Novel Use of Cyanate Esters in Aerospace Applications

(Paper presented International AC Fire & Cabin Safety Conf. October 29-Nov 2, 2007)

Sajal Das
Lonza Inc.
90 Boroline Rd
Allendale, NJ 07401
sajal.das@lonza.com

Alessandro Falchetto
Lonza AG
Wallise & Werke
CH-3930
Visp, Switzerland
alessandro.falchetto@lonza.com

Richard Lyon
FAA Fire Safety Branch
Atlantic City Int'l Airport
Atlantic City, NJ 08405

What are Cyanate Esters?

- Cyanate esters belong to a class of thermoset resins available in di and multifunctional forms. Depending on chemical structure, cyanate esters can be:
  - Solid
  - Liquid
  - Semisolid
- The versatility of physical form gives wide formulation flexibility (similar to epoxy resin) to formulators and crosslink structure makes it inherently flame retardant (similar to phenolic)

What are the Advantages of Cyanate Esters?

Lonza

- Addition cure—no volatility during curing
- Gives high crosslink structure with T_g over 400°C (720°F) depending on chemical structure
- Excellent solvent and radiation resistance
- Very low di-electric constant (D_K) and low-loss (D_f) at high frequency
- Excellent solubility to common organic solvents (suitable for solvent prepregs)
- Low stable viscosity—suitable for hot/melt prepregs
  - RTM/VARTM
  - Filament winding
  - Pultrusion
  - Other liquid casting similar to polyurethane
- Depending on chemical structure, some cyanate esters are inherently flame retardant with excellent FST properties suitable for aircraft and other transportation industries

What are the Known Drawbacks?

Lonza

Past | **Today**

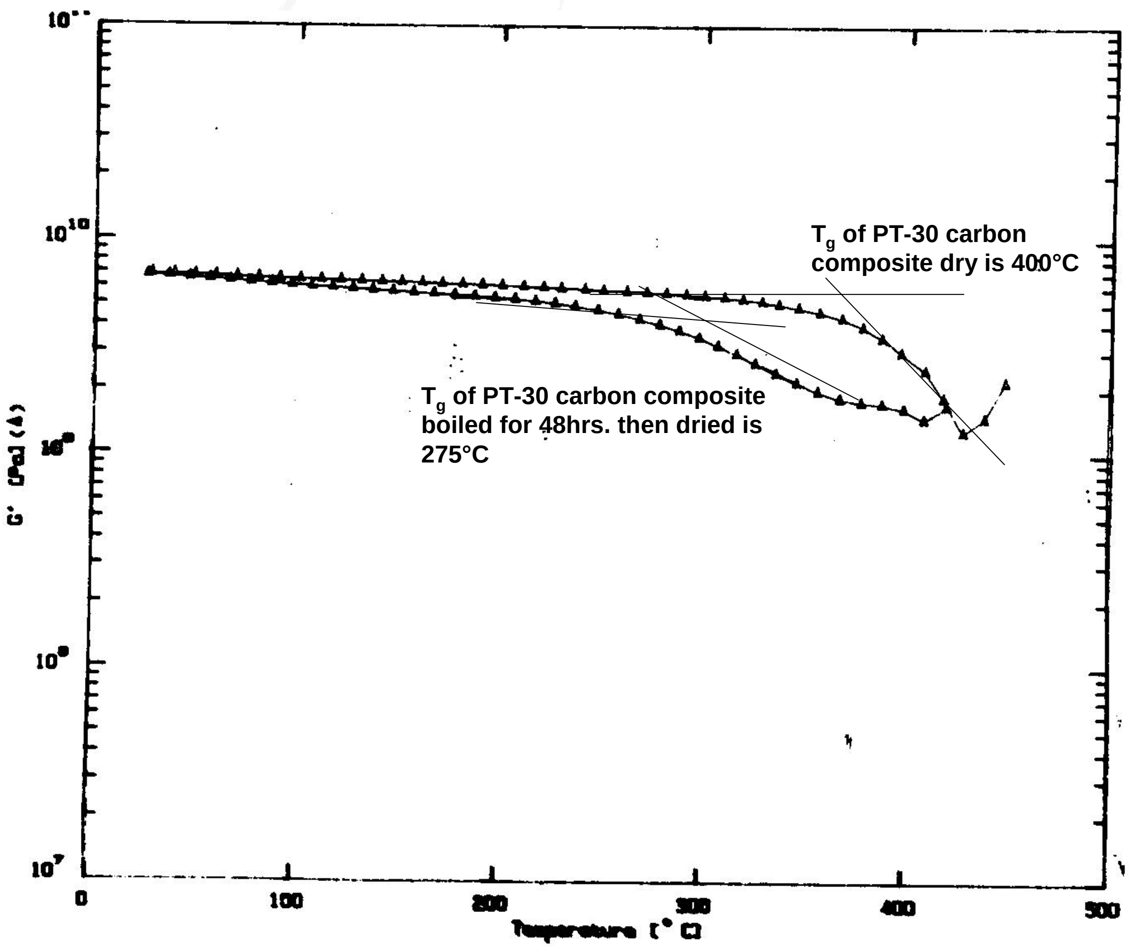
- ☹ Relatively high cost☺😐☹ — 😐
- ☹ High temperature cure cycle — ☺
- ☹ Stability of materials at processing temperature — ☺
- ☹ Lack of formulation knowledge (toughness, moisture problem, etc.) — 😐
- ☹ Lack of material availability and commitment from chemical companies — ☺

Best Known Applications

Today

- High performance Printed Circuit Board (PCB)
- Radomes, low loss at very high frequency (>40-60 GHz) (F-35, F-18, F-22 and other classified programs)
- Satellites
- Air duct in Airbus 340/380
- Formula One racing car and muffler system for motorbike
- Some critical electrical components close to engines (exposed 450°F) in Boeing 737/777
- Laser guided missile hardware

DMA graph of boiled and dry PT/carbon composite



Mechanical properties of PT and PMR-15 carbon-fiber composites (fiber 58-64 vol.-%) of Modern Plastics, Feb, 1999

Lonza

Properties	PT-resin		PMR-15	
	24°C	330°C	24°C	315°C
0°C Flexural Strength, 10^3 p.s.i.	250-360[b]	150-200[b]	220-280[c]	a 140[c]
0°C Flexural Modulus, 10^6 p.s.i.	15-17[c]	16[c]	15-17[c]	15[c]
Short-beam-shear strength, 10^3 psi	21-24[d]	21-22[d]	-	-
	10[e]	7.2[e]	15[f]	7.2[f]

A: PMR-15 (Dexter Composites) is a polyimide produced by the polymerization of methylene dianiline (MDA).

B: Range of data for composites made with Celion (BASF) 6000, T300, and T650 carbon fibers.

C: Celion 6000 fiber.

D: Celion T650/42 fibers. E: Polyimide-sized fibers. F: Unsized fibers.


Lonzagroup
Primaset resin
Muffler of a racing motorbike
Kawasaki
FUCHS
Silkolene
DUNLOP
brembo
NGK

The Focus of Today's Presentation

Lonza

- Use of Cyanate Esters in Aircraft Interiors

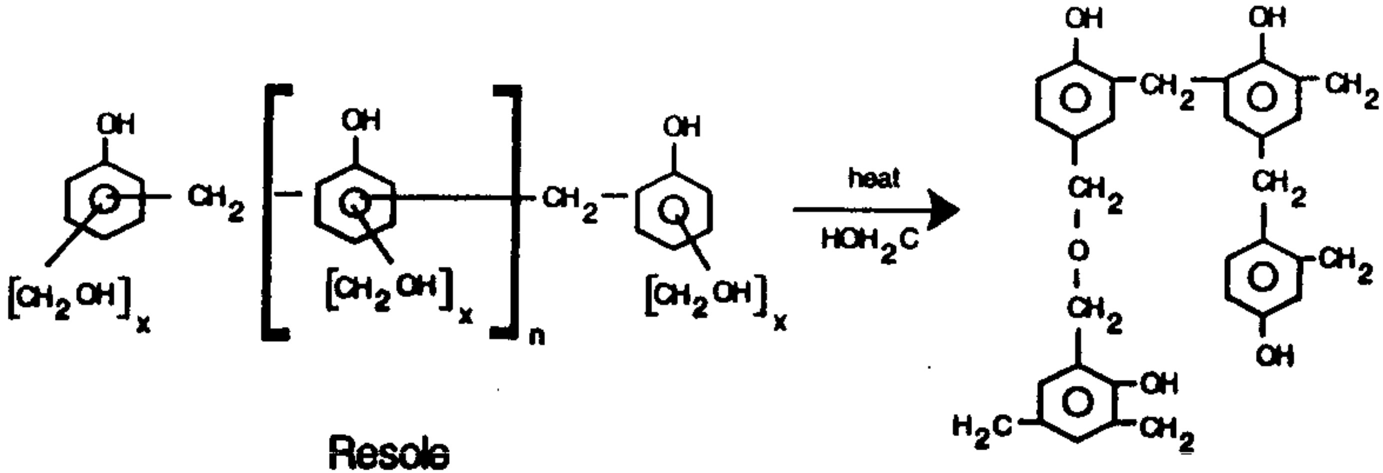
Focus: Weight Reductions / Good Surface Finish / Environmentally Problematic Chemicals

Current Technology

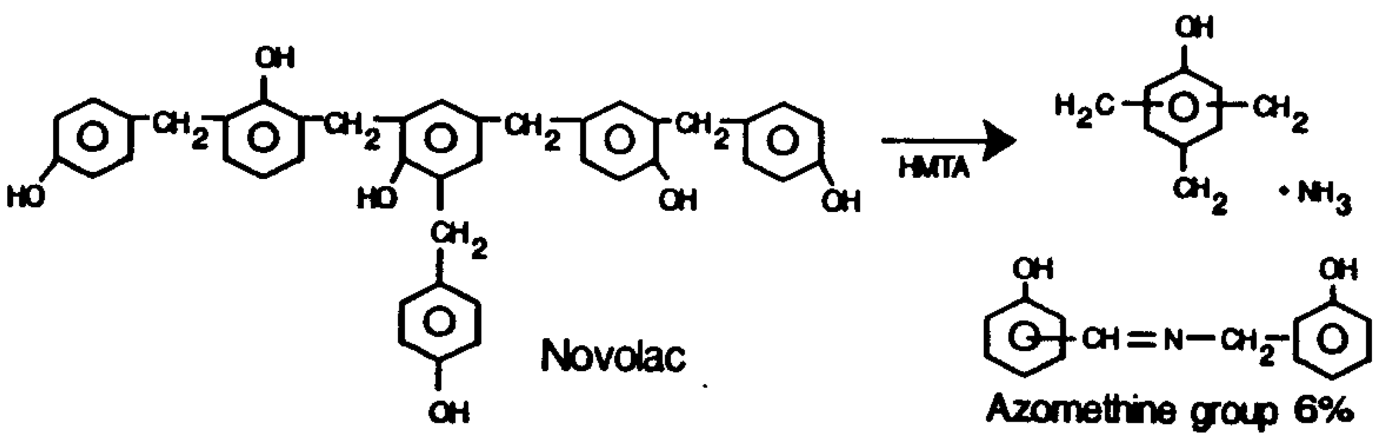
- Phenolic resin (Resole or novolac based) are the primary resin for aircraft interior structures
- Brominated epoxy are used in ducting (mainly USA) and also in aircraft flooring
- Some phosphorous additives are used as flame retardants
- More than 7000-8000MT prepregs are used in only in Aircraft Interiors

Cure Chemistries of PF Resins

Lonza



Resole



Novolac

Azomethine group 6%

Issues with Current Chemistry

- Free phenol and formaldehyde even with excessive B-staging
- Excessive B-staging results low tack in the prepreg and artificial tack is introduced by alcohol
- During curing, volatiles generate from condensation polymerization and from tackifier solvent
- Surface becomes poor for interior applications
- Extra coating polishing required to smooth the surface

Issues with Current Chemistry

- Adds extra weight and additional labor lost
  - Not the best time to add additional weight when fuel cost is skyrocketing
- Airflow Duct with phenol-formaldehyde resin?
- Kevlar duct keeps weight reduction but PF resin required in additional coating (weight!)
- Brominated epoxy or brominated FR cause heavy smoke [Fixing wrong building block, adds weight and cost]

Lonza

Entry of New Chemistry in Aircraft Interiors

→ Cyanate Esters

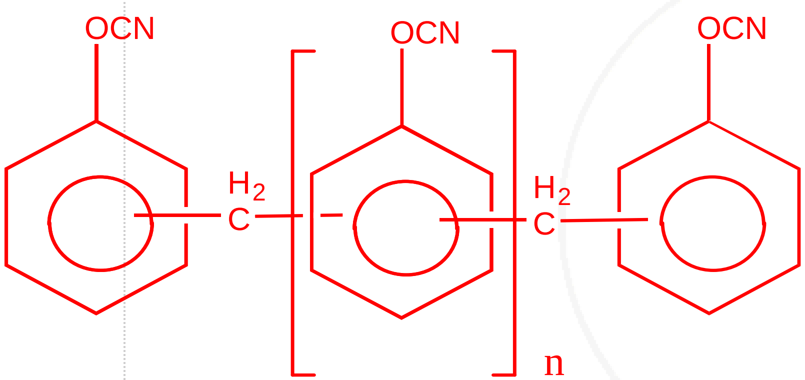
Primaset® PT Resin

- First present at the FAA Conference in 1993
- Major advancements have taken place since then:
  - Lonza built a large dedicated cyanate ester plant in 1999
  - More than 60% of ducting made for A340/380 today is made from a modified PT resin
    - Prepreg available from Gurit

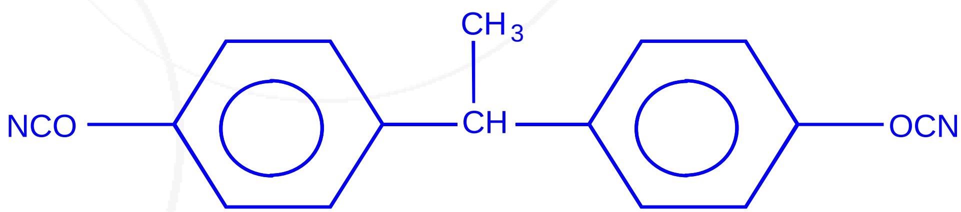
Primaset® PT Resin

- New building block development focusing on environmentally friendly and other regulatory (ROSH, REACH) and FAA material requirements
- Cost effective process to manufacture parts
  - Vacuum bagging
  - RTM
  - VRTM
  - Resin Infusion
  - less additives to pass OSH and FST
  - alternative to thermoplastic (TP)

Structures of Recommended Cyanate Esters for Aircraft Interiors

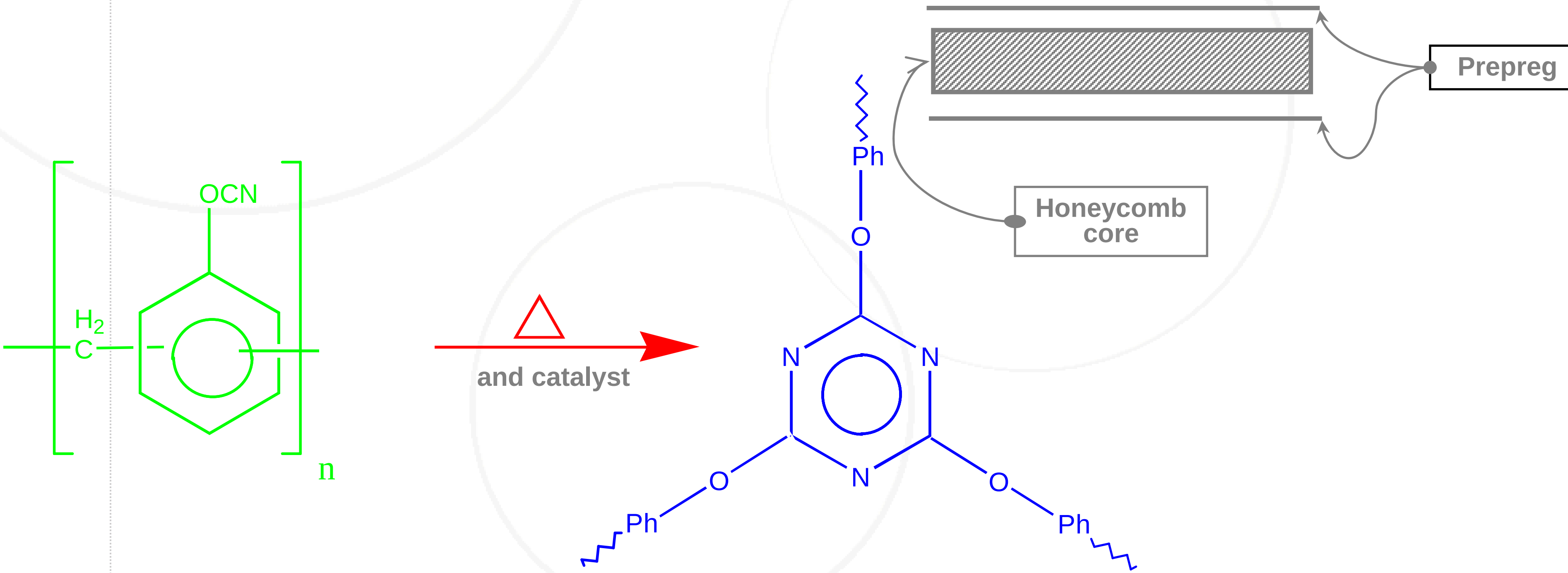


Primaset™ PT-15, PT-30, PT-60
(BASE RESIN)



Primaset™ LECY
(Modifier/tackifier reactive diluent)

A typical homopolymerization structure (CE cure structure).



- Possible to cure 125-135°C prepreg bonding with honeycomb core or crushed core (150°C) technology
- No volatile during cure and gives excellent surface finish

Mechanical properties commercial prepreg

Table 1: Mechanical Properties of Stesapreg EP127-C510-40

Properties	Unit	Value
Ultimate Tensile Strength [1]		
23°C	MPa	840
135°C		800
Tensile Modulus [1]		
23°C	GPa	65
135°C		63
Ultimate Compression Strength [1]		
23°C	MPa	800
135°C		630
135°C HW [2]		530
Ultimate Flexural Strength [1]		
23°C	MPa	1100
135°C		1050
135°C HW [2]		800
Flexural Modulus [1]		
23°C	GPa	64
135°C		61
135°C HW [2]		61
IIS short beam		
23°C	MPa	65
135°C		50
Climbing Drum Peel Strength [3]		
23°C	Nmm/mm	45

1) normalized to 62 Vol. % of fibre
2) HW= Hot-Wet: boiling water until saturation
3) 2 plies of Prepreg material with 50 wt.% of resin
Core material: Nomex honeycomb, cell size 3.2 mm ; 48kg/m^3

Flammability properties of commercial prepreg

Lonza

Table 2: Flammability of Stesapreg EP127-C510-40 in solid laminate consisting of 5 plies

Properties		Unit	Value
Flame Test vert. 60 sec. FAR 25.853			
	Self-Extinguishing Time	sec.	0
	Burn Length	mm	4
	Drip Extinguishing Time	sec	0
NBS Smoke Chamber			
	Flaming mode	D_s	50
Heat Release	**FAR 25.853**		
	Peak	kW/m^2	50
	2 min	$kW/min/m^2$	20

Table 3: Flammability of Stesapreg PN900-68-40 with 2 face sheets on sandwich structure [1)]

Properties		Unit	Value
Flame Test vert. 60 sec. FAR 25.853			
	Self-Extinguishing Time	sec.	2
	Burn Length	mm	4
	Drip Extinguishing Time	sec	0
NBS Smoke Chamber			
	Flaming mode	D_s	30
Heat Release	**FAR 25.853**		
	Peak	kW/m^2	40
	2 min	$kW/min/m^2$	30

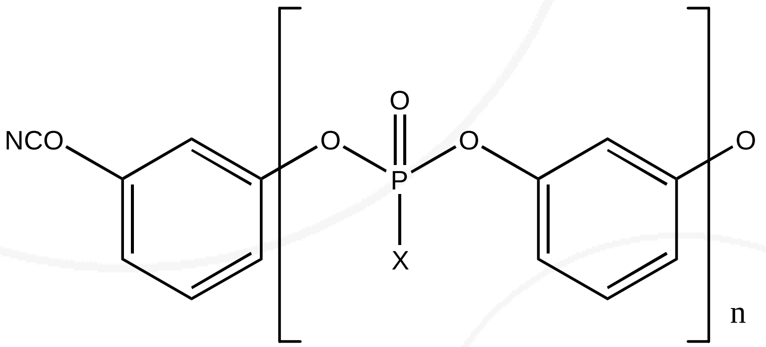
1) Core material: Nomex honeycomb with cell size 3.2 mm; 29 kg/m^3; thickness 5 mm

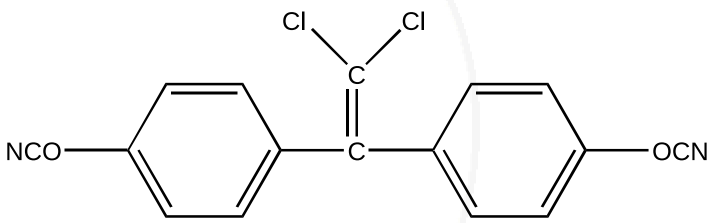
New Development: Targeted to aircraft interiors and other transportation industries

- Primary Goal:
  - Building block chemistry to enhance ultra low OSU and FST properties without free phenol amines and formaldehyde chemicals
  - Auxiliary products compatible with CE, epoxy to provide tack, low temperature cure and toughness is bonded with honeycomb core

New Developments

Lonza





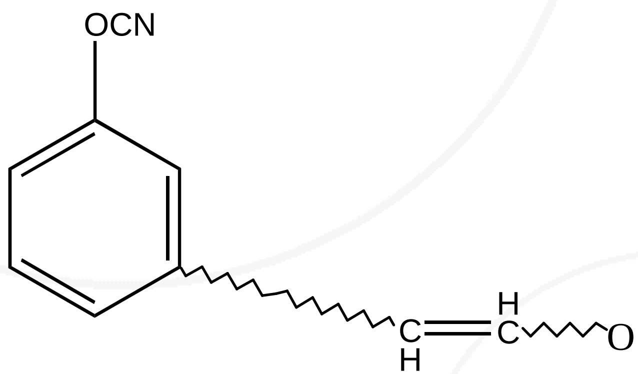
Primaset FR-500

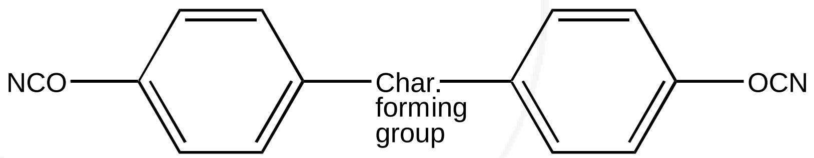
- semi-solid
- soluble in MEK, Acetone
- Additive for CE, epoxy, and other polymers
- sample available

BPC-CE

- developed by FAA/Huntsman
- Ultra low OSU
- halogen derivative
- crystalline solid
- raw material issue?

New development





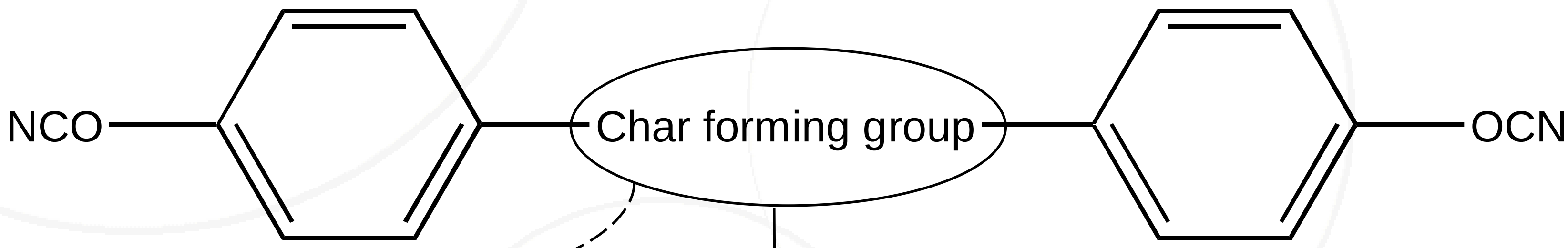
Primaset TC-65

- Long chain low viscosity (<80 CPs) liquid for improved toughness and tackiness
- Compatible with CE, Epoxy
- Low temperature, thermal or free radical cure

Primaset LHR-10

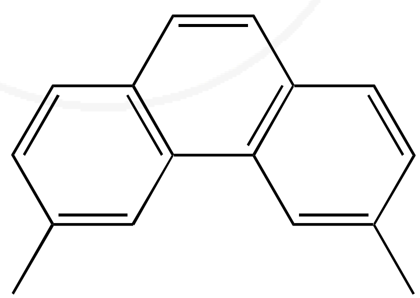
- Low OSU
- No halogen
- Low temperature cure, organic catalyst for CE

Char forming Mechanism



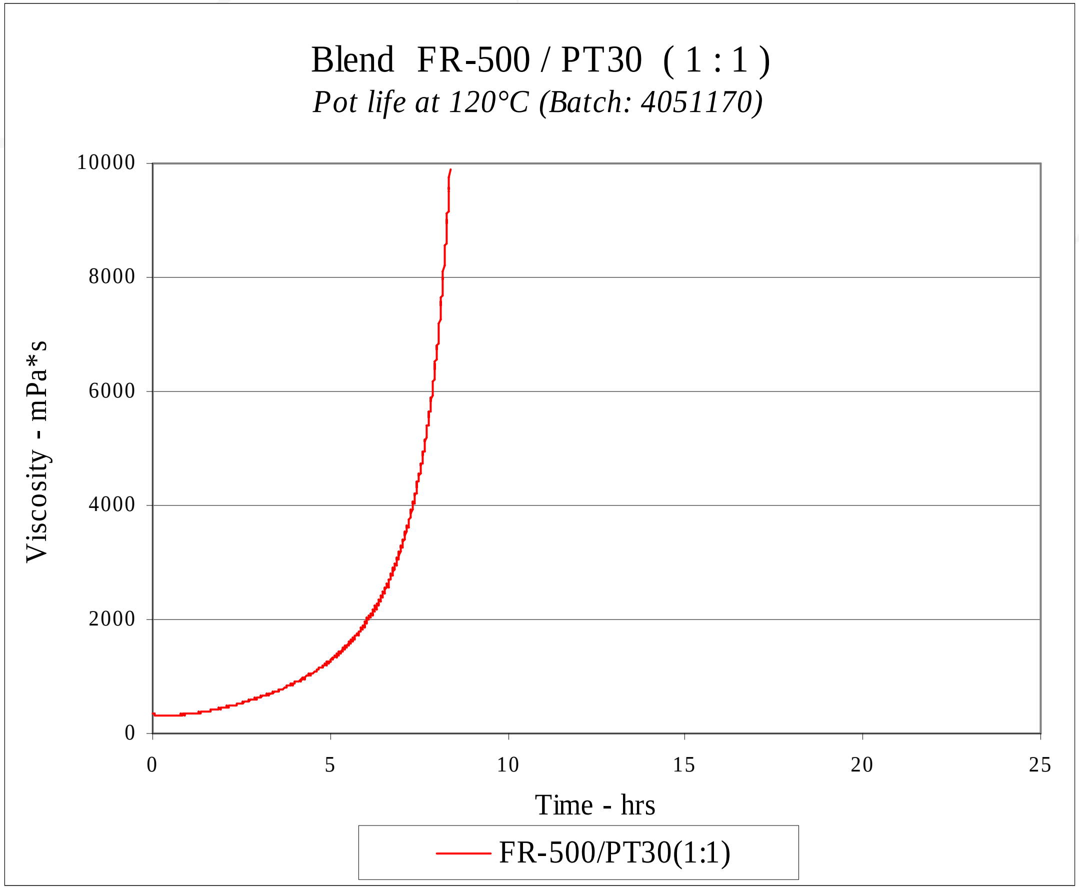
Char forming group:
halogen or
non-halogen

- Low fuel
- Non-combustible chemical(s)

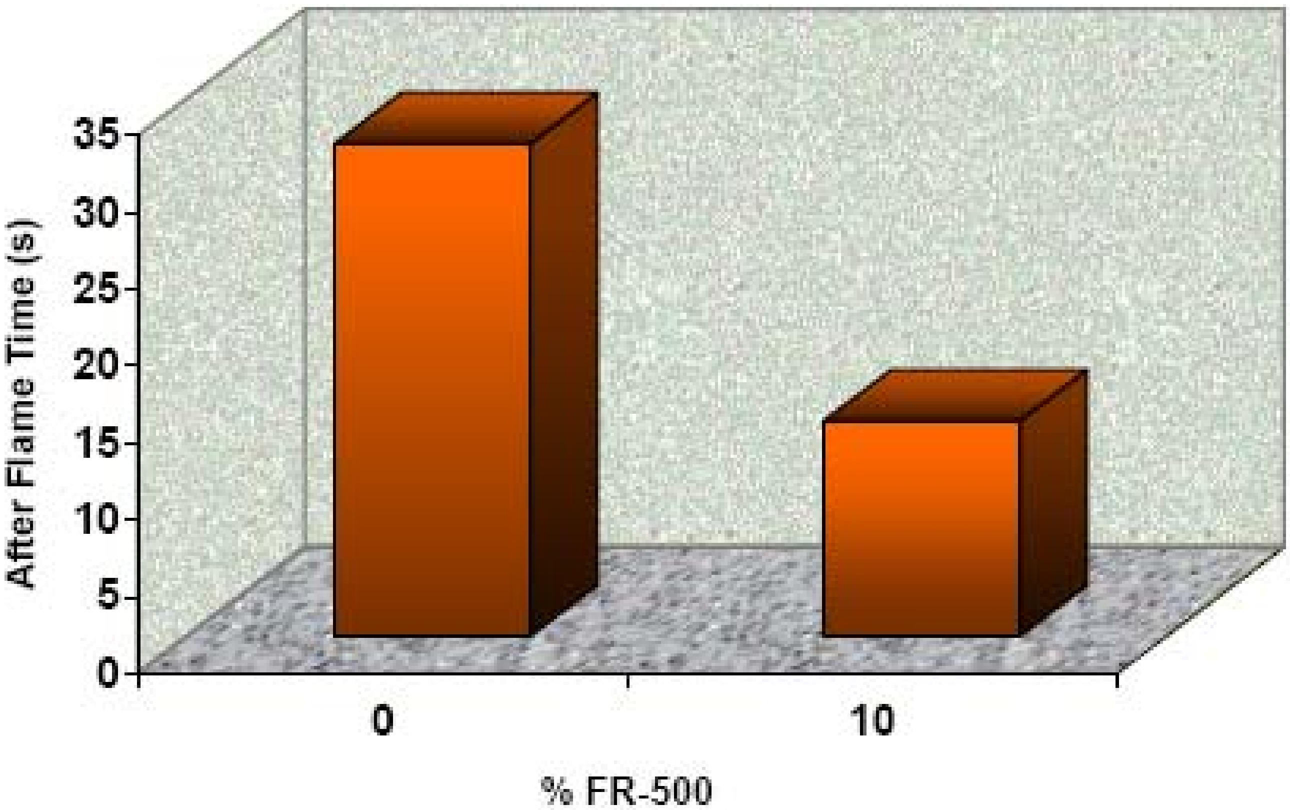


graphite type structure

FR-500 / PT-30 blend viscosity



Effect of FR-500 on Epoxy & CE



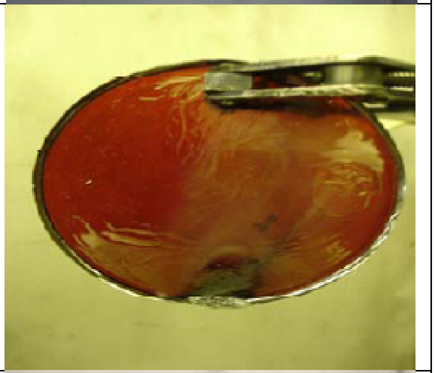
Lonza
CONFIDENTIAL

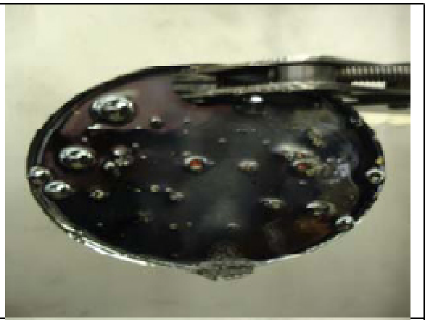
FR 500 / PT 15 blends

1. Sample preparation *(polymerisation at standard conditions).*

Exper #	PT 15 / FR 500 ratio		Polymerisation					
	PT 15 %	FR 500 %	Gel		Cure		Post-cure	
			T. °C	Time min	T. °C	Time min	T. °C	Time min
4640-120- 1	**100**	**---**	**150**	**60**	**200**	**180**	**260**	**60**
4640-120- 2	**90**	**10**	**150**	**60**	**200**	**180**	**260**	**60**
4640-120- 3	**80**	**20**	**150**	**60**	**200**	**180**	**260**	**60**
4640-120- 4	**70**	**30**	**150**	**60**	**200**	**180**	**260**	**60**
4640-120- 5	**60**	**40**	**150**	**60**	**200**	**180**	**260**	**60**

2. Flame test

Experiment #	Flame time *(everage)* sec. 1st	Flame time *(everage)* sec. Time total *(5 specimen)*	Drops	Sample after measurement
4640-121-1	> 100	400	No	
4640-121- 2	2- 4	8	No	
4640-121- 3	0	7- 8	No	

4640-121- 4	0	0	No	
4640-121- 5	0	0	No	

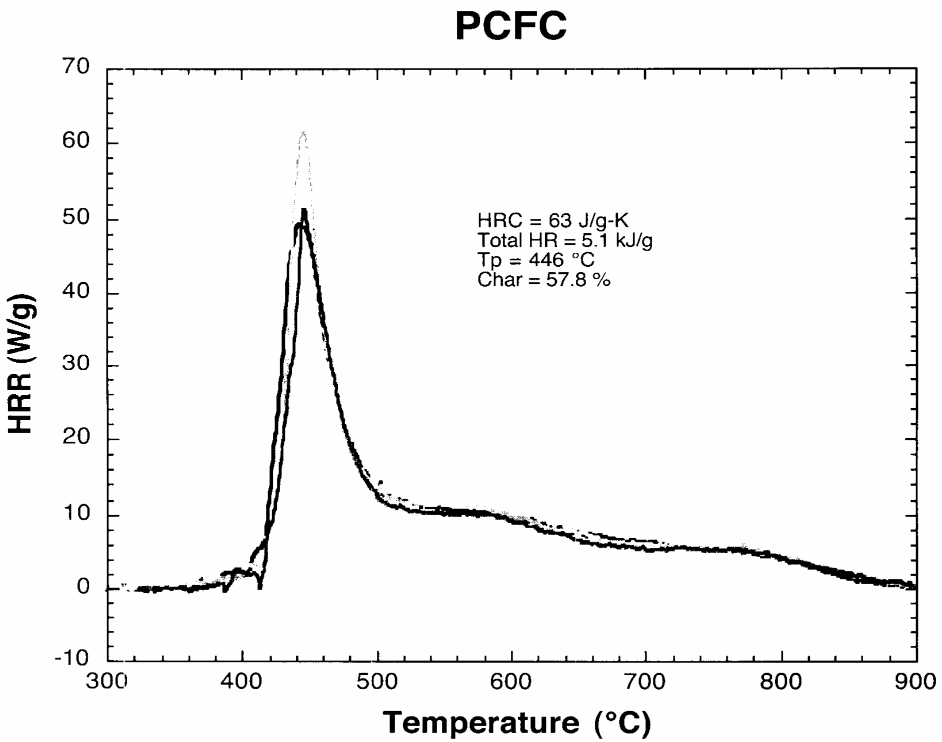
Heat Release Capacity, Total Heat Release, and Char Yield of New Developmental Products

Lonza

Product	Heat Release Capacity (J/g-K)	Total Heat Release (KJ/g)	Char Yield (%)	OSU (single glass ply)
BPC-CE	24	4.2	53	14/13*
LHR-10	89	7.1	49	56/17*
LHR-10 (m)	54	5.1	58	40/10*
PT-30	122	9.9	52	
Ultem™	121	11.0	49	< 65/65**
PEEK	155	12.4	44	≤ 65/65**
Phenolic	50-80	12	44	35/23*
HDPE	1486 ± 20	43.5 ± .1	0	Fail**
PC	359	16.3	21.7	Fail**
FR-500				

*Single ply/glass fabric; ** 1/16-inch sheet

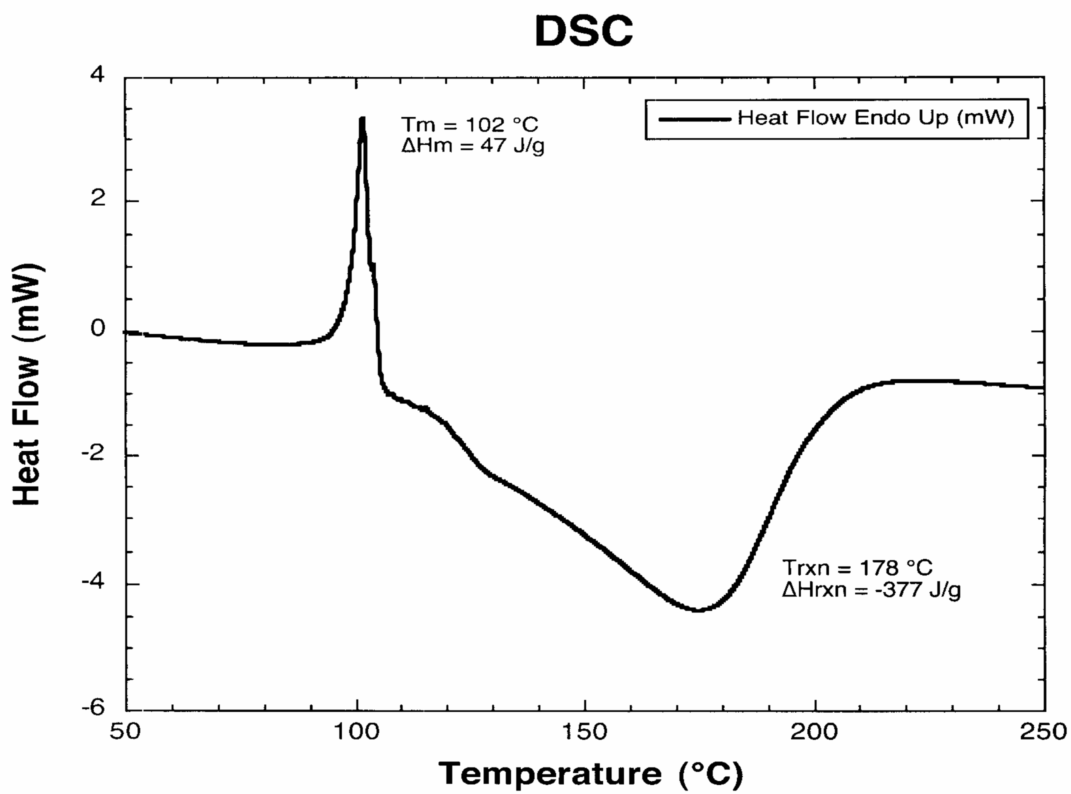
PCFC



Microscale Combustion Calorimeter

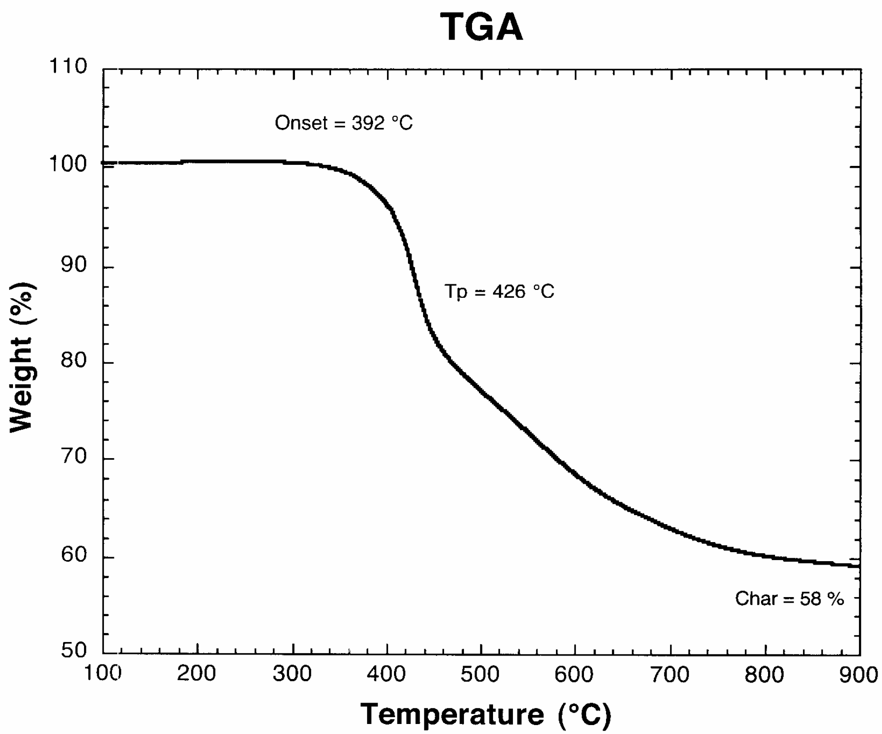
Test	HR Cap (J/g-K)	Peak HRR (W/g)	Total HR (kJ/g)	Tp (°C)	Char (%)
1	59	49	5.2	444	58.5
2	75	62	5.3	446	57.6
3	56	51	4.8	447	57.2
Average	63	54	5.1	446	57.8

LHR-10 DSC



Differential Scanning Calorimetry	
Peak Melting Temperature	102°C
Heat of Melting	47 J/g
Peak Reaction Temperature	178°C
Heat of Reaction	-377 J/g

LHR-10 TGA

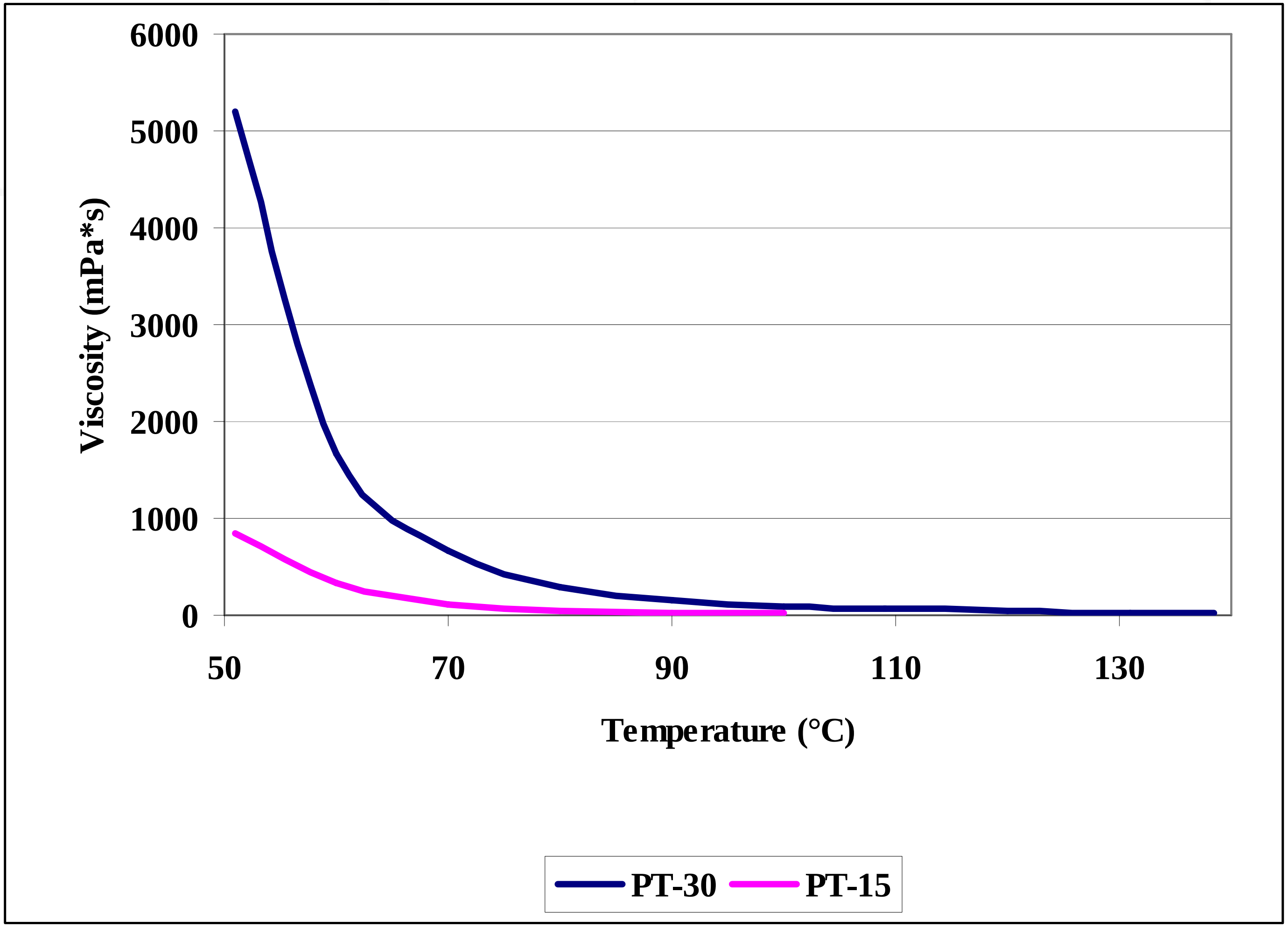


Thermogravimetric Analysis	
Mass Loss Onset Temperature	392°C
Peak Mass Loss Rate Temperature	426°C
Char Yield	58 %

New Process

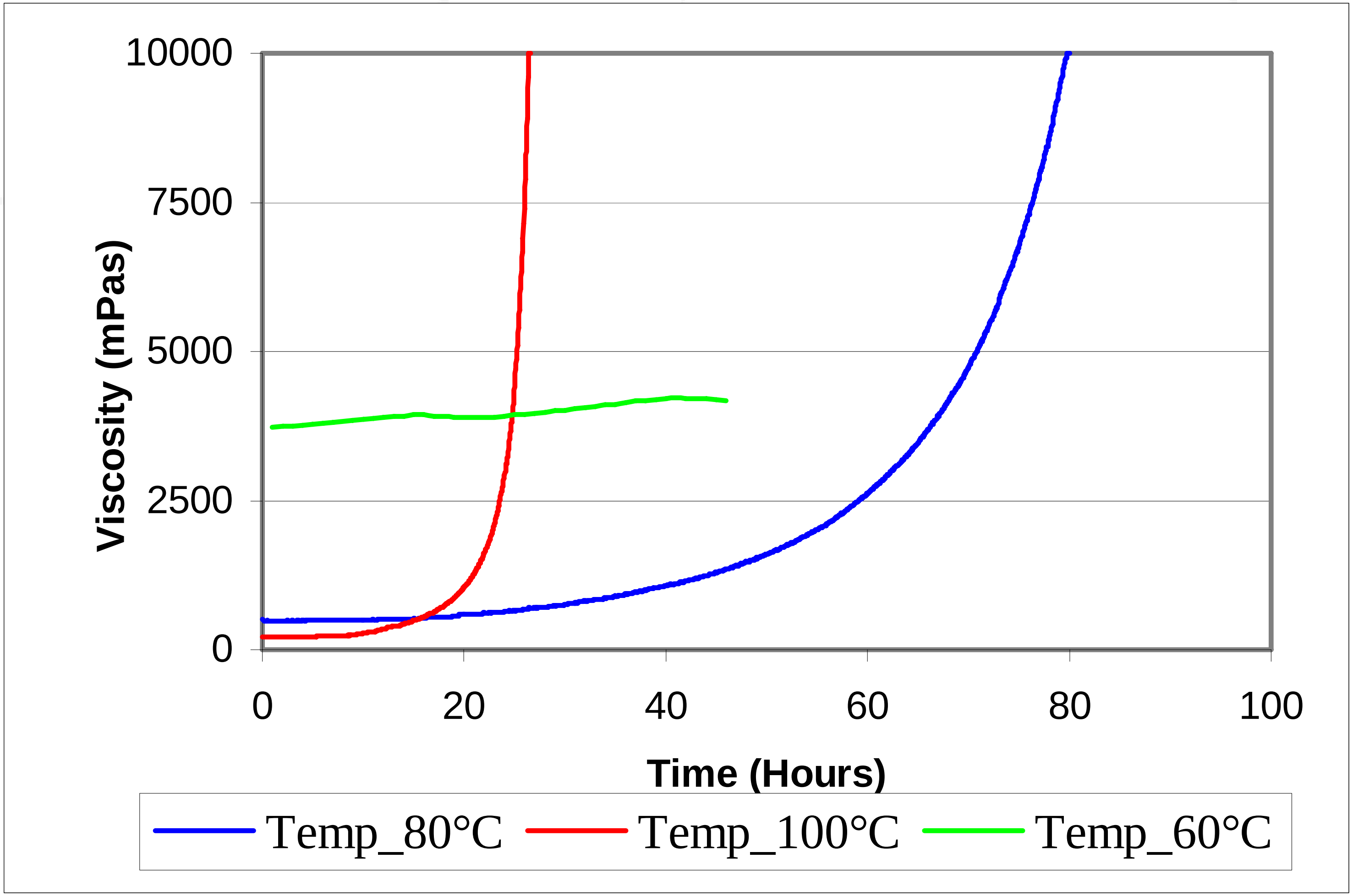
- Hot melt prepreg
- FTM
- VRTM
- alternative to TP process (expensive tooling)

Viscosity Comparison between PT-30 and PT-15 Respect to Temperature.

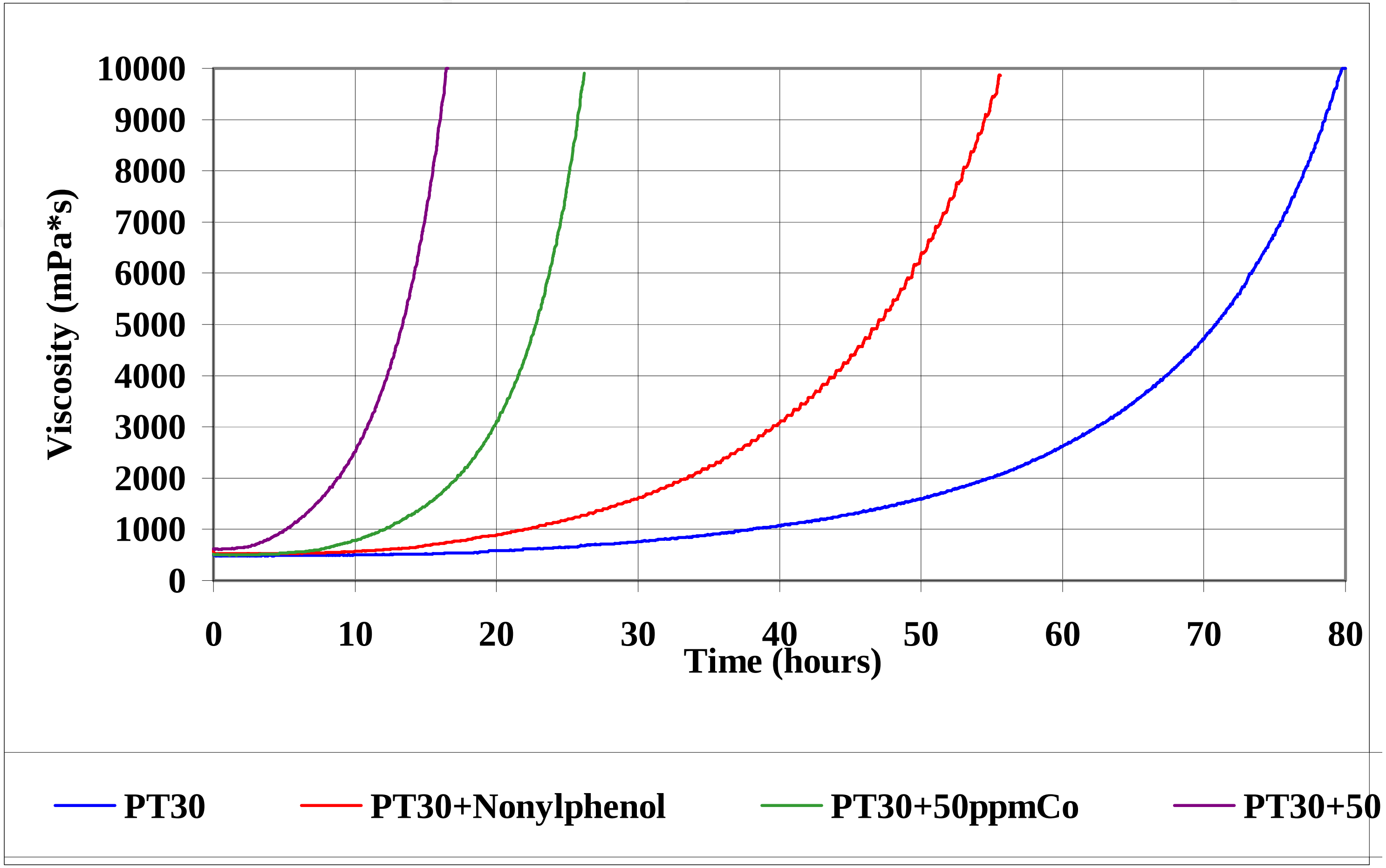


The Influence of Temperature on PT-30 Shelf-life.

Lonza

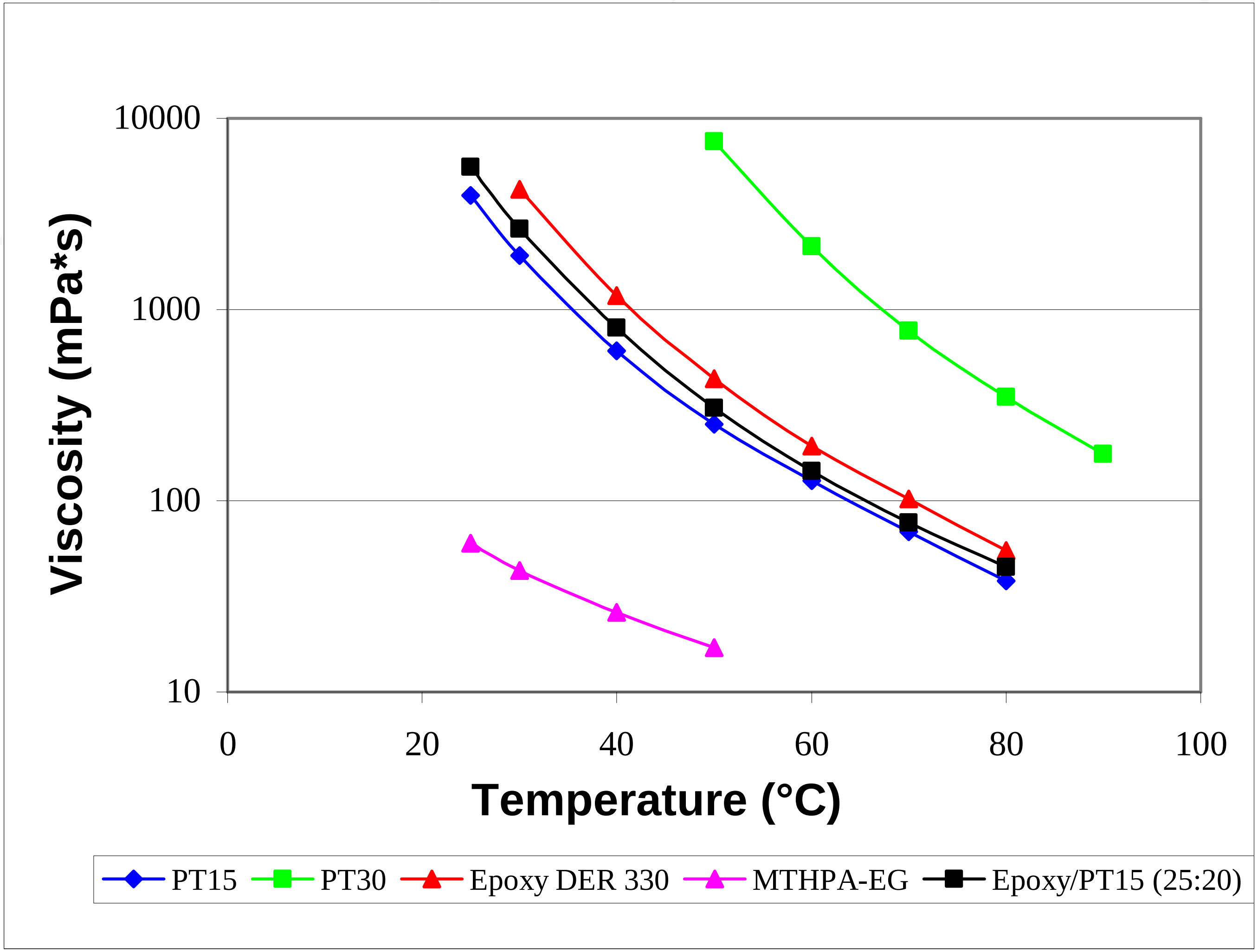


Catalyst effect on Shelf-life of PT-30 at 80°C

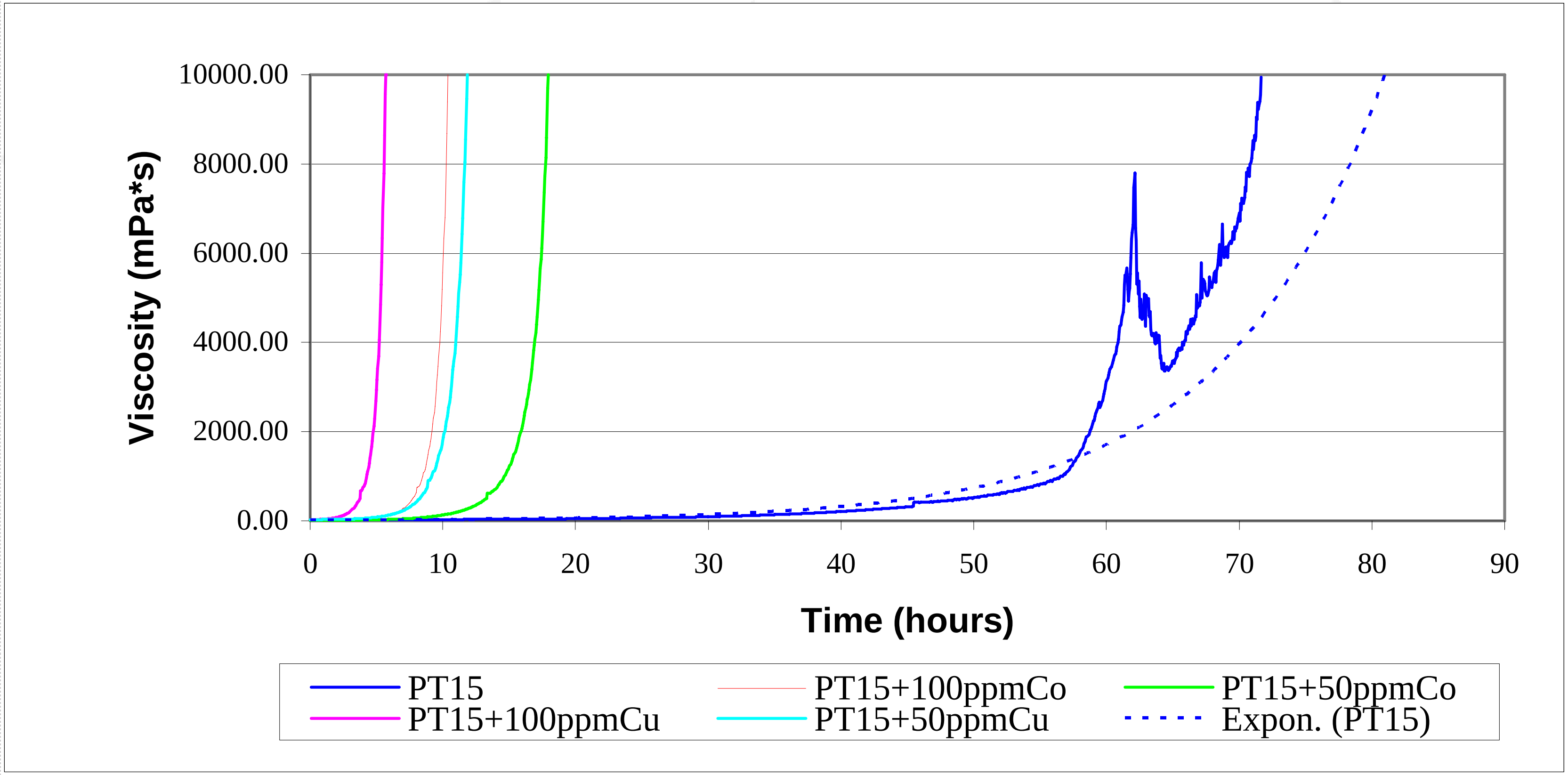


Effect of Epoxy on Viscosity of PT-15 with respect to Temp

Lonza



Catalyst effect on PT-15 Shelf-life



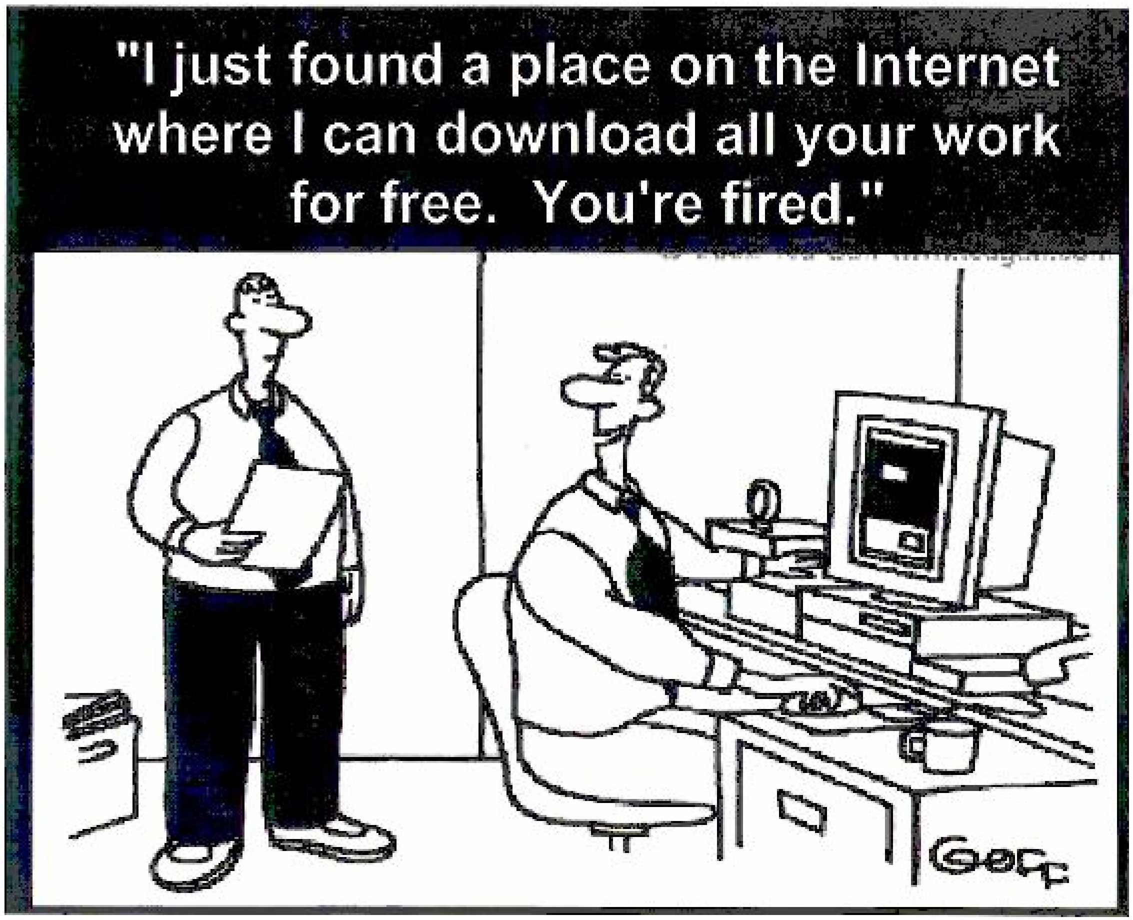
Summary

Lonza

- Phenolic-Triazine (PT Resin) now proven material for aircraft interior applications
- With new char forming building block with and without halogen provides very low heat release and easily passes 65/65 requirements of FAA OSU numbers
- Non-volatile addition polymerization without free phenol formaldehyde and aniline chemistry would be ideal material for mass scale use of aircraft and other transportation industries

Summary

- Weight reduction (no additional coating/ polishing/ painting) would be prompt alternative to phenolic chemistry
- Cost effective manufacturing process such as RTM, vacuum bagging, VRTM, FW and other alternatives to TP process
- Fire resistant spray coating to mold or prepreg


"I just found a place on the Internet where I can download all your work for free. You're fired."