Polyphosphonate Flame Retardants in Aviation Applications

October 24-27, 2016

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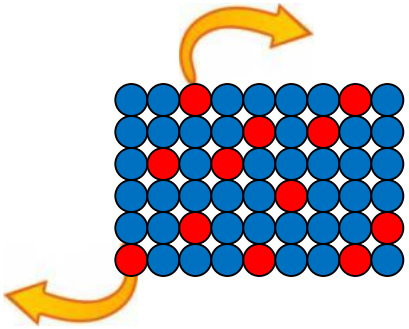
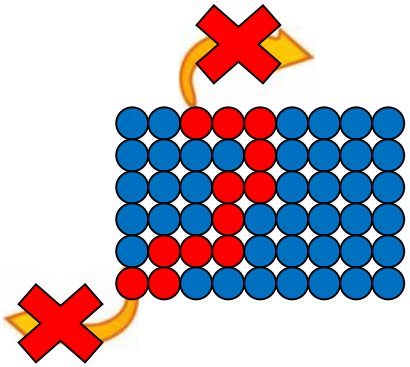
NOFIA Polyphosphonates, A Unique FR Solution



Plastic with current FR additives

Small molecules can end up in environment



Plastic with NOFIA FR

Large molecules trapped in plastic

- Polymer:
  - Permanent and will not migrate out
  - Minimal impact on host plastic properties
  - Possible to use plastic processing methods
- Non-halogen flame retardant
- Extreme FR properties
- High melt flow
- Transparent
- Range of toughness

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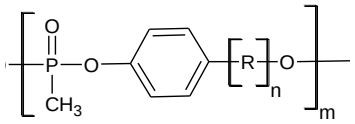
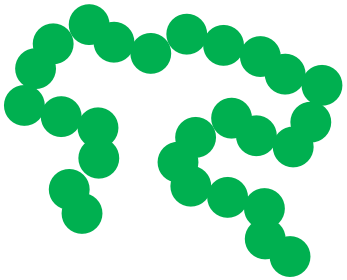
FRX POLYMERS' Products - Characteristics

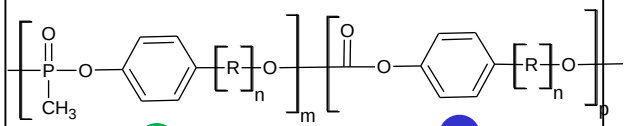
Nofia HM1100

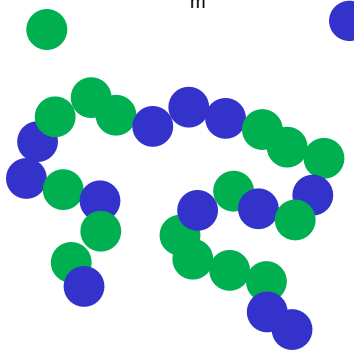




- Polyphosphonate (P ~ 11wt%)
- High molecular weight (40-100,000 g/mole, PS)
- Tg ~ 100-105°C
- Plastic pellets
- Typically used as blend component in plastics

Nofia COPOs

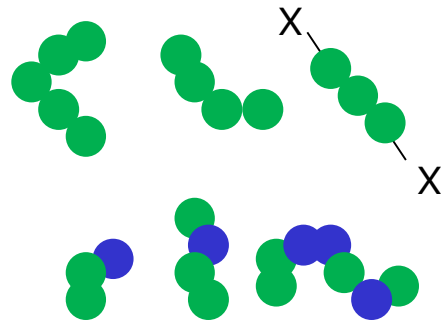




- Polyphosphonate-co-carbonate (P ~ 3-7 wt%)
- High molecular weight (40-100,000 g/mole, PS)
- Tg ~ 120-135°C
- Plastic pellets
- Used as stand alone polymer or blend component in plastics

Nofia Oligomers

-X = different functionalities



- Phosphonate or phosphonate-co-carbonate
- Low molecular weight (1,000 – 6,000 g/mole)
- 5 - 90 mg KOH/g
- Solid white material
- Used as additive or as reactive ingredient in thermoset plastics

Current Markets/Polymer systems

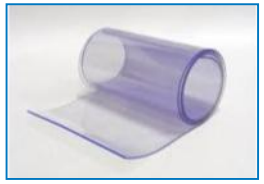
Nofia HM1100

Polymer System
- Polyesters (PET, PBT, PTT)
- TPUs

Markets
- Electrical Equipment
- Consumer Electronics
- Fibers
- Building and Construction

Applications
- Connectors
- Commercial carpet
- Specialty textiles
- TPU films, sheet



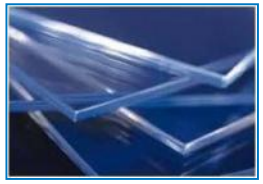
Nofia COPOs

Polymer System
- PC, Polyesters
- PC blends (PC/ABS)

Markets
- Consumer Electronics
- Lighting
- Building and Construction
- **Transportation (aviation)**

Applications
- Housings for electronic equipment
- Light diffusers
- Transparent sheets



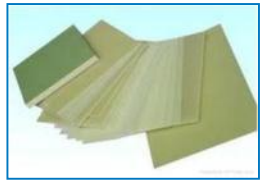
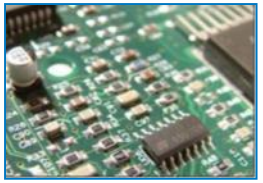



Nofia Oligomers

Polymer System
- Epoxy resins
- Unsaturated polyesters

Markets
- Electronics
- Building and Construction
- **Transportation (aviation)**

Applications
- Printed Circuit boards
- Composites
- Decorative laminates and panels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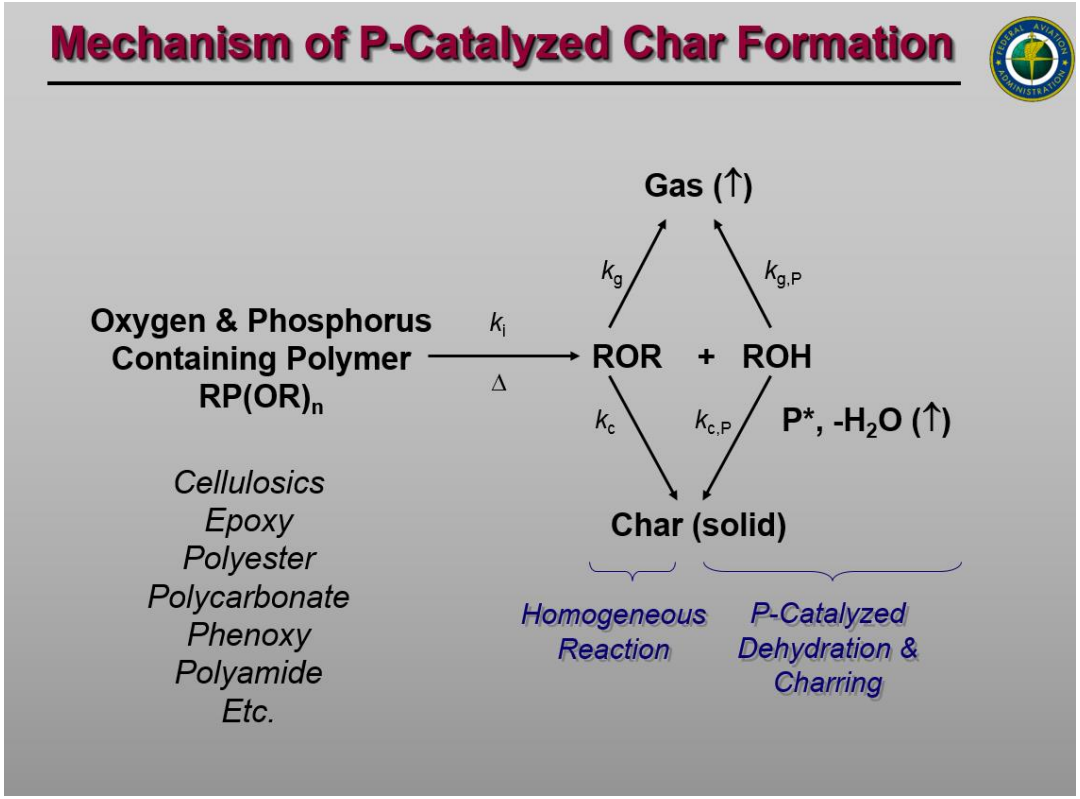
Mechanism of Phosphorus Flame Retardants

- Phosphorus is an element that reduces flammability of certain polymers.
  - Phosphorus can act in the gas phase as a flame inhibitor.
  - Phosphorus can act in the condensed phase as a char promoter.



Gas Phase Activity

R_3P (↑)	Phosphines
R_3PO (↑)	Phosphine Oxides
R_3PO_3	Phosphites
R_3PO_3	Phosphonates
R_3PO_4	Phosphates

Condensed Phase Activity

Richard Lyon, Federal Aviation Administration, 25th Annual BCC Conference on Recent Advances in Flame Retardancy of Polymeric Materials, Stamford, CT, May 19-21, 2014

Aviation Applications

Thermplastics

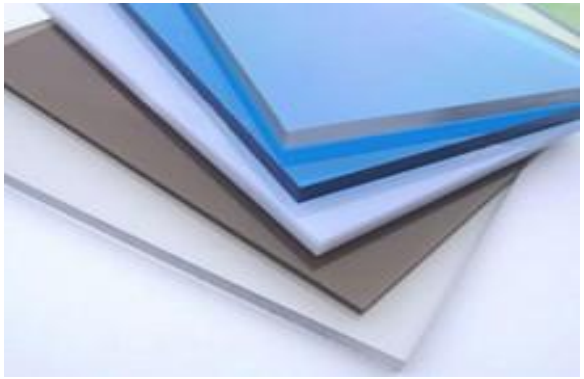
Polyphosphonates in Thermoplastic Applications

Aircraft Interior Parts

Benefits

- Low heat release
- Low smoke density
- Reduced flame spread
- Good impact resistance
- Transparent
- Processable – Film, Sheet

Opaque / Transparent Sheets: Extruded



Thermoformed Products

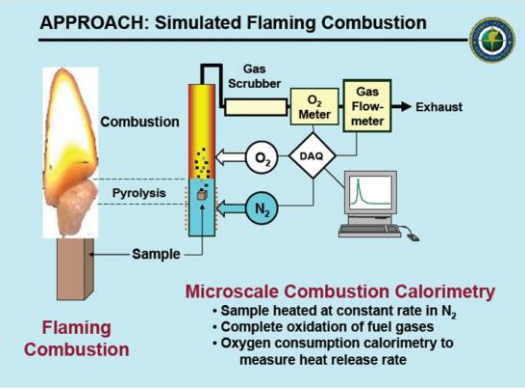
Evaluation of FR Properties

- Heat Release Properties
- Vertical Burn
- Flame Spread
- Smoke density
- Smoke toxicity

Testing Heat Release Properties

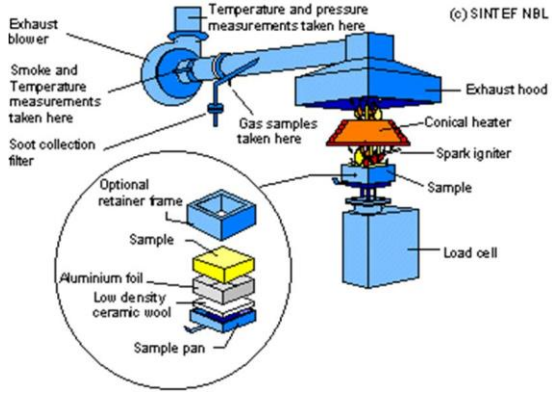
Small Scale

- Pyrolysis Combustion Flow Calorimeter (PCFC), also known as Micro Combustion Calorimetry (MCC)
- ASTM D7309
- Material Needed: Few mg
- Output:
  - Heat of Combustion or Fire Load
  - Ignition Temperature
  - Heat Release Rate
  - Heat Release Capacity: Fundamental Material Property



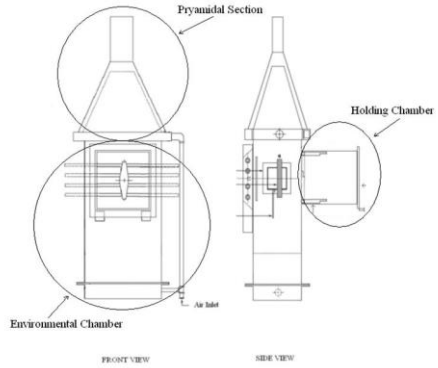
Lab Scale Up

- Cone Calorimeter
- ISO 5660 / ASTM E1354
- Material Needed: 100x100mm plaque
- Output:
  - Rate of heat release
  - Time to ignition
  - Critical ignition flux
  - Mass loss rate
  - Smoke release rate
  - Effective heat of combustion
  - CO2, CO release

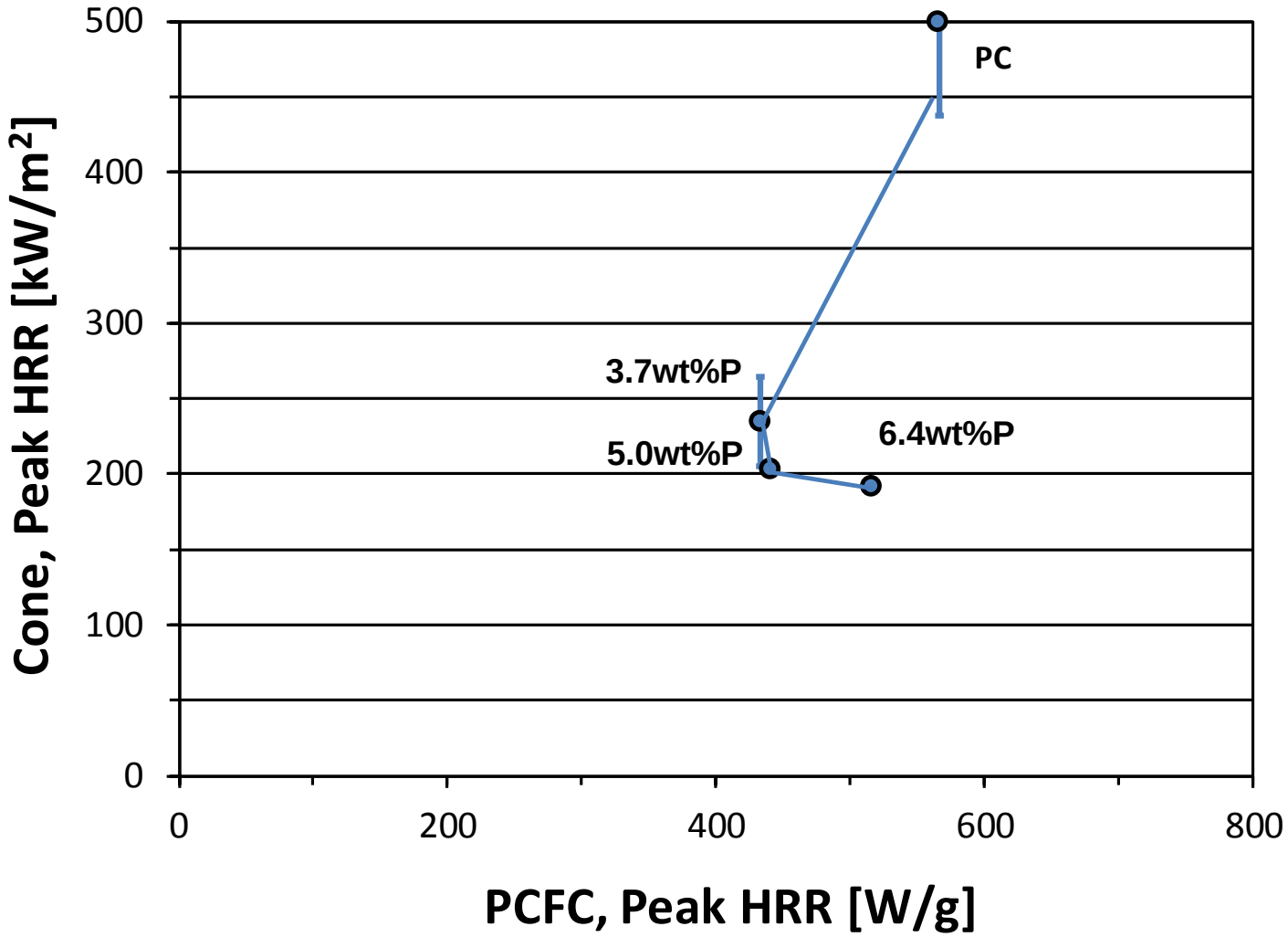


Pilot Plant

- OSU and Smoke Density
- FAR 25.853 / ASTM E906 and ASTM E662
- Material Needed: 150x150mm plaque
- Output:
  - Heat Release (2 min total)
  - Heat Release Rate (peak)
  - Heat Flux Density
  - Smoke Density

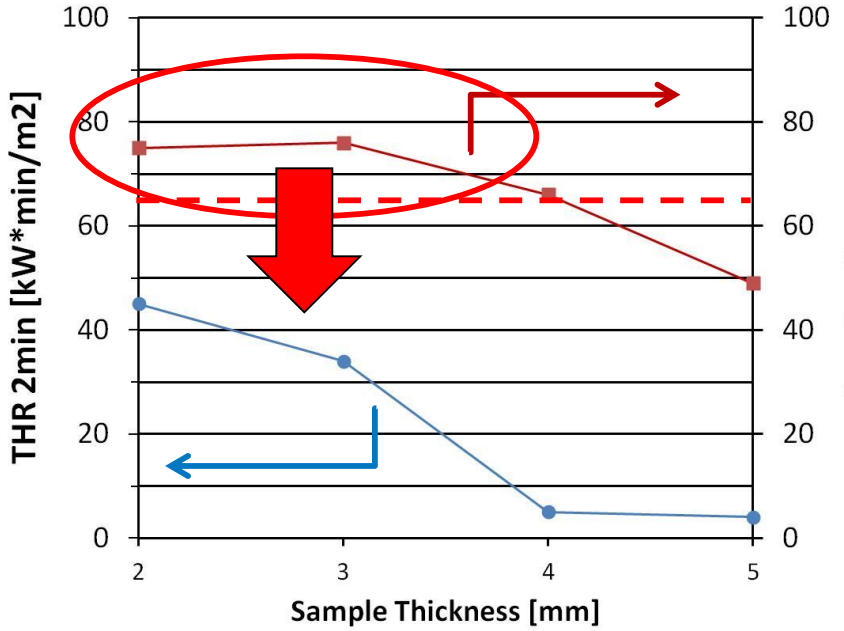


Effect of P-Content on Heat Release Properties

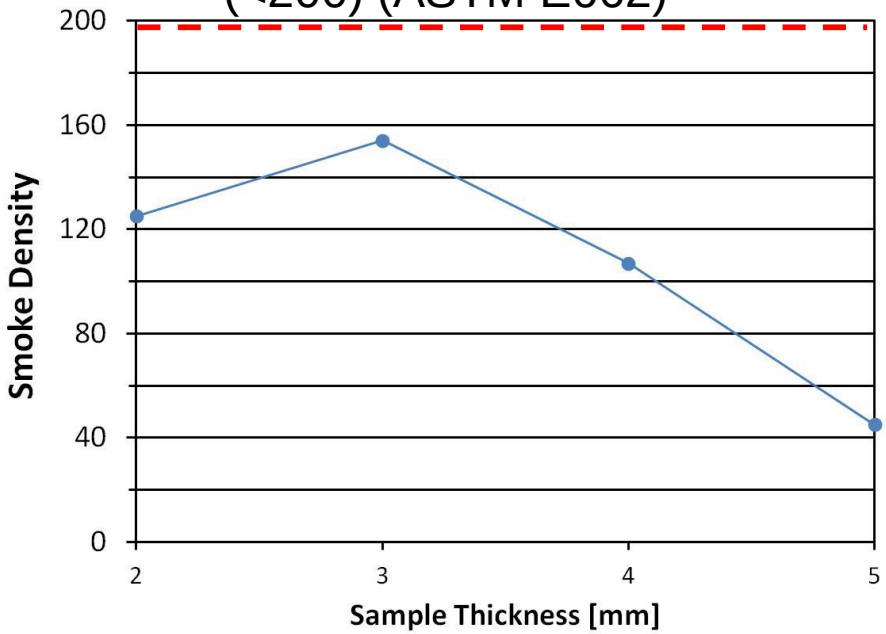


OSU and Smoke Data for 3.5wt% P

OSU (FAR 25.853)

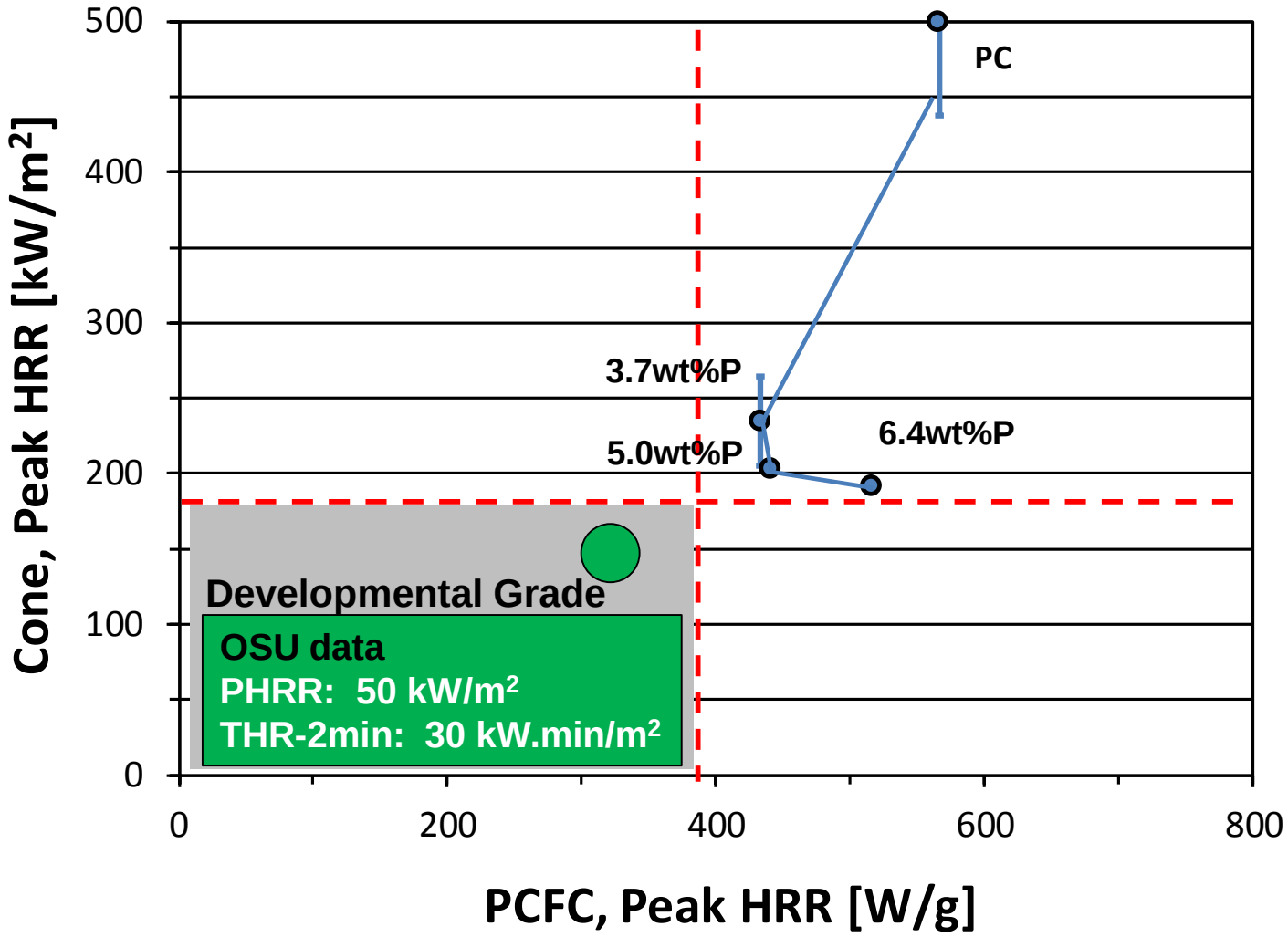


Smoke Density ABD0031 (<200) (ASTM E662)



- Polyphosphonate-co-carbonate has good total heat release and smoke properties that are within spec for OSU (FAR 25.853)
- About ~50% lower Peak Heat Release Rate (PHRR) than PC (150-200 kW/m^2) but not good enough to pass the PHRR specification of 65 kW/m^2
- **<u>Future goal:</u>** Obtain additional improvement (~>12.5 - 25%) in PHRR

Product Optimization



Vertical Burn Test: FAR 25.853 A/B: Nofia Grades

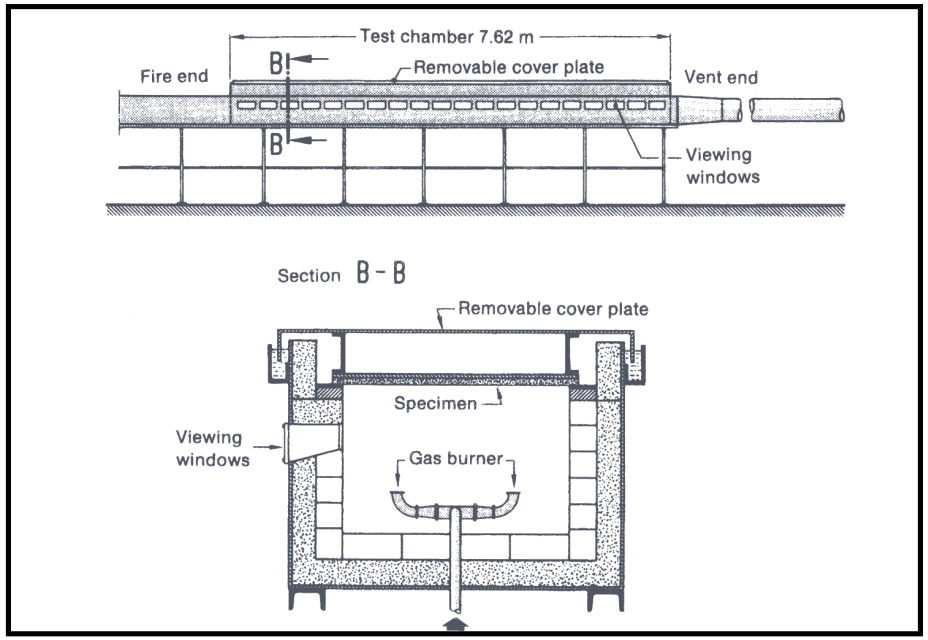
- Test Facility: TTF Aerospace LLC (FAA approved Test Lab), Auburn, WA
- Average of 3 plaques of 3" X 12" (7.5x30cm) at 30 mil (0.76mm)

		A: 60Sec-Vert				B: 12 Sec-Vert			
Nofia Grade	P [wt%]	Burn length [inch]	Exting t [s]	Drip ext t [s]	Smoke	Burn length [inch]	Exting t [s]	Drip ext t [s]	Smoke
EX2111	2.0	5.1±0.3	0.3±0.6	6±1**	Moderate	2.5±0.3	11±3	0.7±0.6**	Moderate
CO3000	4.0	6.5±0.5	0	1±2**	Moderate	2.1±0.3	0.3±0.6	0*	Slight
CO4000	5.0	5.0±0.3	0	0**	Moderate	-	-	-	-

* = Single drip
** = Multiple drips with extinguishing time

- Class A when tested according FAR 25.853 when P ~> 4.5 wt%
- At 2-3.5wt% of P, PC blends / copolyphosphonates (EX2111) obtain class B in the FAR 25.853

Flame Spread: ASTM E 84-15 (Steiner Tunnel Test)



Classification for Interior Finishes	Flame Spread Index	Smoke Developed Index
Class A:	0 – 25	0 – 450
Class B:	26 – 75	0 – 450
Class C:	76 – 200	0 – 450

ASTM E84 equivalent to
- NFPA 225
- UL 723

Flame Spread: ASTM E 84 -15 Data*

- Samples: 0.8mm and 1.6mm sheets
- Sheets are supported with ¼” diameter steel rods spaced 24 inches on center and 2” hexagonal wire mesh

SAMPLE	%P	Thickness [mm]	Flame Spread Index	Smoke Developed Index	Melting / Dripping	Melting Distance	CLASS
Nofia CO3000	4.0	0.8	5	170	Yes	24’	A
Nofia CO4000	5.0	0.8	5	185	Yes	22’	A
Nofia CO4000	5.0	1.6	5	300	Yes	24’	A

* Artificial support due to melting/dripping of thermoplastic may interfere with test, additional testing to validate FSI results may be required

Thermoplastic Polyurethane (TPU) Applications

Aircraft Interior Parts

Benefits

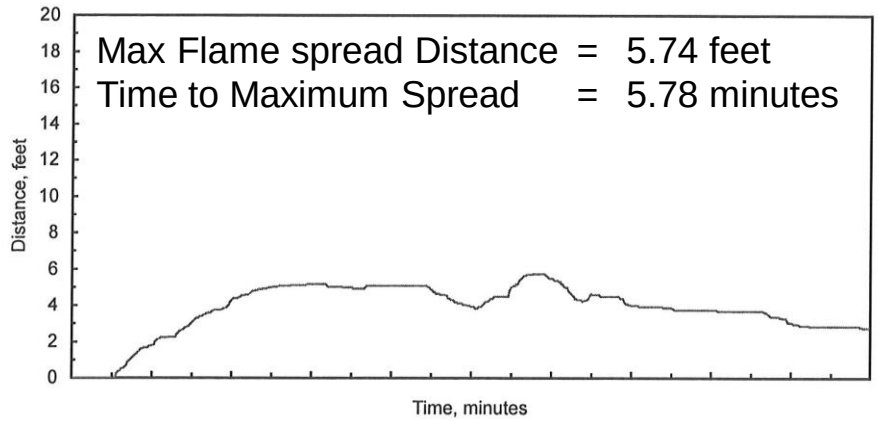
- Low heat release
- Reduced flame spread
- Low smoke
- Melt processable
- Halogen free alternative to existing materials

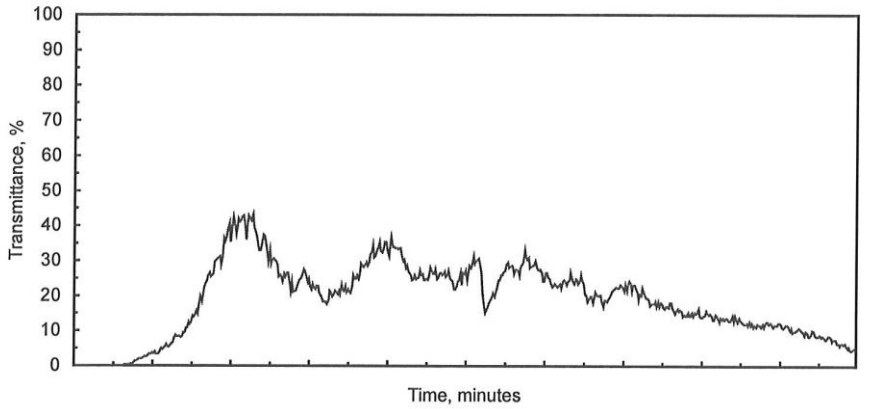
Non-textile Floor Coverings

Aircraft Seats

Polyphosphonates in TPU Applications

Flame Spread Test ASTM E 84 - 10b		Test Specimen		
		Fiber-Reinforced Cement Board, Grade II	Red Oak Flooring	TPU w/ HM1100 (0.7mm)
ASTM E84	Classification			
Flame spread Index (Is)	A: 0-25 B: 26-75 C: 76-200	0	100	24
Smoke Developed Index	A: 0-450 B: 0-450 C: 0-450	0	100	189 **Class A**





Aviation Applications

Thermosets

Polyphosphonates in Thermoset Applications

Composites

Thermoset Prepregs

Epoxy

Phenolic

Cyanate-Ester

Benzoxazines

Reinforcements

Carbon, Aramid and Glass fiber

Benefits

- Excellent flame retardancy
- High heat resistance
- Improved mechanical strength
- Improved adhesion to glass fiber
- Low dielectric properties (Dk/Df)

Wall and ceiling panels, cabin dividers, galleys

Benefits of Polyphosphonates in:

Epoxy-based systems

- Highly soluble in epoxy resins
- Dual purpose as **flame retardant** and **hardener** for epoxy resins
- Multi-functional reactivity with epoxy resulting in high crosslink density
- Strengthens adhesion to glass fabric used in composites
- Maintains Transparency

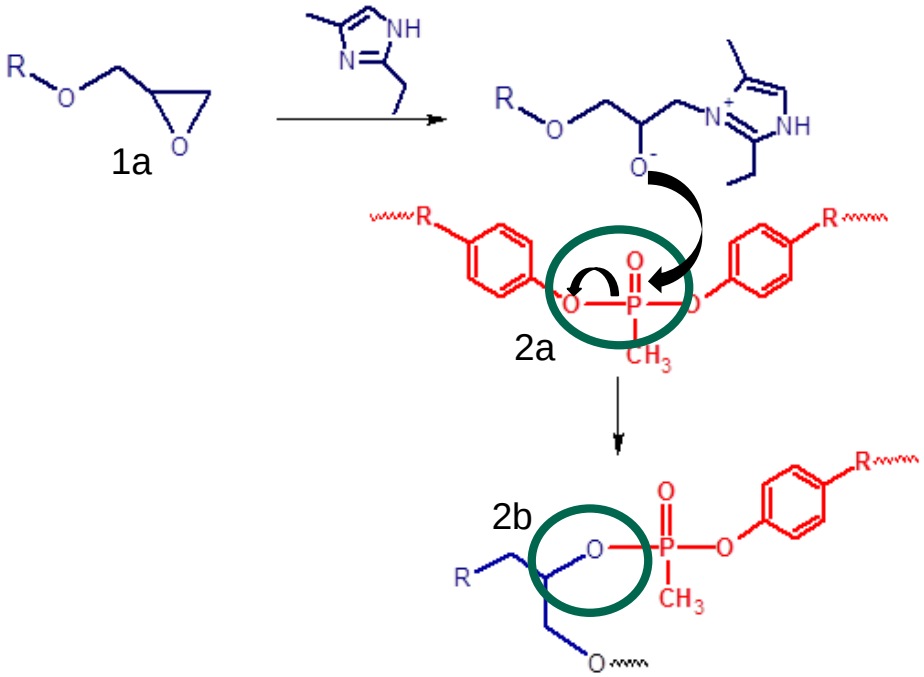
Phenolic prepregs

- Good compatibility with phenolic resins
- Reduces smoke

Phosphonates Oligomers: Hardener for Epoxy

Monitor Curing Reaction with FTIR

Starting Formulation		Upon Reaction
1a. Epoxy ring (916 cm^{-1})	→	1b. Loss of epoxy ring peak
2a. P-O-Ar (930 cm^{-1}) Ar = aromatic	→	2b. P-O-CHR (985, 1050 cm^{-1}) CHR = aliphatic



FTIR Bruker Tensor 27

Attenuated Total Reflectance Mode (ATR)

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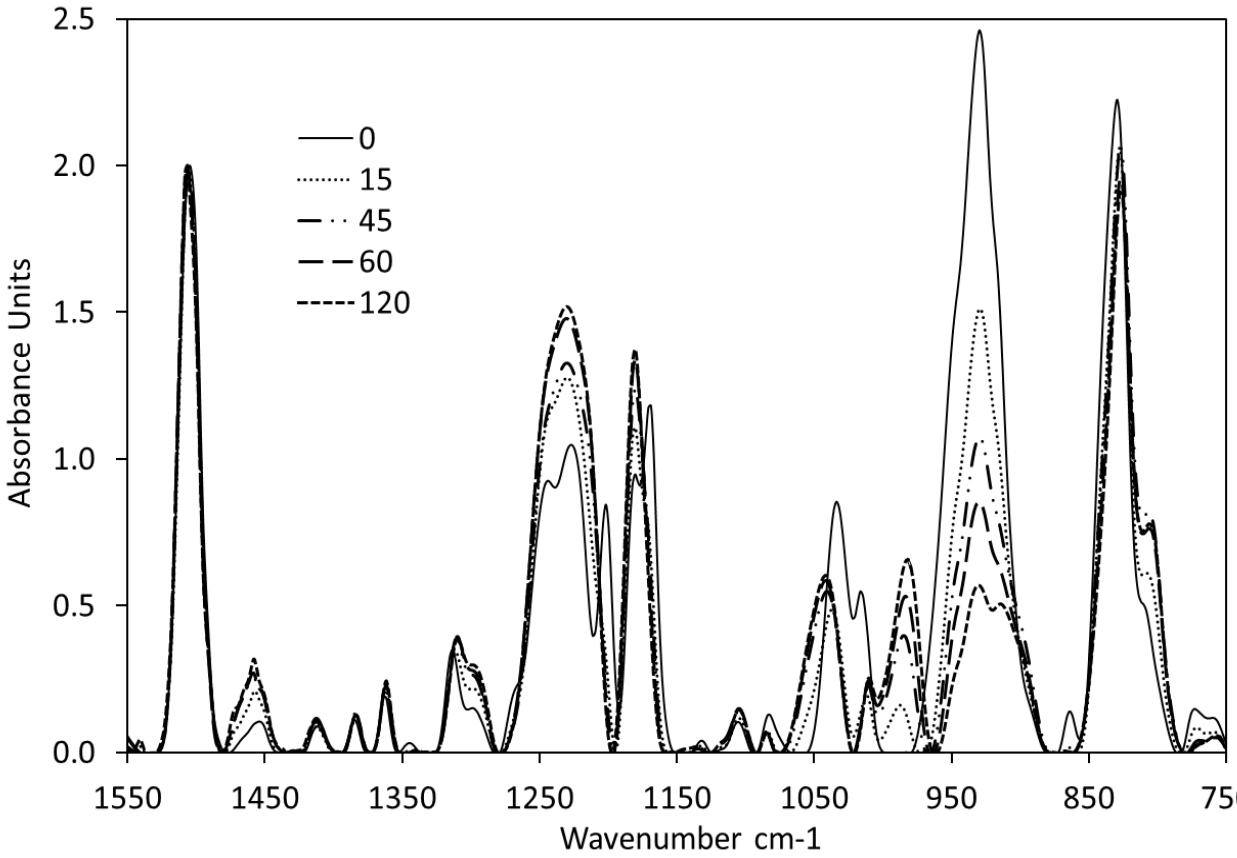
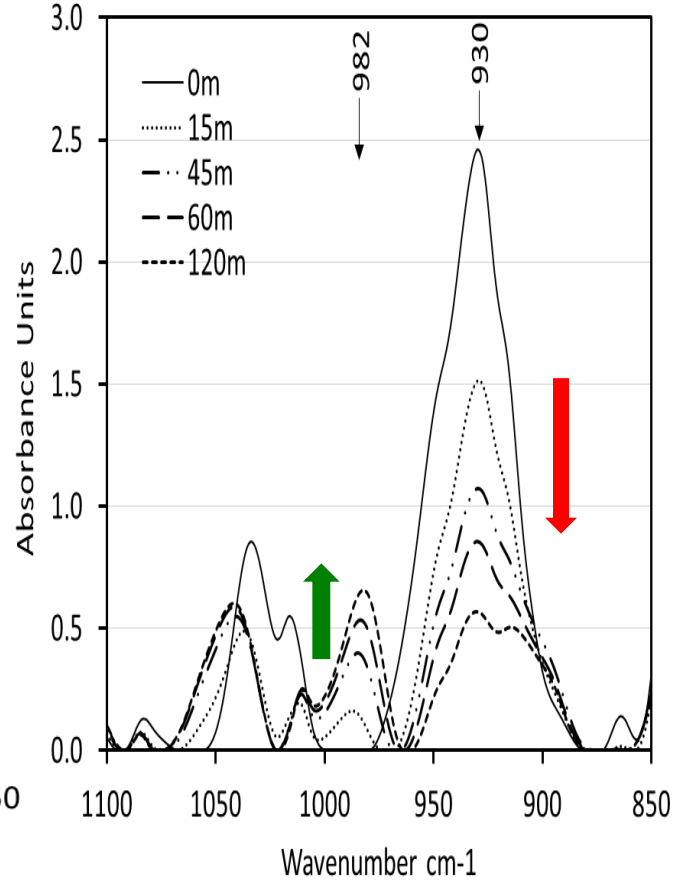
Monitoring the Curing Reaction using FTIR





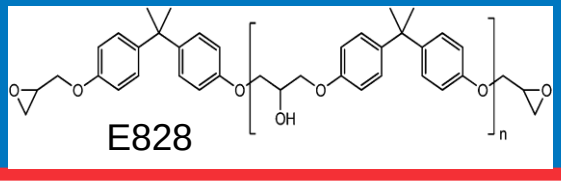
Extent of curing reaction (conversion) (α): = $\frac{A(ti) - A(t0)}{A(t0)}$

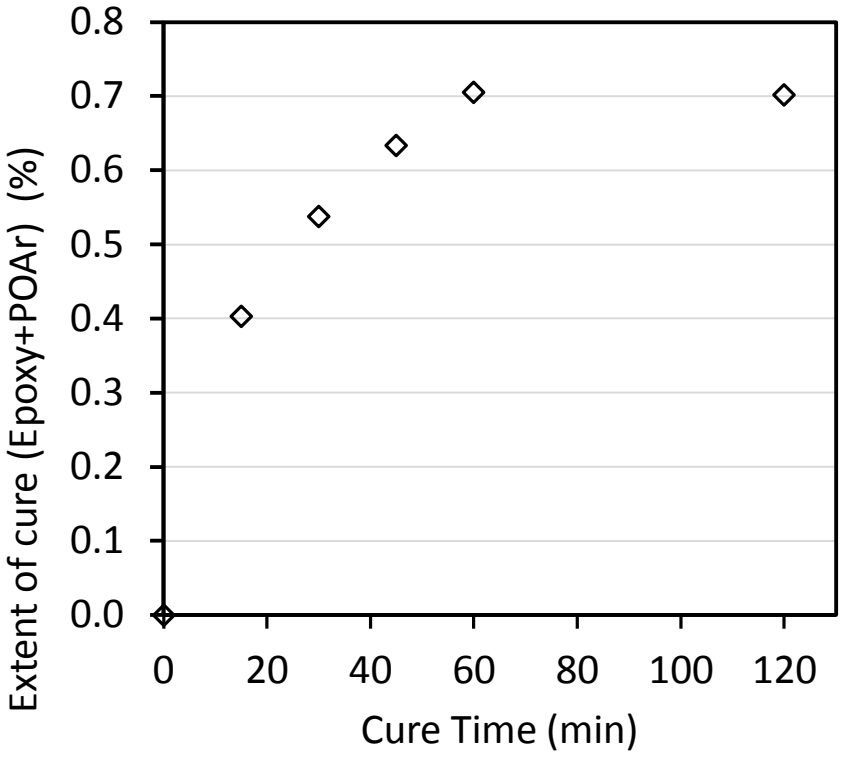
A (t0) - absorbance peak area at initial time "0"

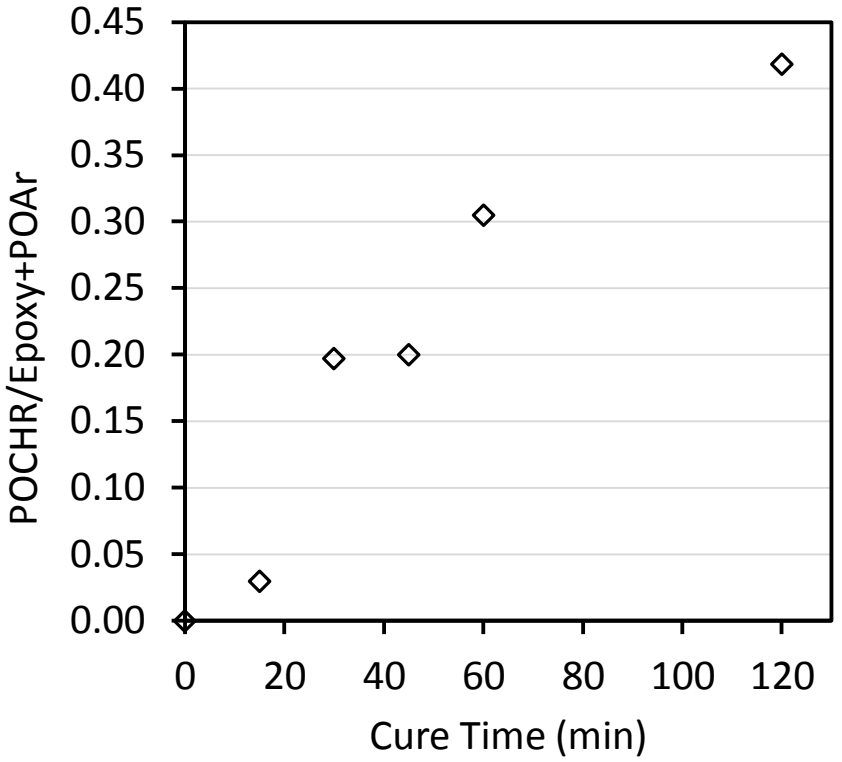
A (ti) - absorbance peak area at time "t"

Normalize to reference peak at 1507 cm^{-1} (C=C aromatic stretching)

Curing Reactions



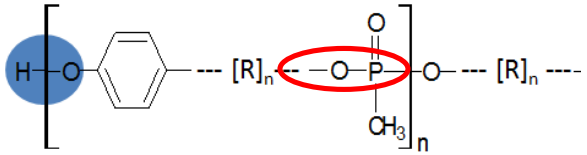




1:1 equiv weight [OL3001]:[E828], 0.2wt% 2E4MI catalyst, 165ºC

Summary of Phosphonate Oligomer-Epoxy Curing Reaction

- FTIR provides evidence of the curing reaction: formation of the P-O-C (aliphatic) group generated by the reaction of the alkoxide group ($^{-}$OR) of epoxy at P-O-Ar site of oligomer
- Curing reaction is temperature dependent, minimum temp ~160ºC
- Imidazoles are effective catalysts for the phosphonate curing reaction
- Reactive equivalent of phosphonate oligomer is calculated based on both phenolic-OH and P-O-Ar reaction sites but P-O-Ar sites dominate

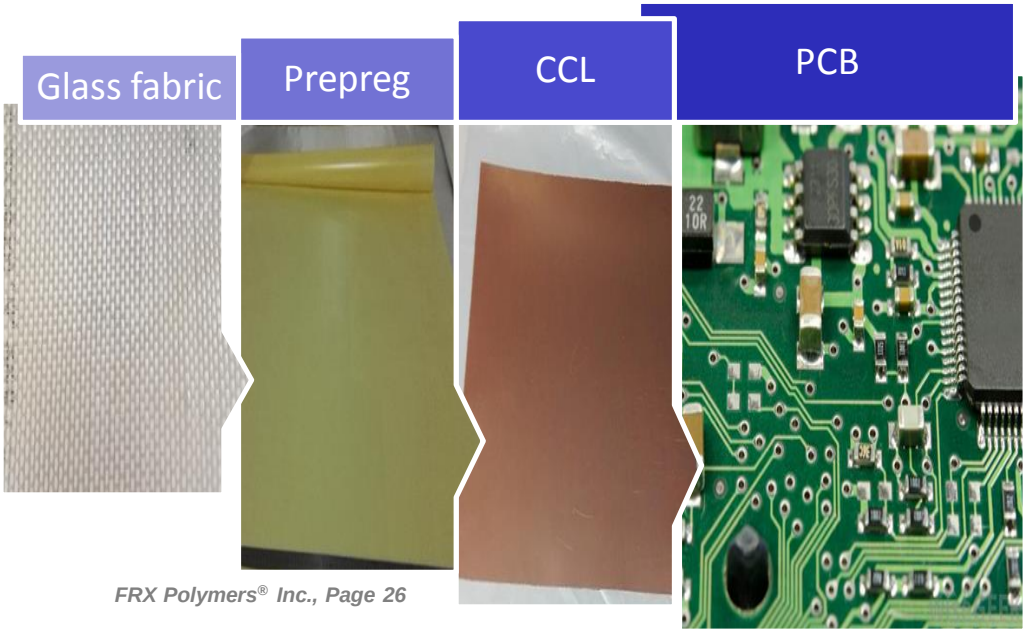


Product	OH Equiv weight (g/eq)	Total Reactive Equiv weight (g/eq)
Phosphonate oligomer (OL3001)	1240	141

Comparative Example in Epoxy based Electronic Laminate Applications

Benefits of Phosphonate Oligomer vs current Halogen-Free (Phosphorus) FRs used in CCL

- Excellent thermal stability - Td (5%) >400°C
- Increased peel strength – very good adhesion to glass fabric
- Improved dielectric properties (low Dk <3.9/Df <0.009 @ 10GHz)
- Increased toughness – 45% increase storage modulus (50-150°C)
- Improved moisture and heat resistance (passes 3 hr pressure cooker test/288°C solder dip



FRX Polymers' Plant in Antwerp

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