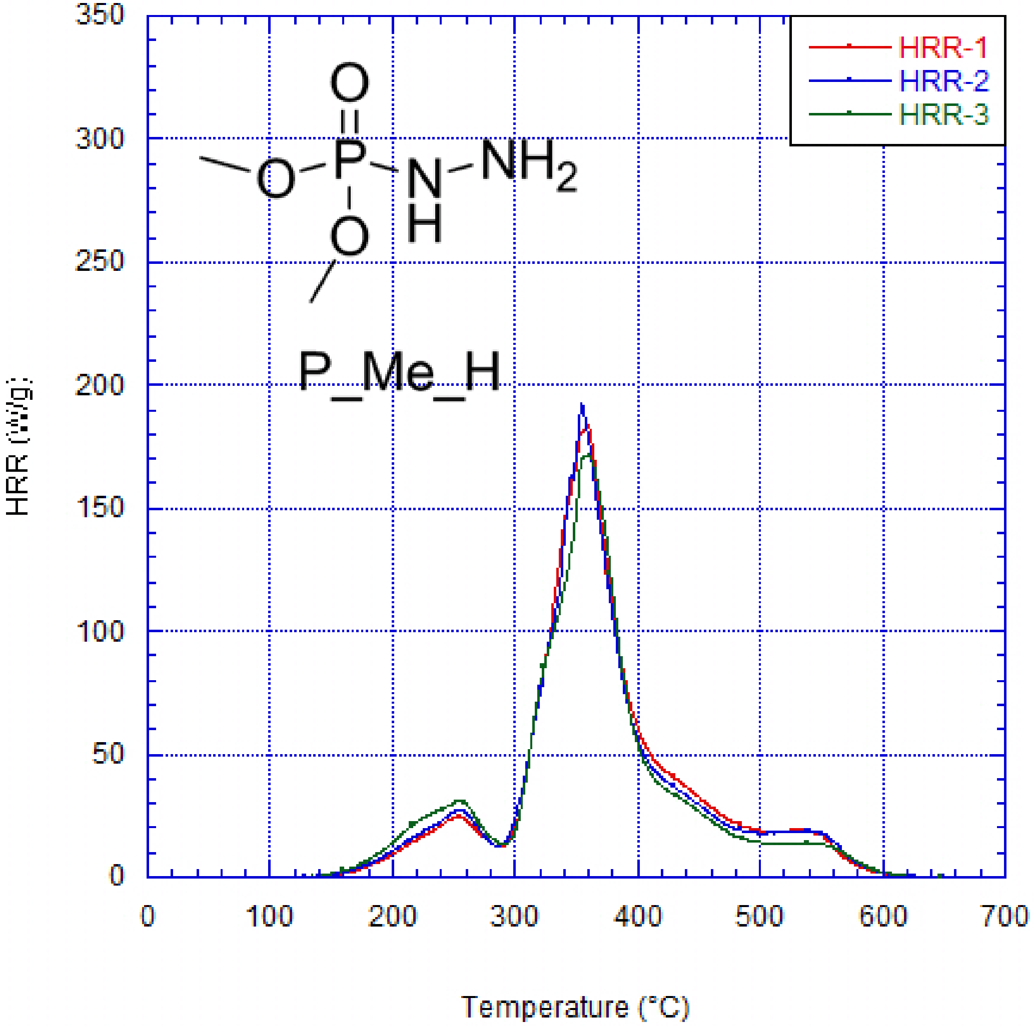


Epon/Epikure + 2P-Et-Me
(cure RT + 140C/1hr)

Heat Release Curves – MCC Testing



Epon/Epikure + 2P-cyc-Me
(cure RT + 140C/1hr)



Epon/Epikure + P-Me-H
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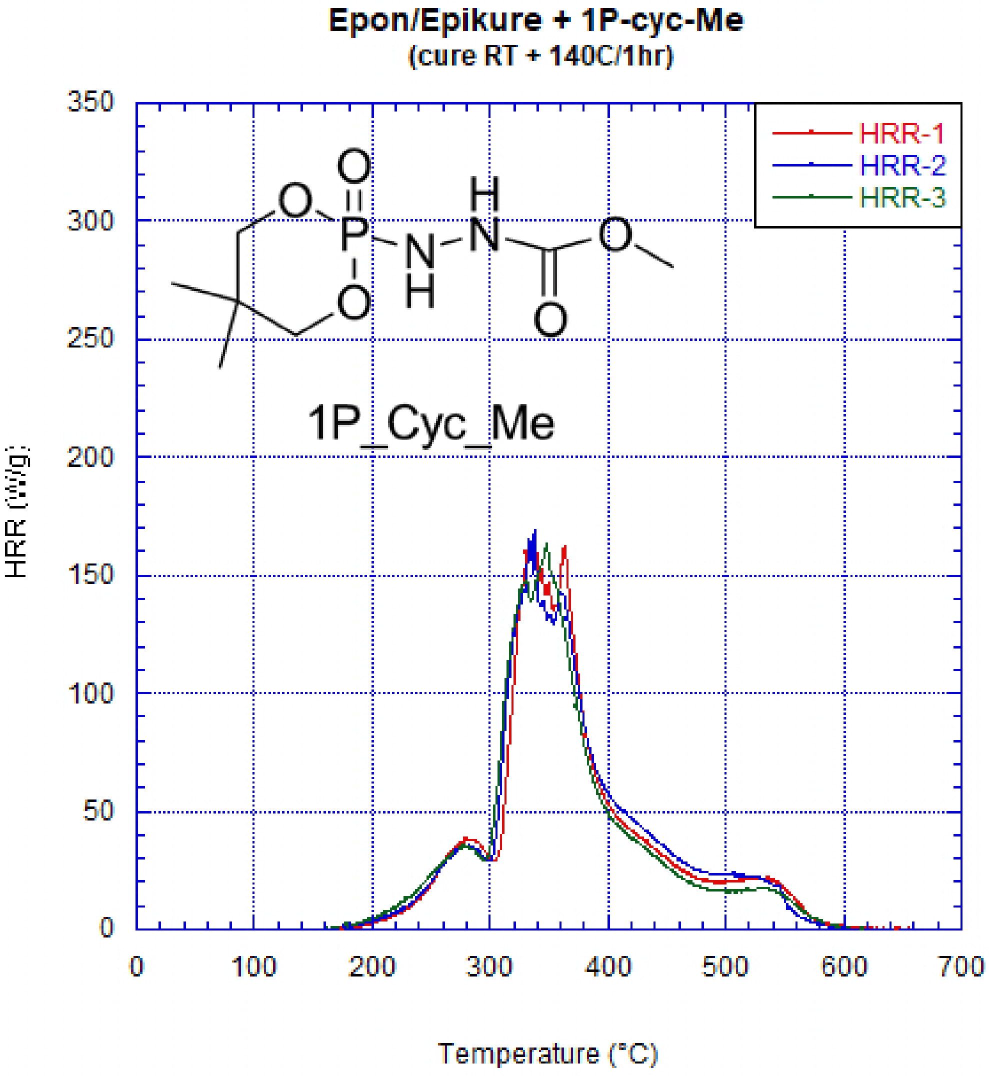
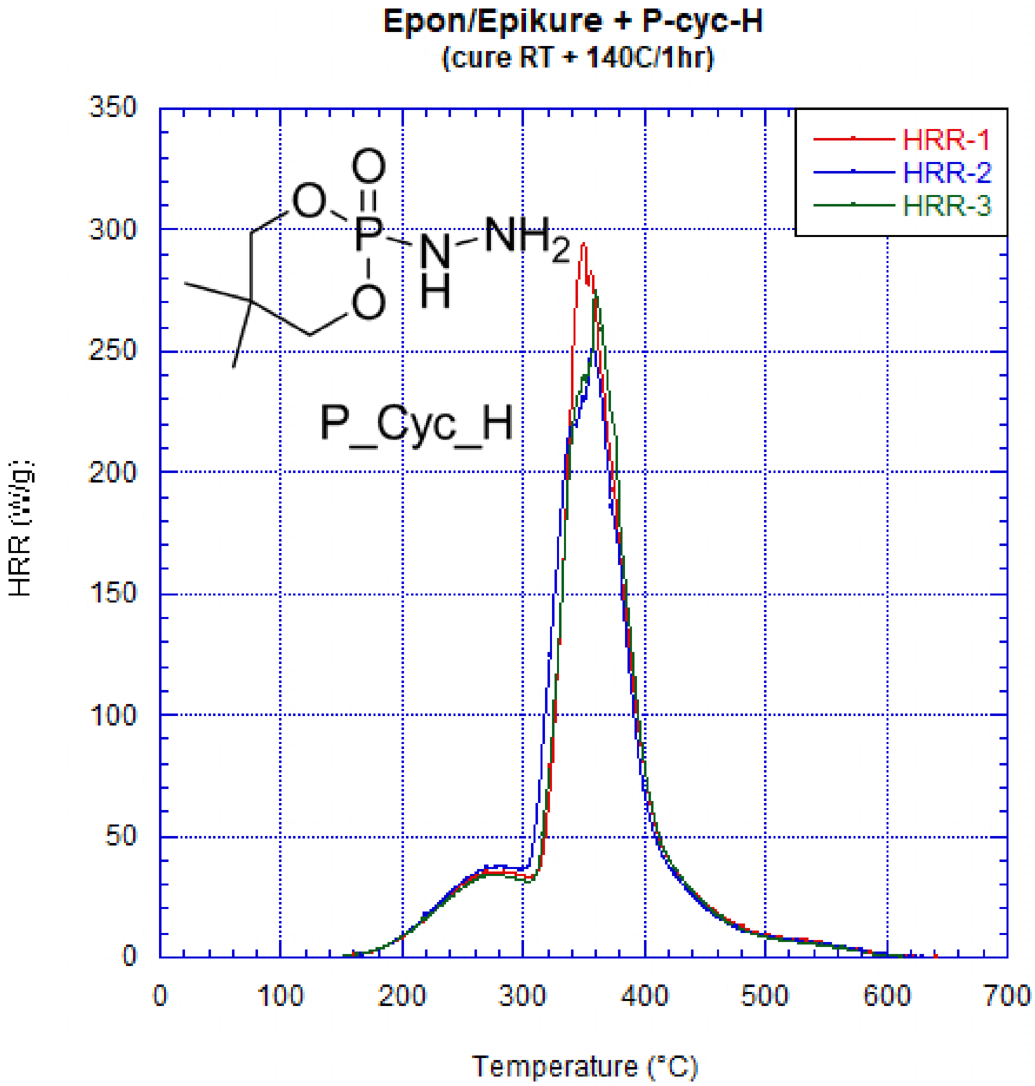
Heat Release Curves – MCC Testing



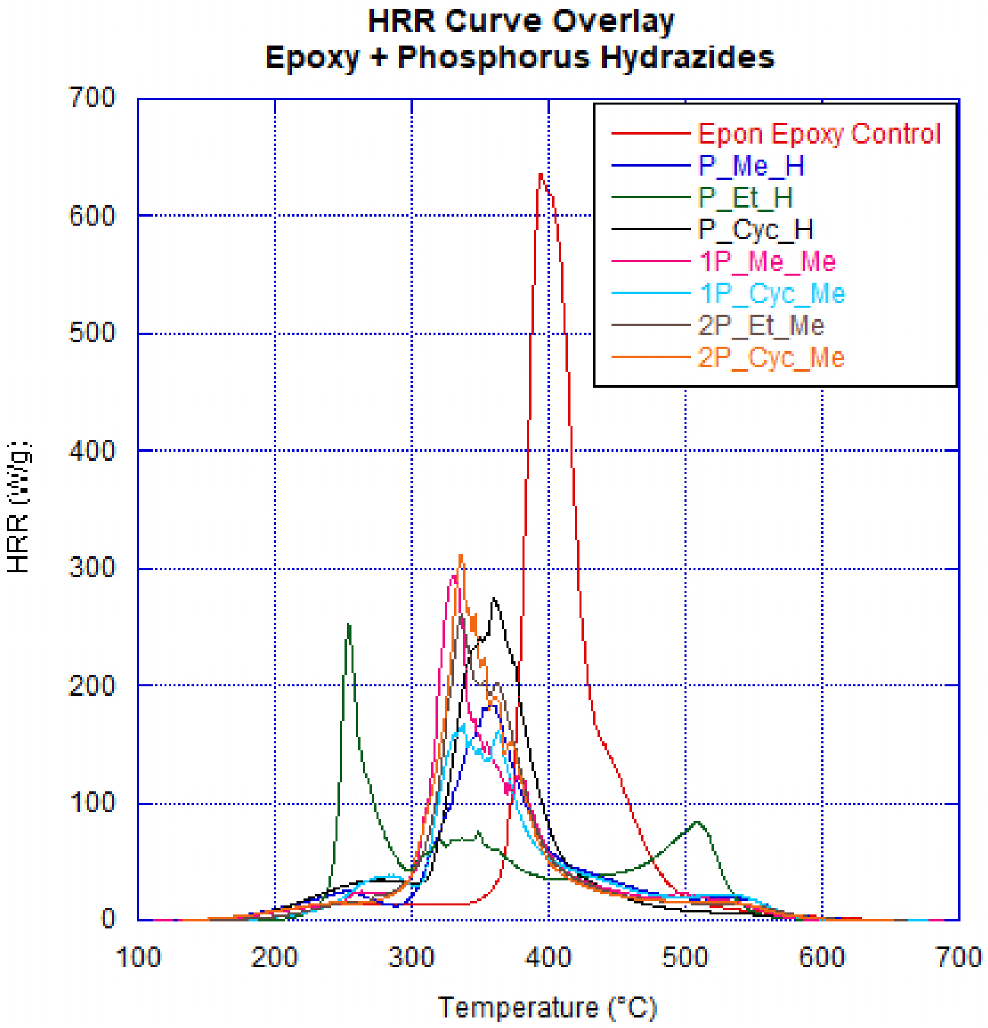
Epon/Epikure + 1P-cyc-Me
(cure RT + 140C/1hr)

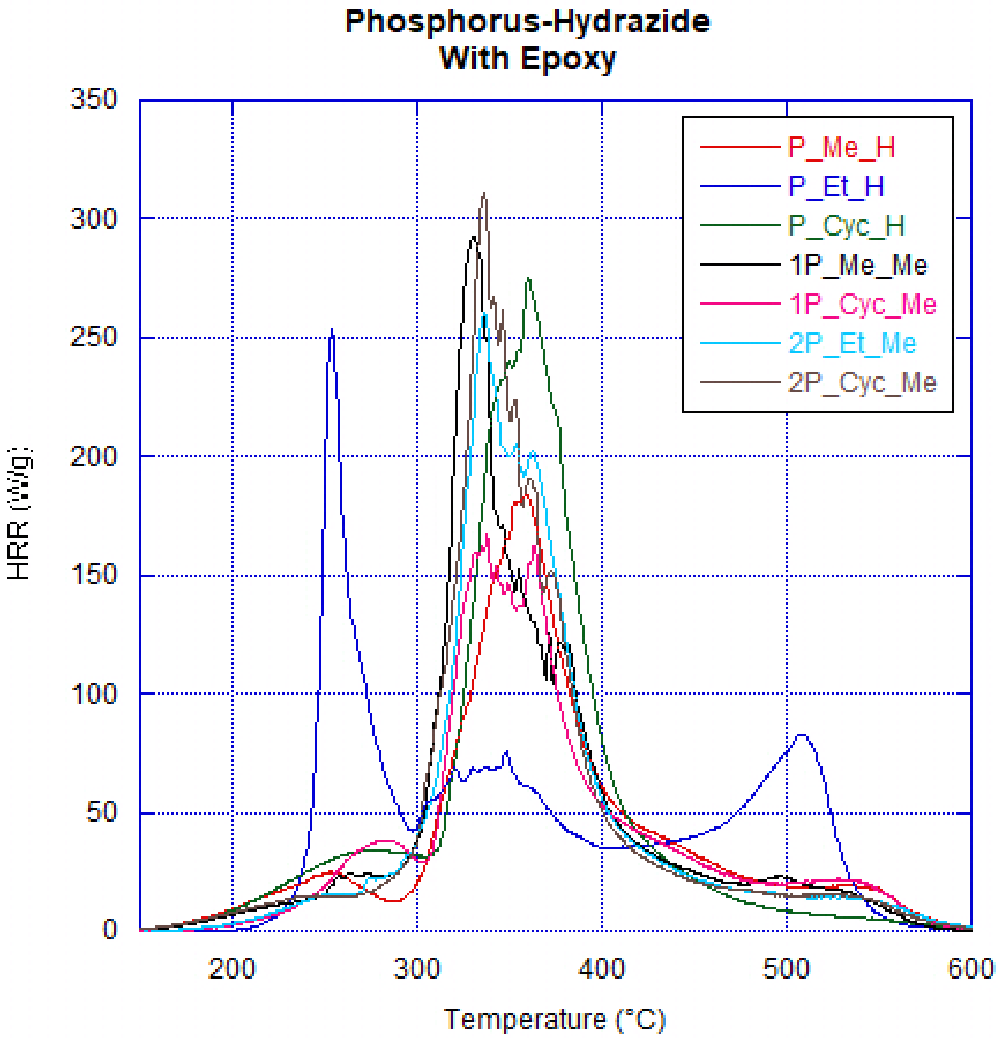


Epon/Epikure + P-cyc-H
(cure RT + 140C/1hr)

MCC Summary of Results

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

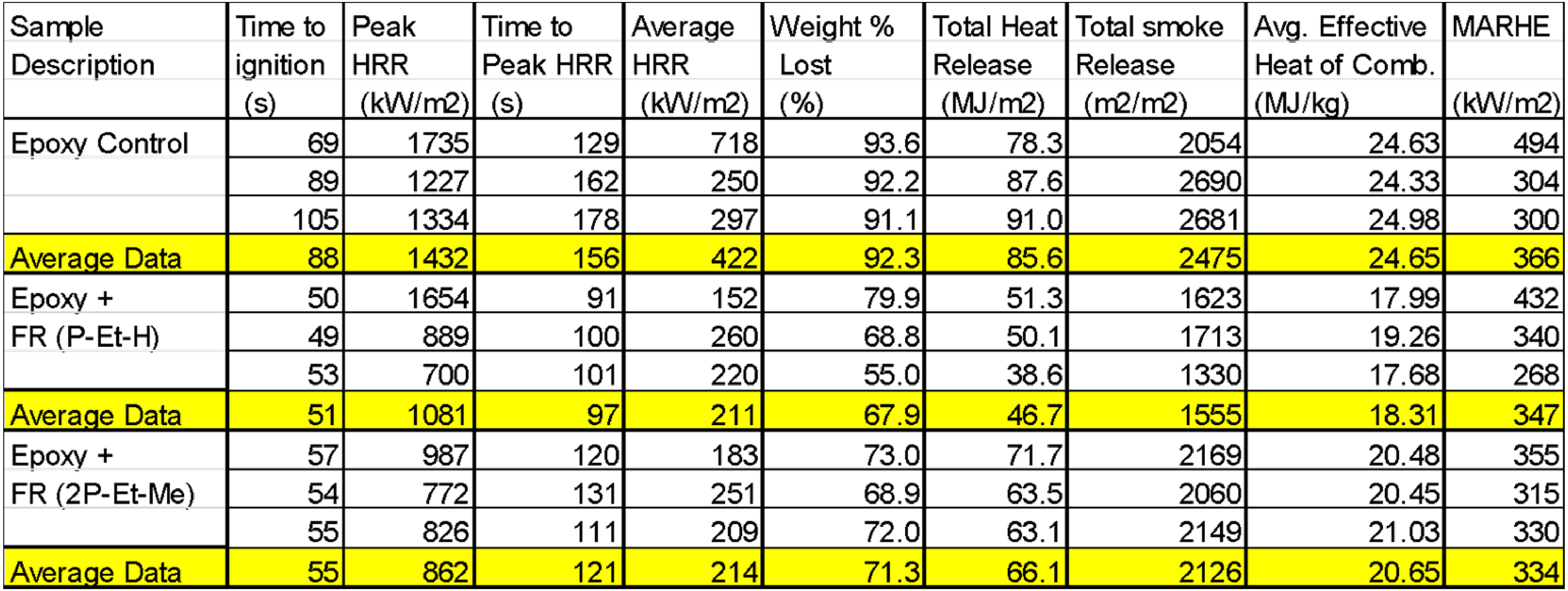

HRR Curve Overlay
Epoxy + Phosphorus Hydrazides


Phosphorus-Hydrazide
With Epoxy

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

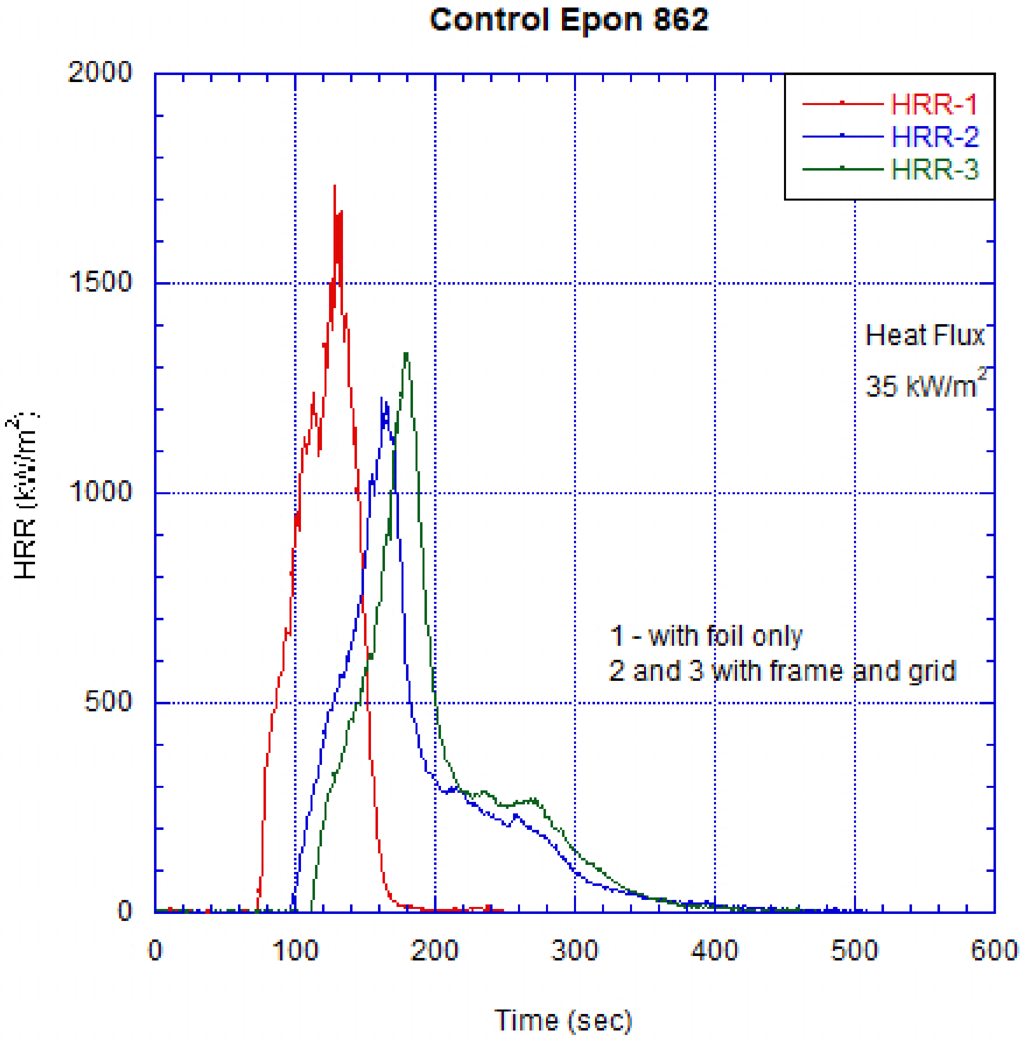


Sample Description	Time to ignition (s)	Peak HRR (kW/m2)	Time to Peak HRR (s)	Average HRR (kW/m2)	Weight % Lost (%)	Total Heat Release (MJ/m2)	Total smoke Release (m2/m2)	Avg. Effective Heat of Comb. (MJ/kg)	MARHE (kW/m2)
Epoxy Control	69	1735	129	718	93.6	78.3	2054	24.63	494
	89	1227	162	250	92.2	87.6	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 + FR (P-Et-H)	50	1654	91	152	79.9	51.3	1623	17.99	432
	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 + FR (2P-Et-Me)	57	987	120	183	73.0	71.7	2169	20.48	355
	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

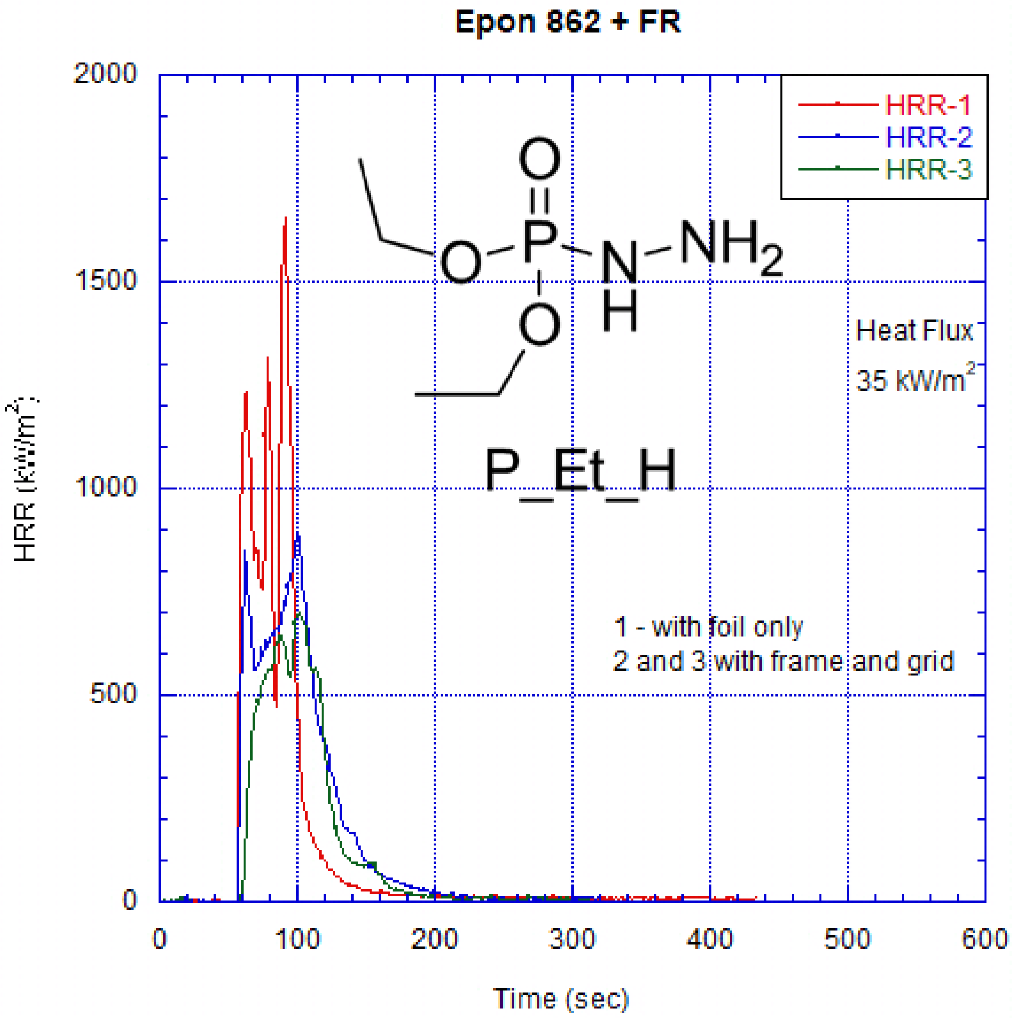
- Erratic results due to strong physical effects of burning



Control Epon 862

Heat Flux 35 kW/m^2

1 - with foil only
2 and 3 with frame and grid



Epon 862 + FR

P_Et_H

Heat Flux 35 kW/m^2

1 - with foil only
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Cone Calorimeter Results

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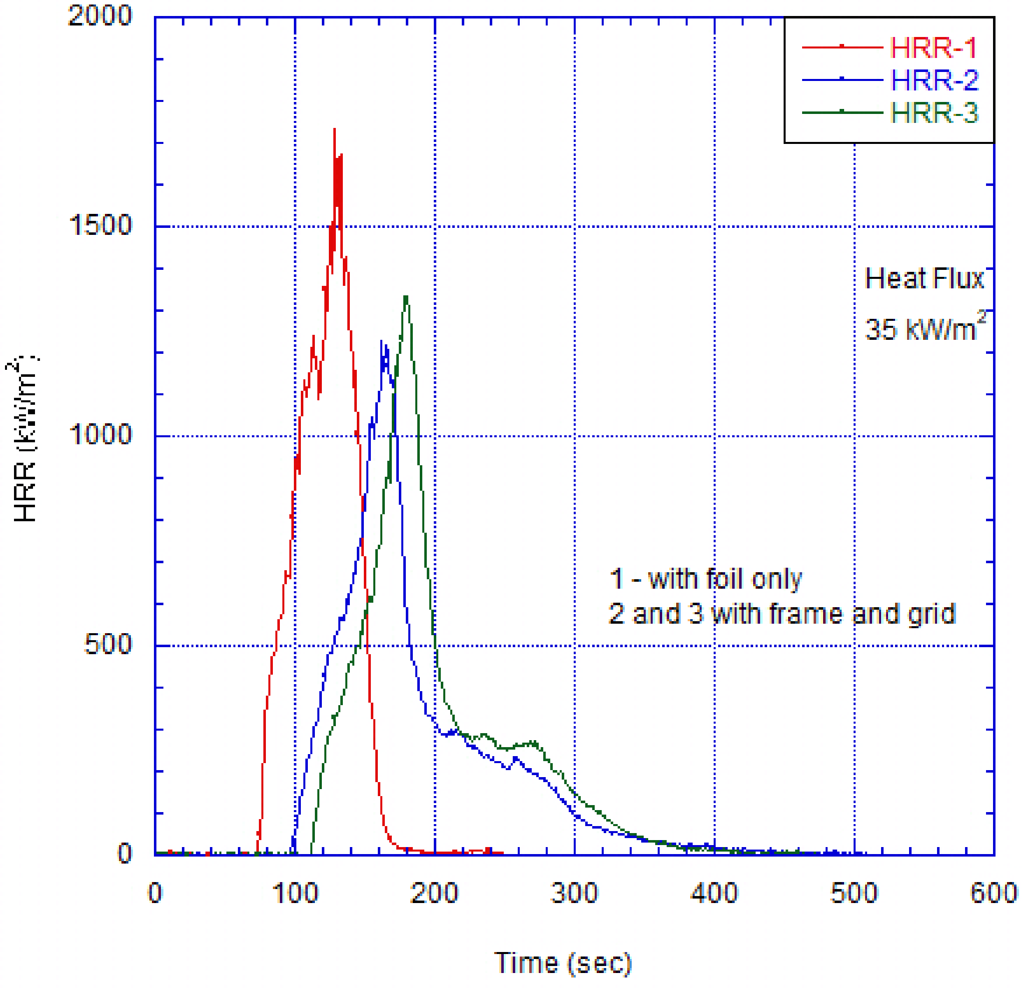
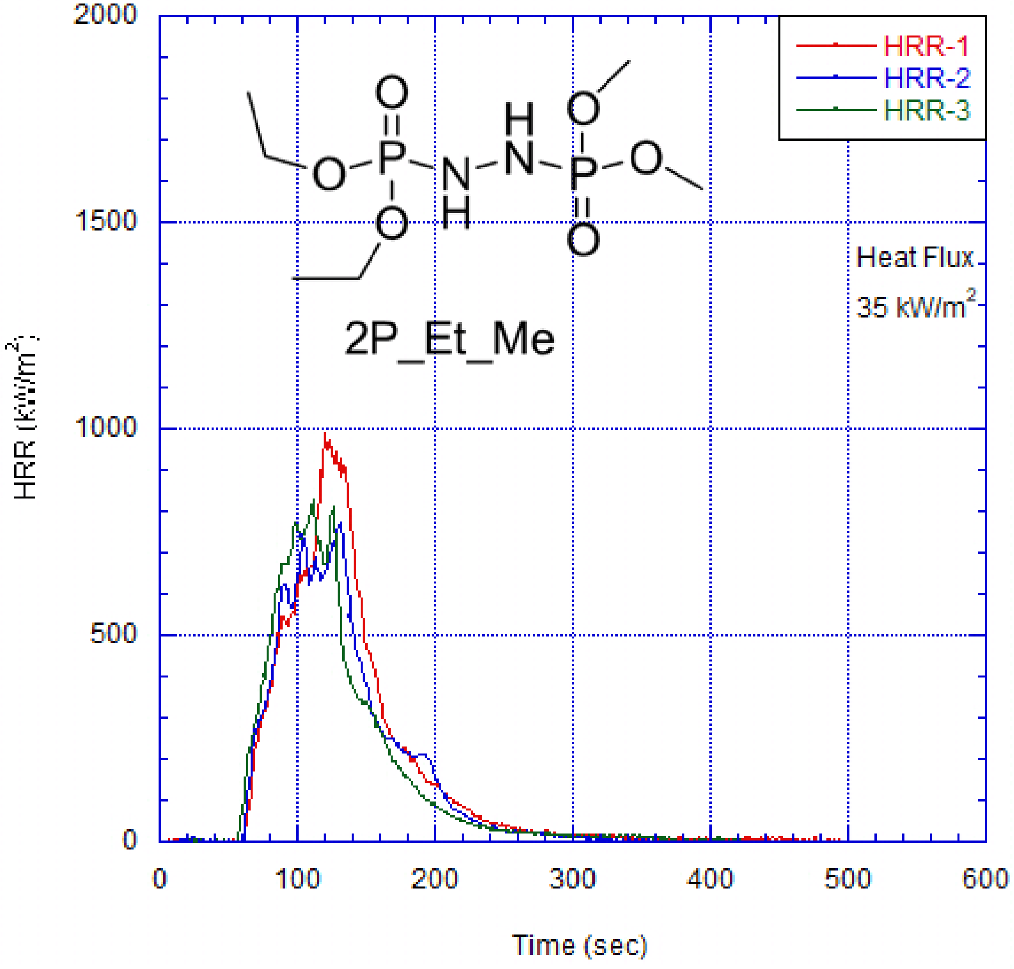


Heat Flux 35 kW/m^2

1 - with foil only
2 and 3 with frame and grid

Epon 862 + FR5



Heat Flux 35 kW/m^2

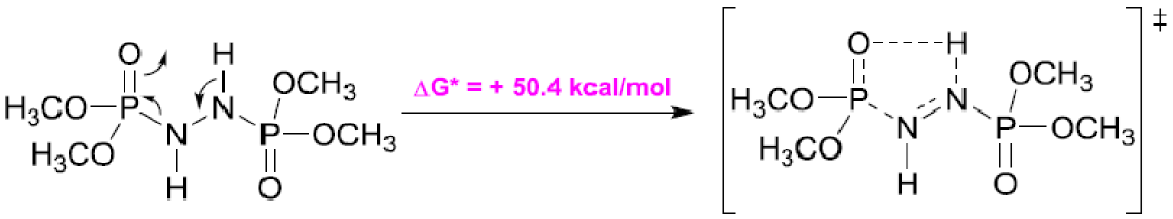
Cone Calorimeter Chars

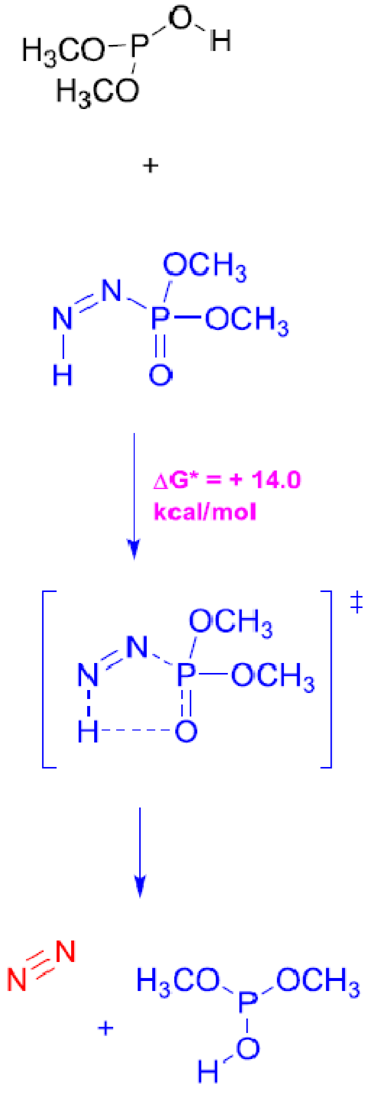
Control Sample

Epoxy + P-Et-H

Epoxy + 2P-Et-Me

Mechanism of Flame Retardancy





- 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.

Phosphorus Hydrazide Conclusions

- 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.

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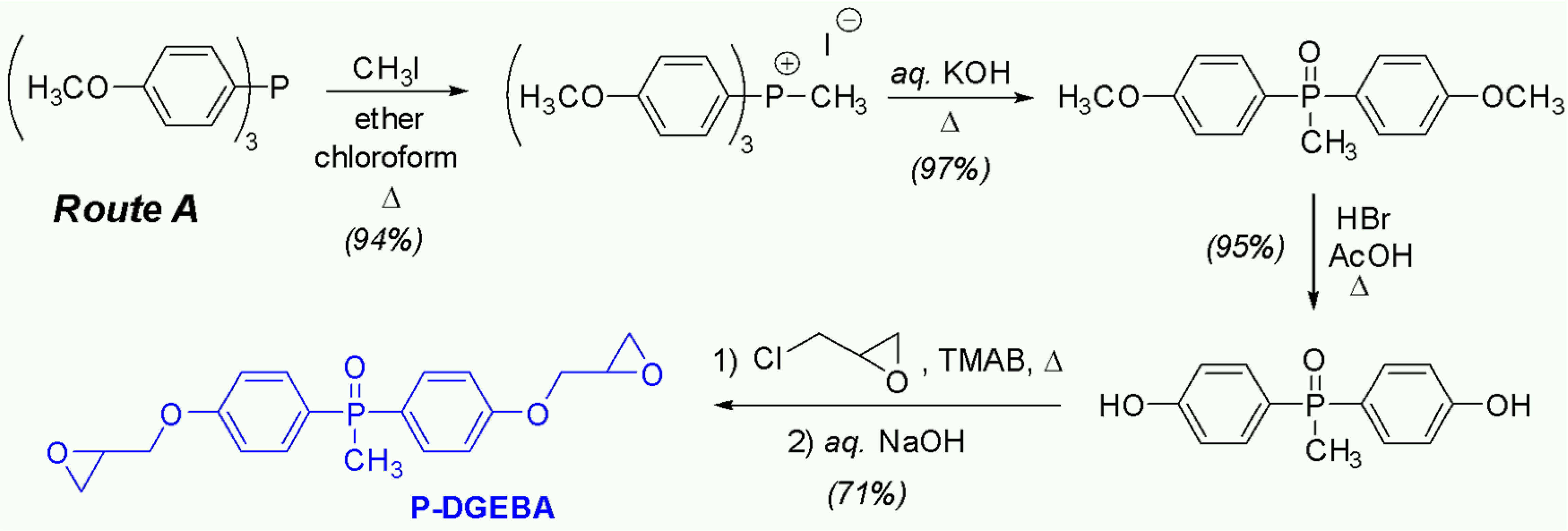
Phosphine Oxide Bisphenol A Epoxy (P-DGEBA)



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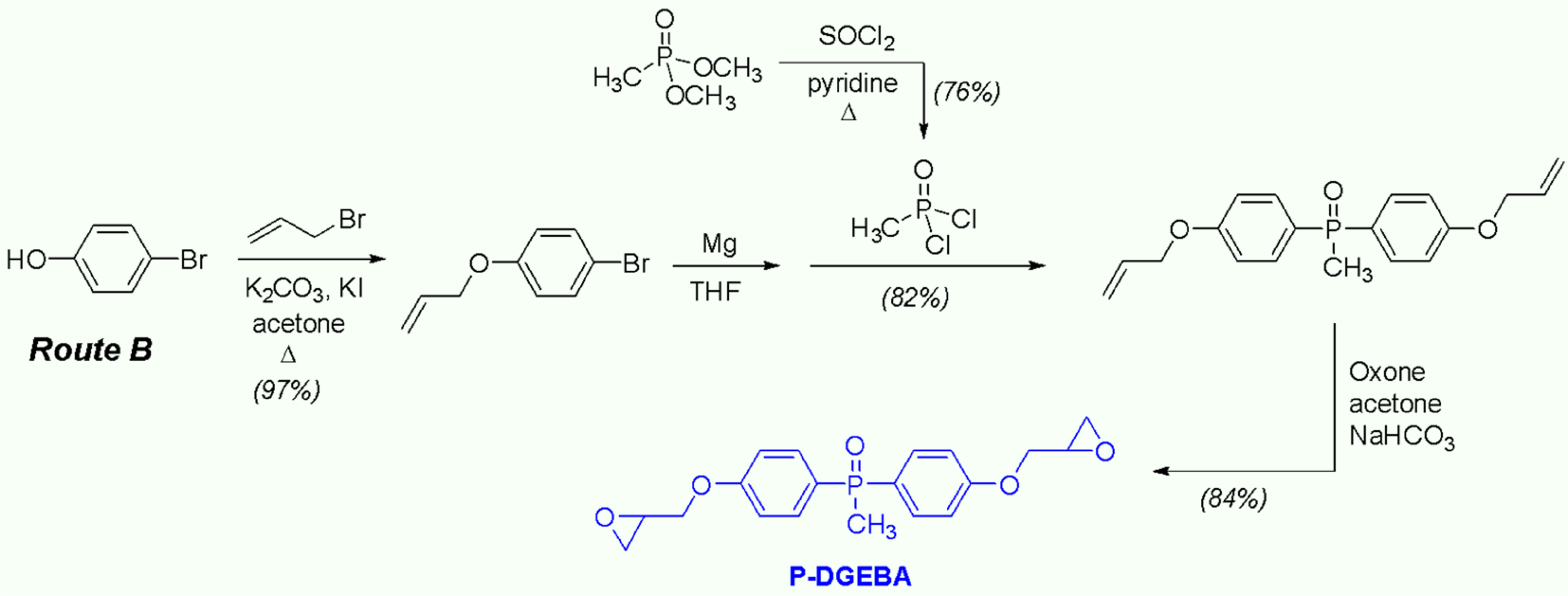
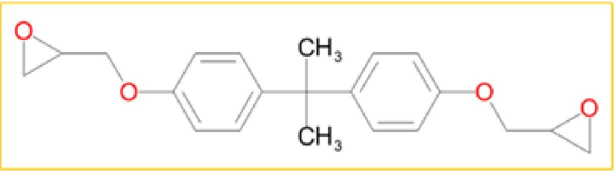
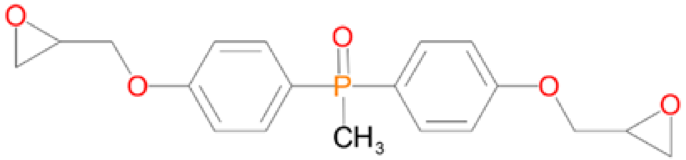


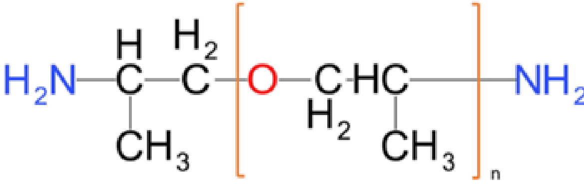
P-DGEBA Polymerization and Properties



A. Epoxy resin
EPON 825 (DGEBA) (liquid)



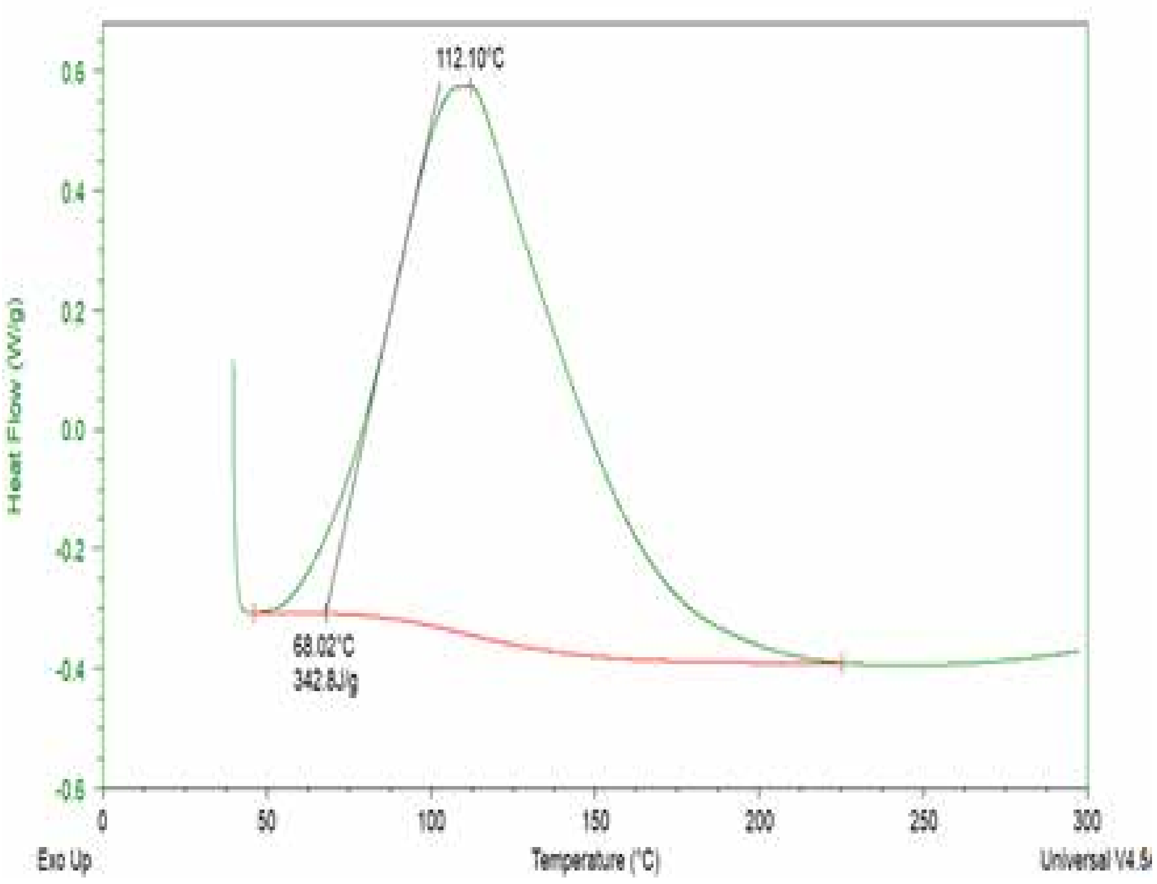
B. Flame Retardant (P-DGEBA)
Phosphorus-Diglycidyl Ether of Bisphenol A (Synthesized by UD Chemistry Dept. faculty)

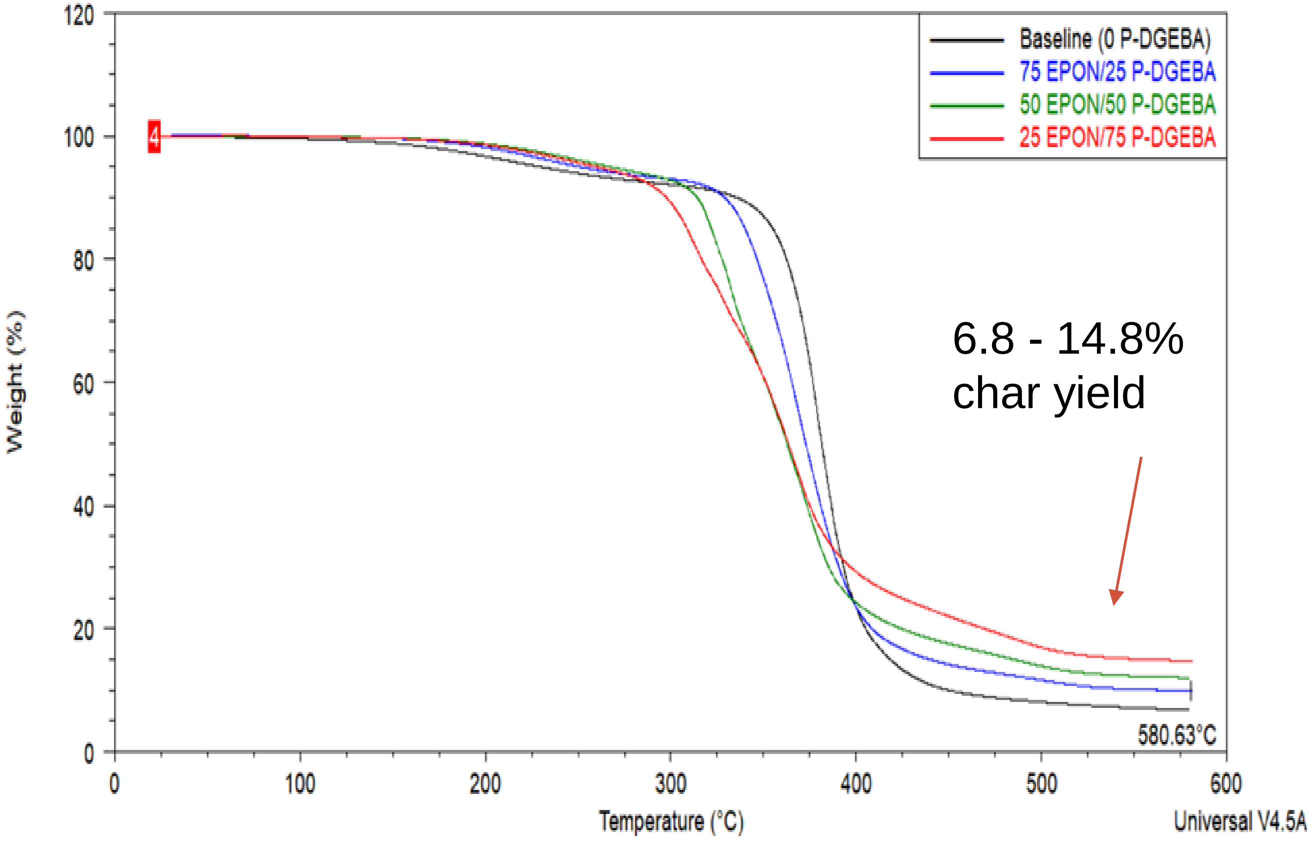


C. Curing Agent
Epikure 3274 (liquid)

- 4 blends produced:
  - 100 A / 0 B + C (at stoichiometric balance) → control
  - 75 A / 25 B + C (at stoichiometric balance)
  - 50 A / 50 B + C (at stoichiometric balance)
  - 25 A / 25 B + C (at stoichiometric balance)
- small samples (< 1g) mixed by hand to minimize usage
- DSC and TGA used to analyze

DSC and TGA results (resin blends)



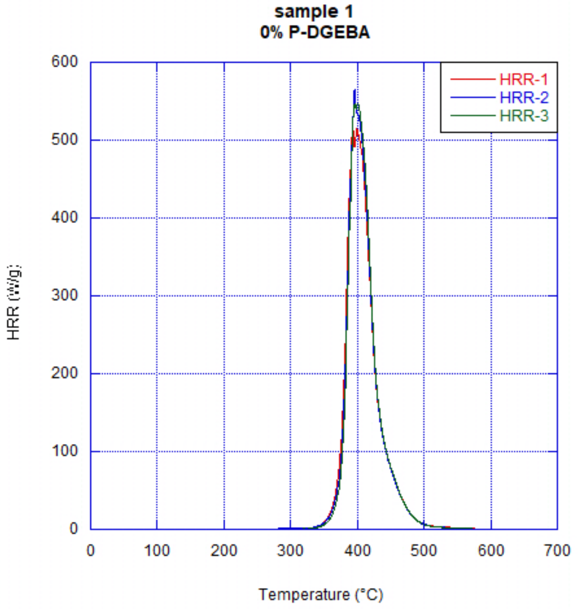


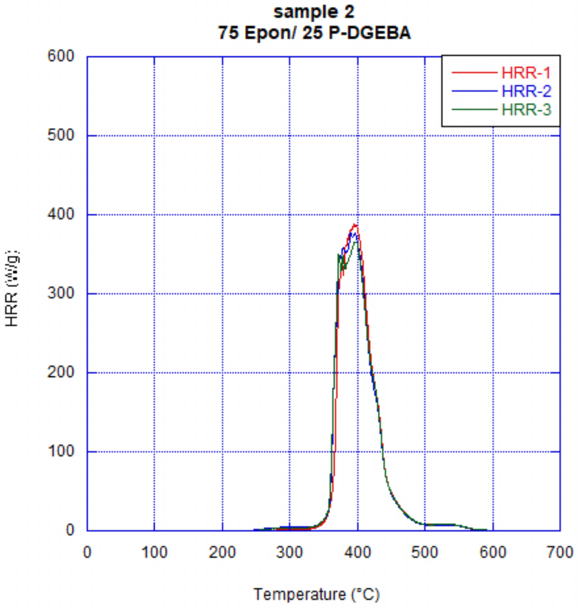
6.8 - 14.8%
char yield

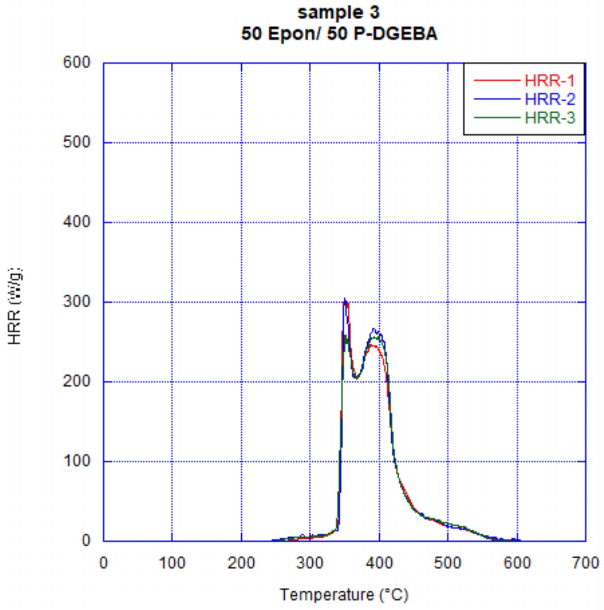
- Good cure characteristics at all ratios
- Tg slightly increased with increased P-DGEBA (68.5 to 76.1 °C)

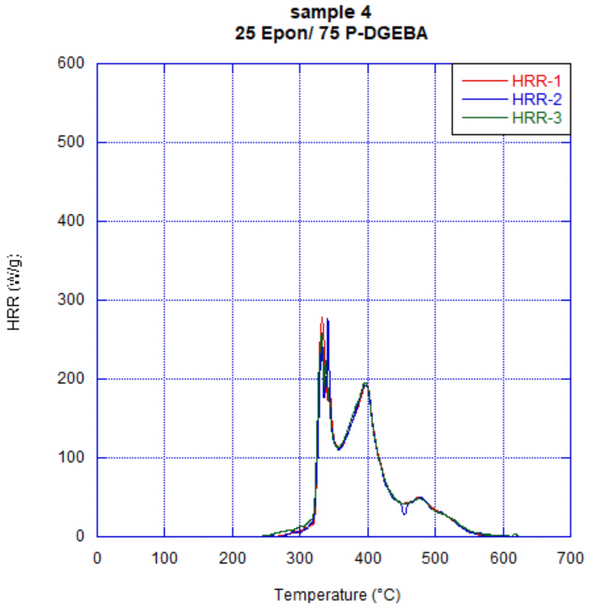
- Char yield increased with increased P-DGEBA
- 50/50 blend determined to be best candidate

P-DGEBA + Epoxy Heat Release - MCC


sample 1
0% P-DGEBA


sample 2
75 Epon/ 25 P-DGEBA


sample 3
50 Epon/ 50 P-DGEBA

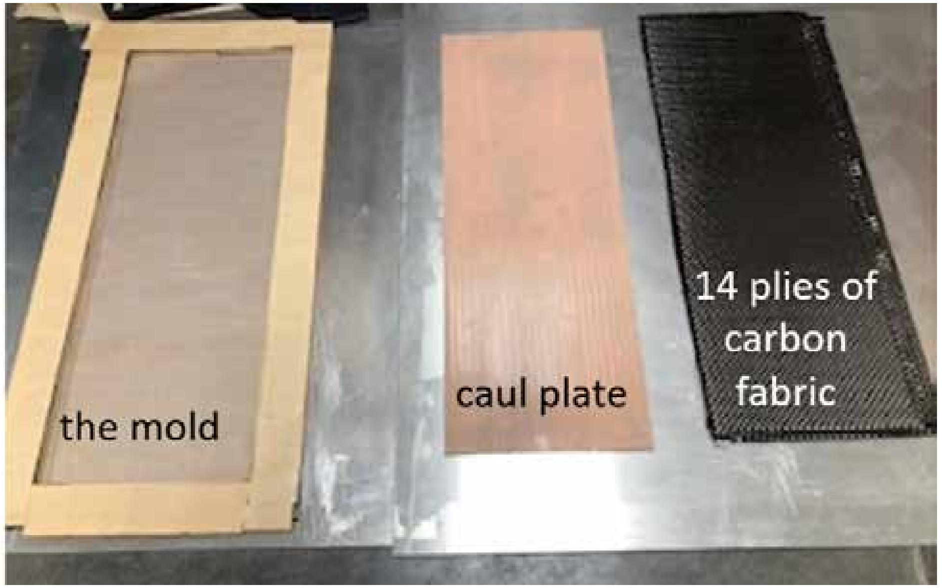

sample 4
25 Epon/ 75 P-DGEBA

Sample	Char Yield (%)	HRR Peak(s) Value (W/g)	HRR Peak(s) Temp(s) (°C)	Total HR (kJ/g)
sample 1	5.66	514	399	25.2
0% P-DGEBA	5.34	535	395	25.5
	5.30	547	401	25.3
sample 2	10.41	388	396	23.6
75 Epon/25 P-DGEBA	10.46	375	390	24.1
	10.74	365	396	24.0
sample 3	13.64	304, 246	351, 388	22.3
50 Epon/50 P-DGEBA	13.39	304, 260	350, 393	22.8
	13.18	258, 255	351, 393	22.6
sample 4	15.86	278, 192, 49	332, 398, 475	20.5
25 Epon/75 P-DGEBA	15.75	277, 192, 50	332, 398, 477	20.2
	16.30	269, 196, 48	332, 397, 477	21.1
PS std 4-9-21	0.06	1046	444	39.1
	0.03	1057	444	39.3
	0.05	1075	445	39.2

- Increasing P-DGEBA use does increase char yield, lowers heat release, changes decomposition pathways.

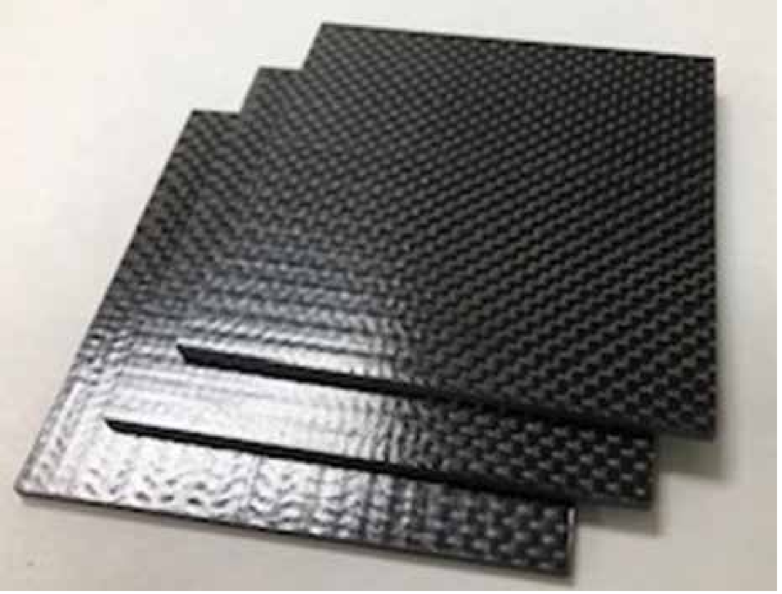
P-DGEBA + Carbon Fiber Composites

- Goal: produce aerospace quality composites for cone calorimeter testing
    - limited supply of P-DGEBA available < 23 g !
- Formulation: 50/50 P-DGEBA / EPON 825 (+ curing agent) → over 60 g of resin
- Process: carbon fabric wet-layup, autoclave curing

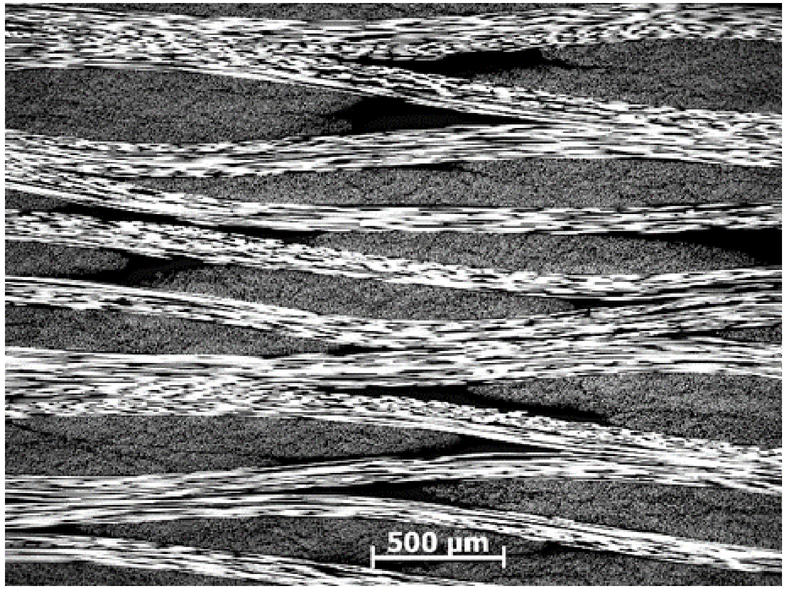


Flacktek mixer:
prepare blend

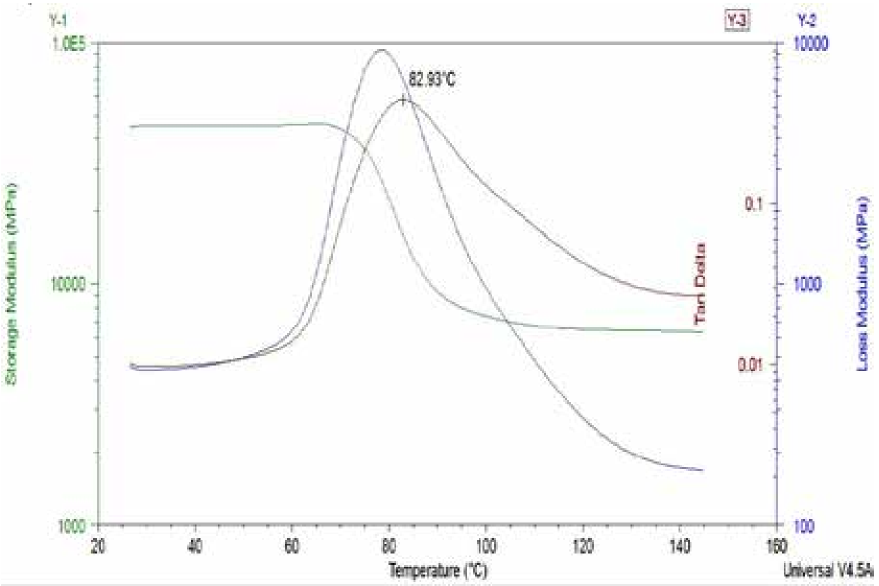
Composite Panels



3.5 in x. 3.5 in.



well consolidated
Vf ~ 0.5



DMA results, Tg:

Control	72 °C
P-DGEBA	82 °C

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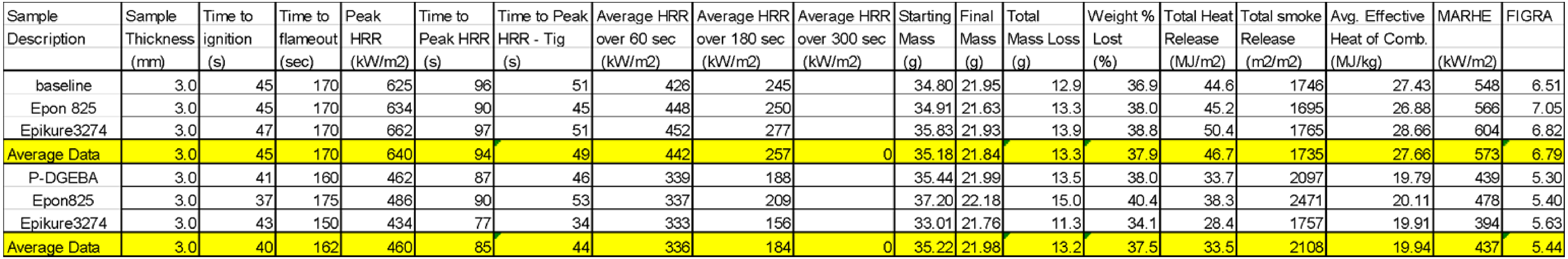
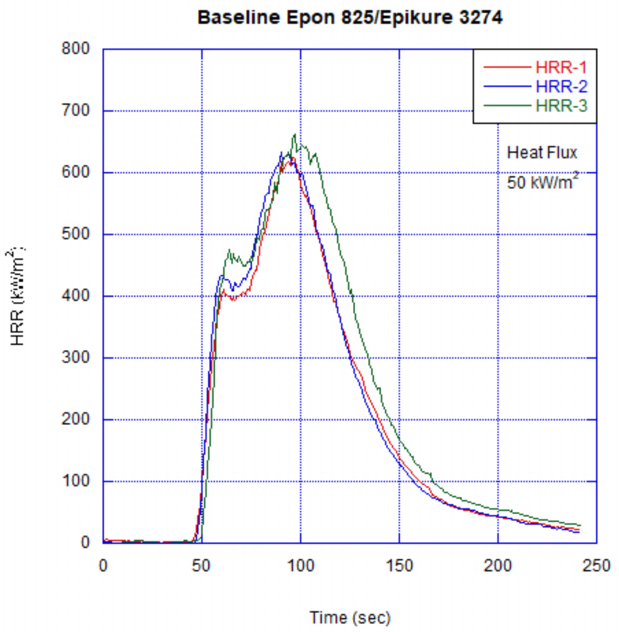
P-DGEBA + Carbon Fiber Epoxy Heat Release – Cone Calorimeter

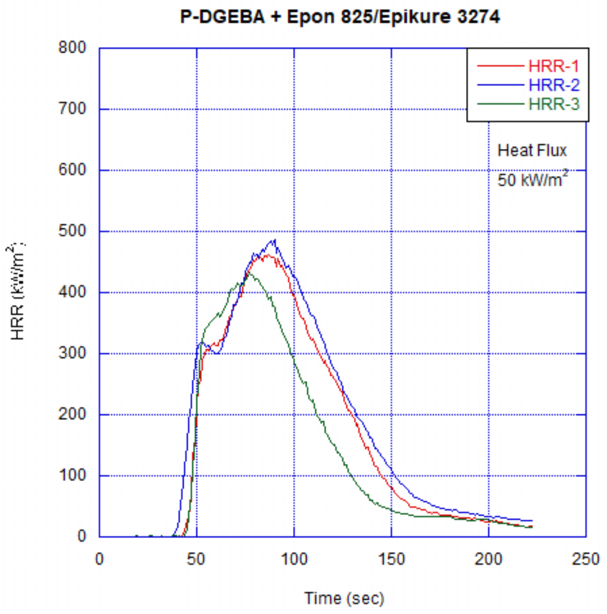


Sample Description	Sample Thickness (mm)	Time to ignition (s)	Time to flameout (sec)	Peak HRR (kW/m2)	Time to Peak HRR (s)	Time to Peak HRR - Tig (s)	Average HRR over 60 sec (kW/m2)	Average HRR over 180 sec (kW/m2)	Average HRR over 300 sec (kW/m2)	Starting Mass (g)	Final Mass (g)	Total Mass Loss (g)	Weight % Lost (%)	Total Heat Release (MJ/m2)	Total smoke Release (m2/m2)	Avg. Effective Heat of Comb. (MJ/kg)	MARHE (kW/m2)	FIGRA
baseline	3.0	45	170	625	96	51	426	245		34.80	21.95	12.9	36.9	44.6	1746	27.43	548	6.51
Epon 825	3.0	45	170	634	90	45	448	250		34.91	21.63	13.3	38.0	45.2	1695	26.88	566	7.05
Epikure3274	3.0	47	170	662	97	51	452	277		35.83	21.93	13.9	38.8	50.4	1765	28.66	604	6.82
Average Data	3.0	45	170	640	94	49	442	257	0	35.18	21.84	13.3	37.9	46.7	1735	27.66	573	6.79
P-DGEBA	3.0	41	160	462	87	46	339	188		35.44	21.99	13.5	38.0	33.7	2097	19.79	439	5.30
Epon825	3.0	37	175	486	90	53	337	209		37.20	22.18	15.0	40.4	38.3	2471	20.11	478	5.40
Epikure3274	3.0	43	150	434	77	34	333	156		33.01	21.76	11.3	34.1	28.4	1757	19.91	394	5.63
Average Data	3.0	40	162	460	85	44	336	184	0	35.22	21.98	13.2	37.5	33.5	2108	19.94	437	5.44



Baseline Epon 825/Epikure 3274

- Minor reductions in heat release noted.
- Flame retardant effect appears to be solely vapor phase (no char formation)
- Char formation effect seen in MCC not seen in cone calorimeter testing.
- Carbon fibers may be interfering with char formation effect, or there is not enough “residence” time in cone calorimeter testing for stable chars to form.



P-DGEBA + Epon 825/Epikure 3274

Outline

- Review of Epoxy + Carbon Fiber Systems in Aircraft and Fire Hazards
  - Fire Hazards & Emissions from Epoxy + Carbon Fiber Composites
  - Commercially available reactive flame retardants for epoxy

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

- Phosphine Oxide “Bisphenol A” Epoxy
  - Synthesis Details
  - Heat Release Reduction Results

- Conclusions & Acknowledgements

Conclusions

- Reactive FRs for epoxy have been documented in the open literature, but very few have been commercialized.
  - Little to no studies of these reactive materials on aerospace grade carbon fiber composites.
- Results in this presentation represent basic research (TRL1) being advanced to higher TRL.
  - These chemistries would not be used by themselves, but would be combined with other fire protection schemes to improve properties and fire performance.
  - Example: P-DGEBA for vapor phase effect + char formation FR + co-bonded/cured fire protection barrier.
- More research needed, as well as funding
  - Very little to no research for aerospace-grade fire safe epoxy composites in US academia.

Acknowledgements

- UDRI/UD
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  - Dr. Richard E. Lyon – technical discussions on aircraft fire hazards.

Questions?