HUNTSMAN

Enriching lives through innovation

“Novel Benzoxazine Based Systems for Flame Retardant Aircraft Interior Prepreg Applications”

Jim Hoge
Huntsman Corporation

The Sixth Triennial International Aircraft Fire and Cabin Safety Research October 2010

Disclaimer

HUNTSMAN
Enriching lives through innovation

:

- The slides following hereafter contain information that is confidential and proprietary to Huntsman Corporation, and/or its appropriate affiliate(s) (“Huntsman”) Recipients of this presentation and the information contained herein shall not copy or replicate the same by any means whatsoever and shall not share or show such information to third patties..
- While the information contained herein is, to the best of Huntsman’s knowledge, accurate as of the date of its presentation, it is the responsibility of recipients to determine the applicability and/or suitability of such information for their own particular purpose Huntsman accepts no responsibility for any damages of any kind incurred by recipient and/or third patties resulting from the use of, reliance upon, or the misuse of such information for any purpose.
- All information contained herein is provided “as is” without any warranties, express or implied, and under no circumstances shall the authors or Huntsman be liable for any damages of any nature whatsoever resulting from the use or reliance upon such information. Nothing contained in this publication should be construed as a license under any intellectual property right of any entity, or as a suggestion, recommendation, or authorization to take any action that would infringe any patent. The term “Huntsman” is used herein for convenience only, and refers to Huntsman Corporation, its direct and indirect affiliates, and their employees, officers, and directors

Agenda

HUNTSMAN
Enriching lives through innovation

- Introduction
- Chemistry Description
- Benzoxazine Monomer Types – Solids / Liquids
- Attributes and Limitations
- Curing of Benzoxazines
- Benzoxazines & Aircraft Interiors
- Flammability of Benzoxazines
- Formulations & Testing results
- Summary and Conclusions

Huntsman Development Program _ Benzoxazines

HUNTSMAN
Enriching lives through innovation

- Huntsman Benzoxazine Development Program
- Began in the 1990's
- Introduced a number of commercial products since 2000 through today
  - 5 new monomers benzoxazine solids
  - Several new development materials
  - 2 catalysts for benzoxazine curing
- Development continues for applications in
  - Electronics [nonhalogen materials]
  - Adhesives [high temperature]
  - Composites [industrial, aerospace, and others]
  - Coatings [powder]
  - Energy [fuel cells]
  - Materials for Flame, Smoke, and Toxicity applications

HUNTSMAN

Enriching lives through innovation

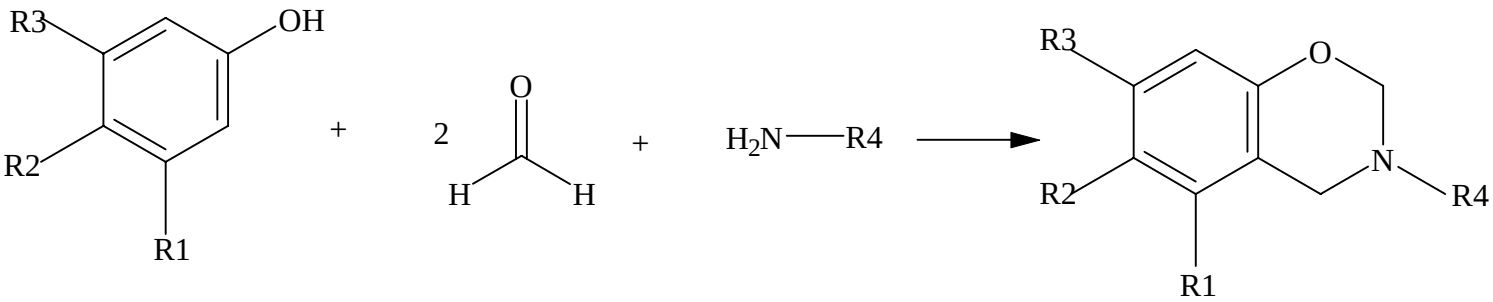
Chemistry of Benzoxazines

What are Benzoxazines ?

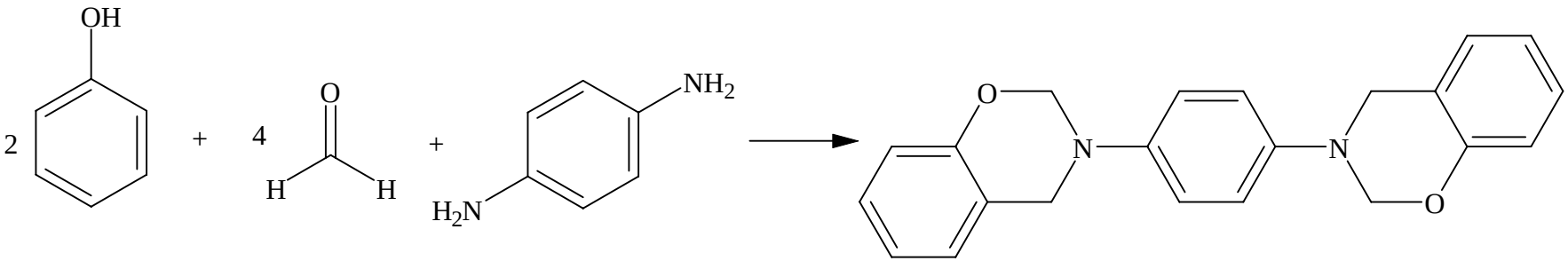
HUNTSMAN
Enriching lives through innovation

- **Benzoxazines are the reaction products of an amine, a phenol and formaldehyde**

Reaction Scheme # 1



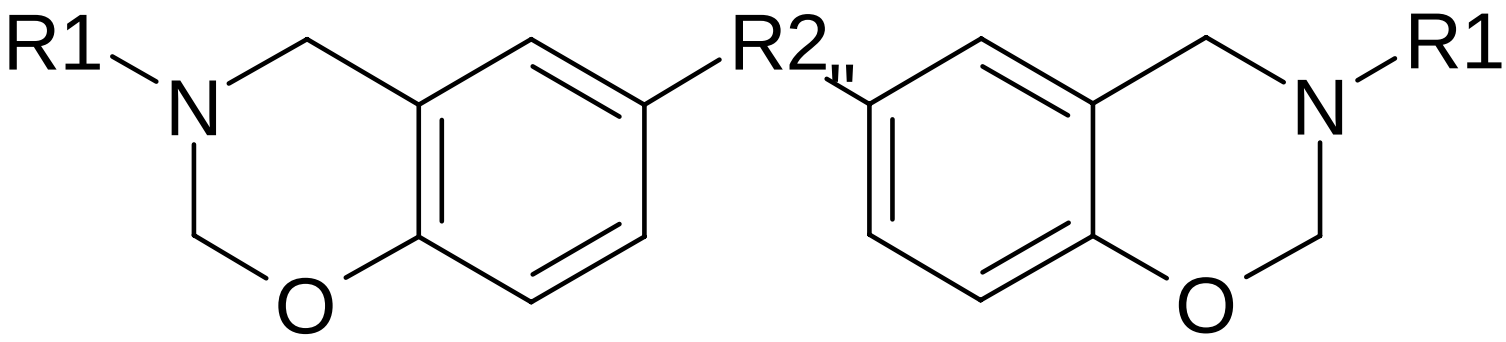
Reaction Scheme # 2



Typical Benzoxazine

HUNTSMAN
Enriching lives through innovation

Di-functional Benzoxazines for crosslinked network



R1 = alkyl, phenyl, alkenyl, alkoxy, OH, halogen …etc

R2 = single bond, alkyl (CH_2, $C(CH_3)_2$ …) , O, S, SO_2, …etc

HUNTSMAN

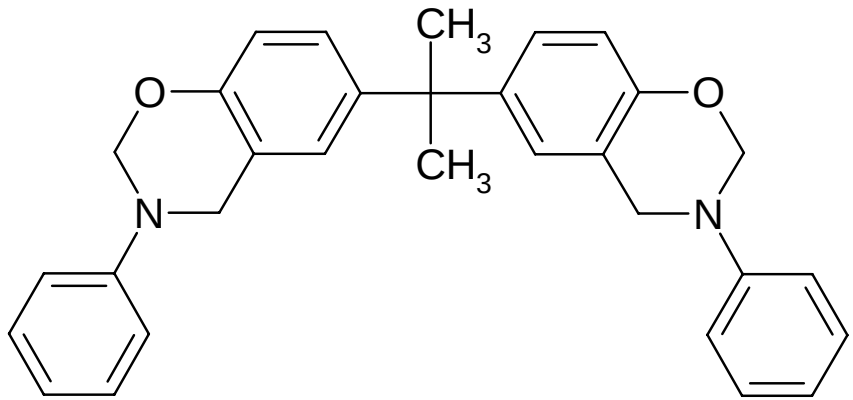
Enriching lives through innovation

Benzoxazine Monomers

Bisphenol A Benzoxazine

HUNTSMAN
Enriching lives through innovation

- Only Fair Flammability Resistance
- High Tg properties
- Low water absorption
- High Modulus Properties
- Excellent chemical resistance
- Semisolid with melt point [58°C – 70°C]

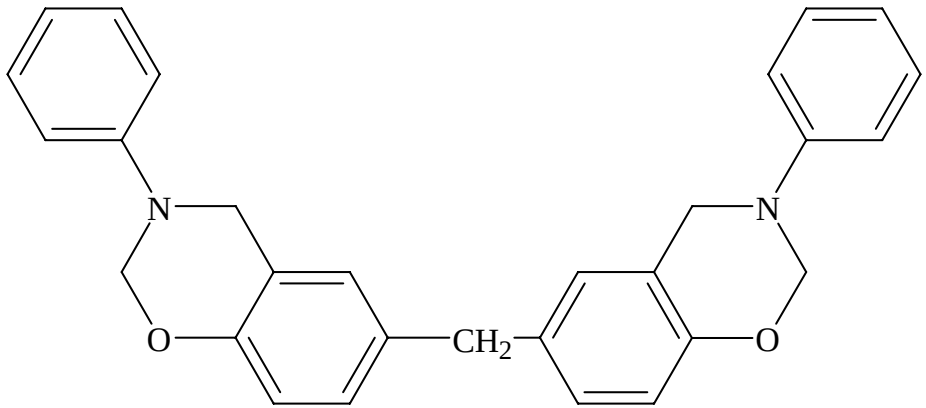


Araldite® MT 35600
N-Phenyl Bis A Benzoxazine

Bisphenol F Benzoxazine

HUNTSMAN
Enriching lives through innovation

- Good Flammability resistance [UL94 V1]
- High Tg properties
- Low smoke generation
- Low smoke toxicity
- Low Water Absorption
- High Modulus Properties
- Excellent chemical resistance
- Semisolid with melt point [55°C – 65°C]



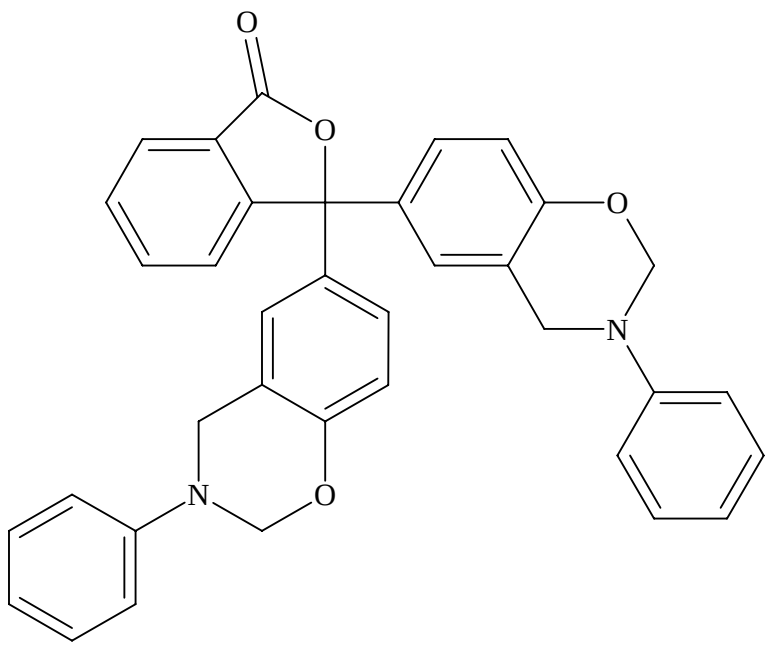
Araldite® MT 35700
N-Phenyl Bis F Benzoxazine

Phenolphthalein Benzoxazine

HUNTSMAN
Enriching lives through innovation

- Excellent (best) Flammability resistance [UL94 V0]
- High Tg properties
- Low smoke generation
- Low smoke toxicity
- Low water absorption
- High modulus properties
- Good chemical resistance
- Non sintering solid with high melt point [98 - 103°C]

Patented

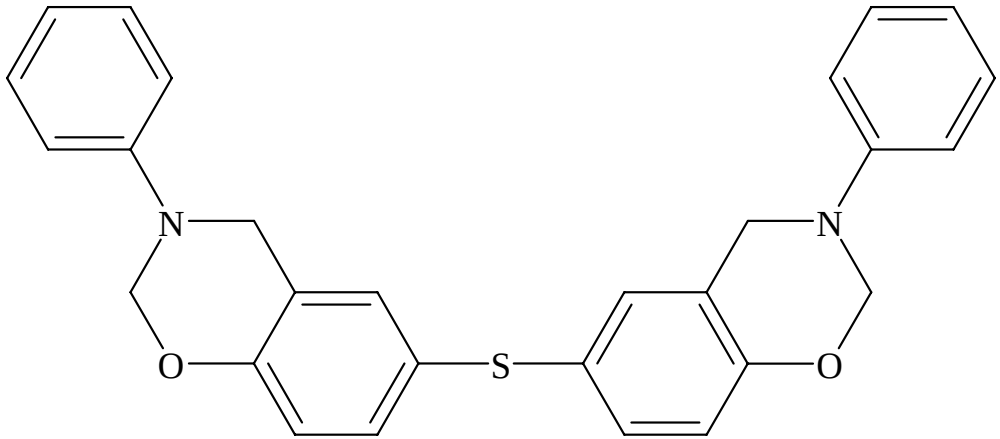


Araldite® MT 35800
N-Phenyl Phenolphthalein Benzoxazine

Thiodiphenol Benzoxazine

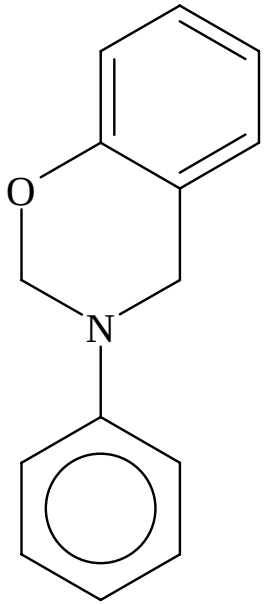
HUNTSMAN
Enriching lives through innovation

- Good flammability resistance [UL94 V1]
- Higher reactivity
- Low water absorption
- High modulus properties
- Good chemical resistance

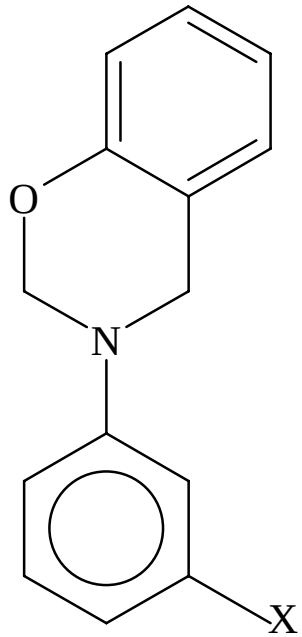


Araldite® MT 35900
N-Phenyl Phenolphthalein Benzoxazine

Liquid Benzoxazines – (Formulating)



RD 2007- 027
Phenol Benzoxazine
MW = 211
Liquid resin ; will crystallize upon standing
MP = 40°C - 60°C



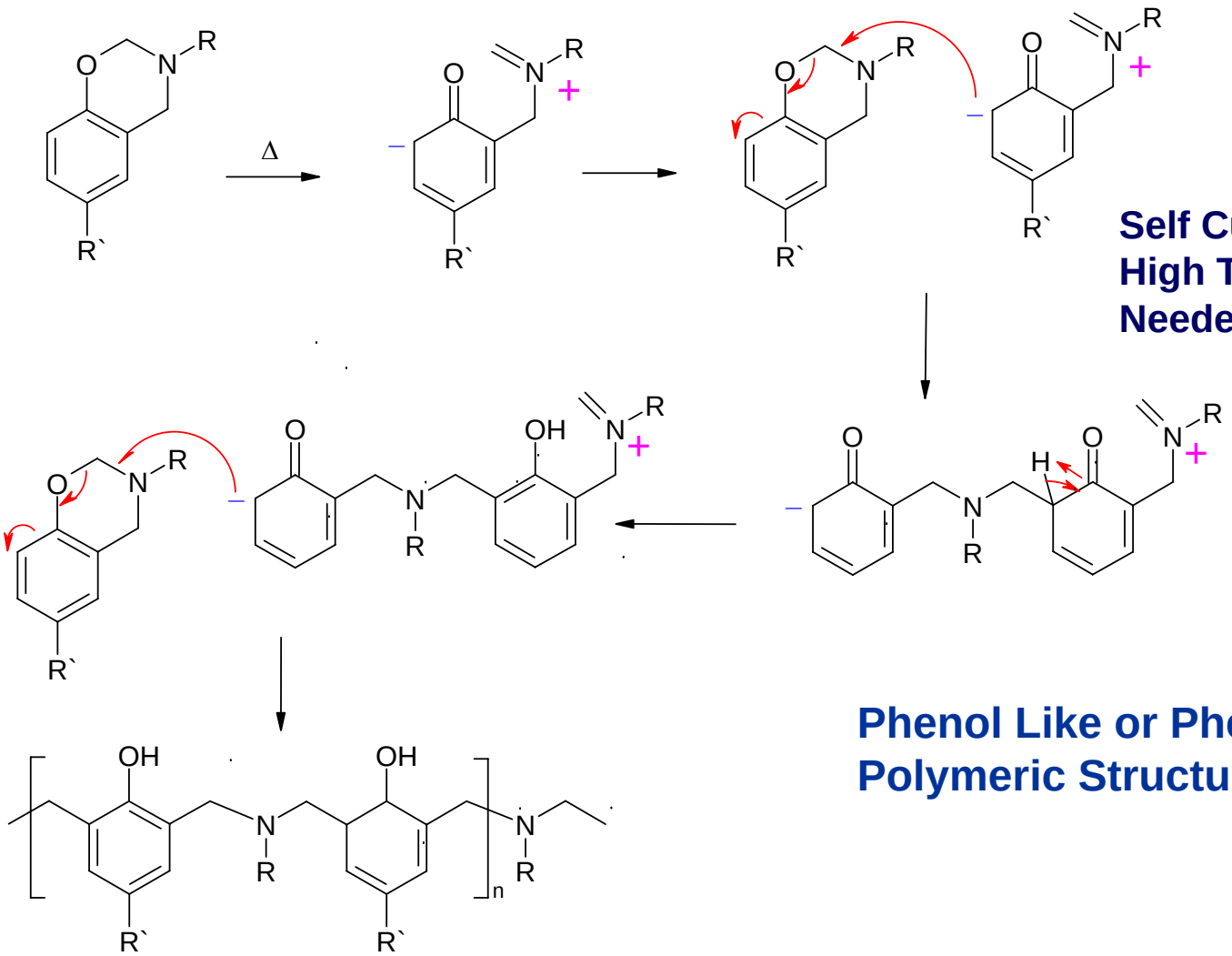
RD2009 - 008
MW = 419
Liquid resin
Visc @ 25°C = 105 cps
Stable liquid

HUNTSMAN

Enriching lives through innovation

Curing of Benzoxazines

Curing of Benzoxazine Resins



Self Curing Mechanism
High Temperatures (≥ 200°C)
Needed for Complete Cure

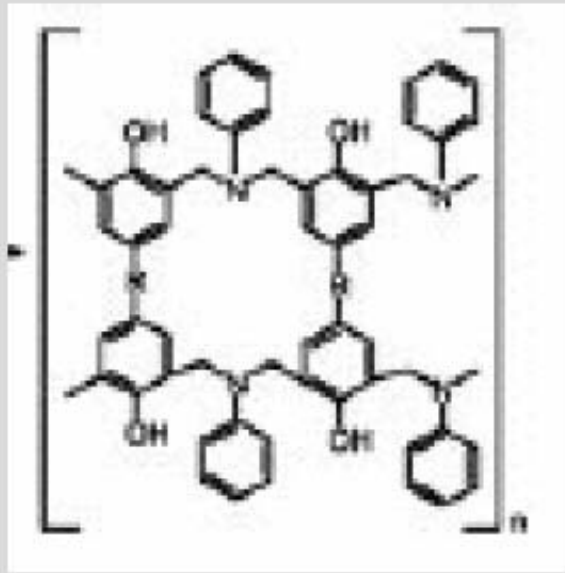
Phenol Like or Phenolic Like
Polymeric Structures

Benzoxazine Curing

HUNTSMAN
Enriching lives through innovation

On curing, Benzoxazine resins create a Phenolic like structure with inherent Flame retardant properties …

… strongly influenced by the backbone



BENZOXAZINE PROPERTIES

HUNTSMAN
Enriching lives through innovation

ADVANTAGES

- Low cost materials.
- No volatile release during cure.
- High Tg.
- Excellent thermal properties.
- Good flame retardant properties.
- Low water absorption / moisture pick-up.
- Excellent mechanical properties (modulus).
- Good electrical properties.
- Near zero shrinkage of resin.
- Storage stable at room temperature.
- Compatible with various thermosetting resins.

BENZOXAZINE PROPERTIES

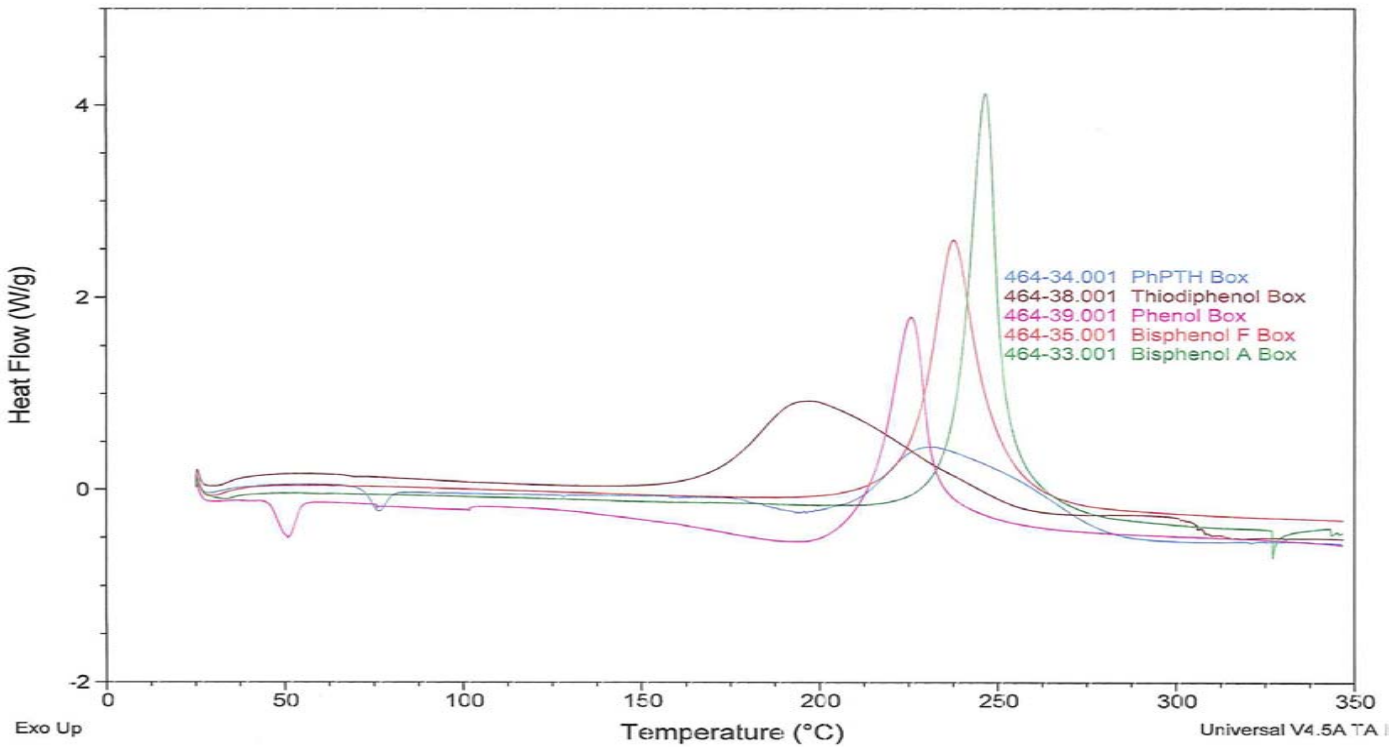
HUNTSMAN
Enriching lives through innovation

Limitation

- **Require high temperatures (min ≥ 190°C) for self curing**
  - → **Catalysts for curing available (≥ 150°C)**
  - → **Catalysts for very low temperature (<150°C) cure work is ongoing**

Reactivity of Several Neat Benzoxazines - DSC Analysis

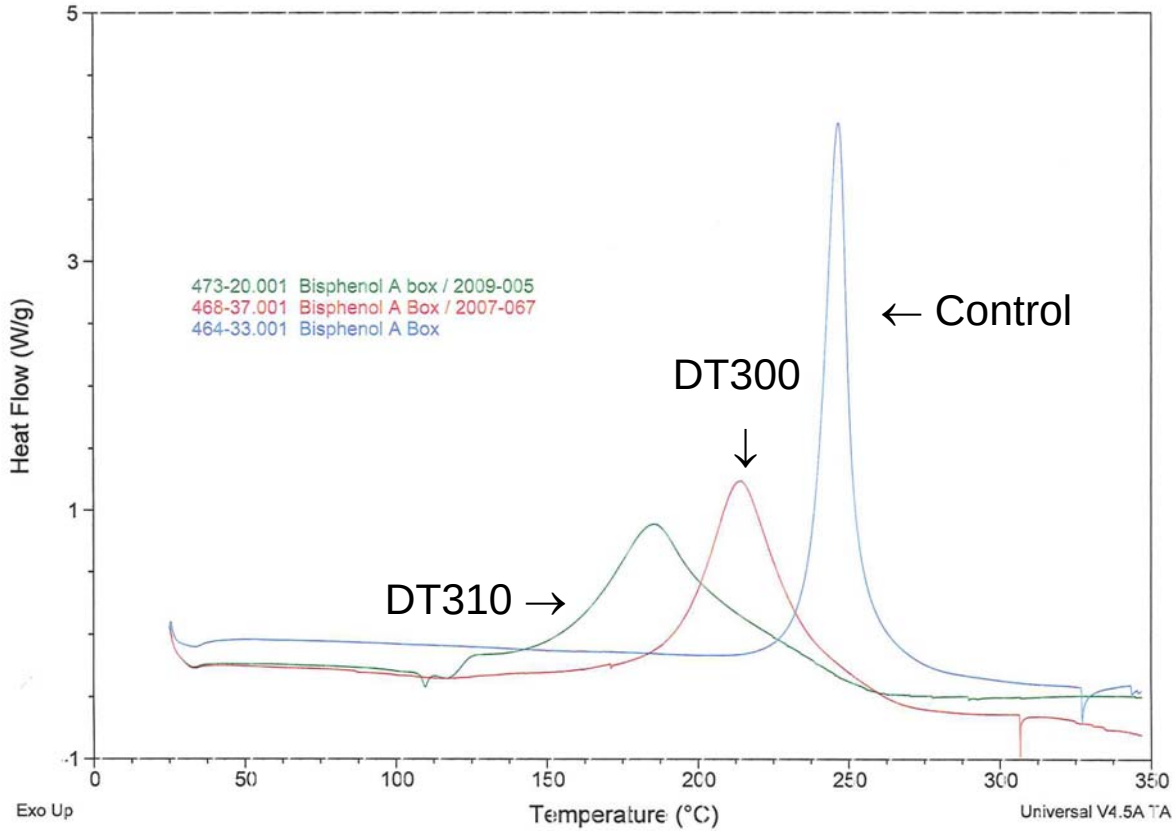
HUNTSMAN
Enriching lives through innovation



- Benzoxazines are materials that typically need high temperatures for curing to develop their properties.
- Onset and Peak temperatures for different benzoxazines shown here are typically are above 200°C
- Most reactive Benzoxazine is the thiodiphenol

DSC analysis – Catalyzed Bisphenol A Benzoxazine (Formulating)

HUNTSMAN
Enriching lives through innovation



- Catalysis of benzoxazines will reduce the cure temperatures and shorten the curing time.
- Examples of 2 such catalysts are DT300 and DT310.

Huntsman Commercial Catalysts

HUNTSMAN
Enriching lives through innovation

- Huntsman Catalysts
  - DT300 – Standard curative for benzoxazines. Good mechanical properties and doesn't detract from flammability resistance.
  - DT310 - Standard curative for benzoxazines. Very fast curative. May have small effect on flammability resistance. Not as soluble in MEK.

HUNTSMAN

Enriching lives through innovation

Flammability of Benzoxazines

HUNTSMAN
Enriching lives through innovation

UL94-V0 Test Results

Resin System	Typical Burn Time	Rating
Bisphenol A Epoxy / Dicy	n/a	Burned to clamp
MY 720 (TGMDA epoxy) / DDS	n/a	Burned to clamp
Bisphenol A Benzoxazine	> 250 seconds	burning
Thiodiphenol Benzoxazine	120 - 130	V1
Bisphenol F Benzoxazine	75 - 95	V1
Phenolphthalein Benzoxazine	30 – 40	V0

Flame Retardant Systems For Aircraft Interior Projects

HUNTSMAN
Enriching lives through innovation

Formulation Work

Objectives:

- Develop materials with good properties for interior applications
  - Low heat release
  - Minimal smoke generation
  - Flame retardant
  - Low toxicity byproducts
- Improved Toughness / Adhesion
- Similar or improved composite properties compared to phenolics
- Low Temperature cures
- Versatile for manufacturing processes
  - Systems for Solvent based and Non-Solvent based resins for prepreg, pultrusion, filament winding, RTM and infusion

HUNTSMAN

Enriching lives through innovation

Formulation and Test Results

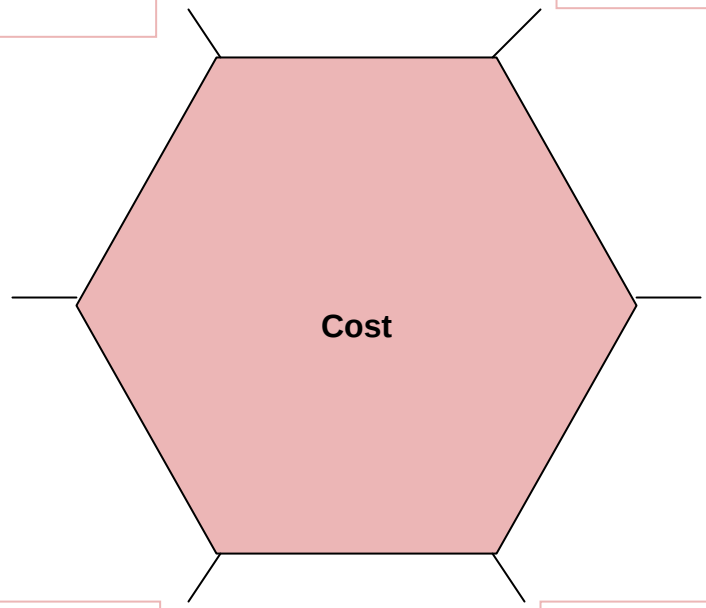
System Requirements - Formulating

HUNTSMAN
Enriching lives through innovation

Goals & Variables – Meet or Exceed Phenolic Properties

Composite Physical Properties
- Flexural
- Compressive
- Tensile
- ILSS
- Toughness

Tg Build @ Temperature
- Crosslink density
- Use Temperature
- Physical Property Build



Composite Quality
- Resin Content
- Good Wetting
- Void Content (No Off-gassing)
- Consistency

Cure Kinetics
- Cure Speed (Time/Temp.)
- Viscosity Profile
- Gel Time
- B-staged Tack/Drape

Adhesion to Core
- Nomex Core
- Other Cores

FST Properties
- Flame Retardant
- Smoke Density
- HRR
- Toxicity

Liquid Benzoxazines (Formulating)

HUNTSMAN
Enriching lives through innovation

The needs for liquid benzoxazines are:

Viscosity modification of solid benzoxazines for

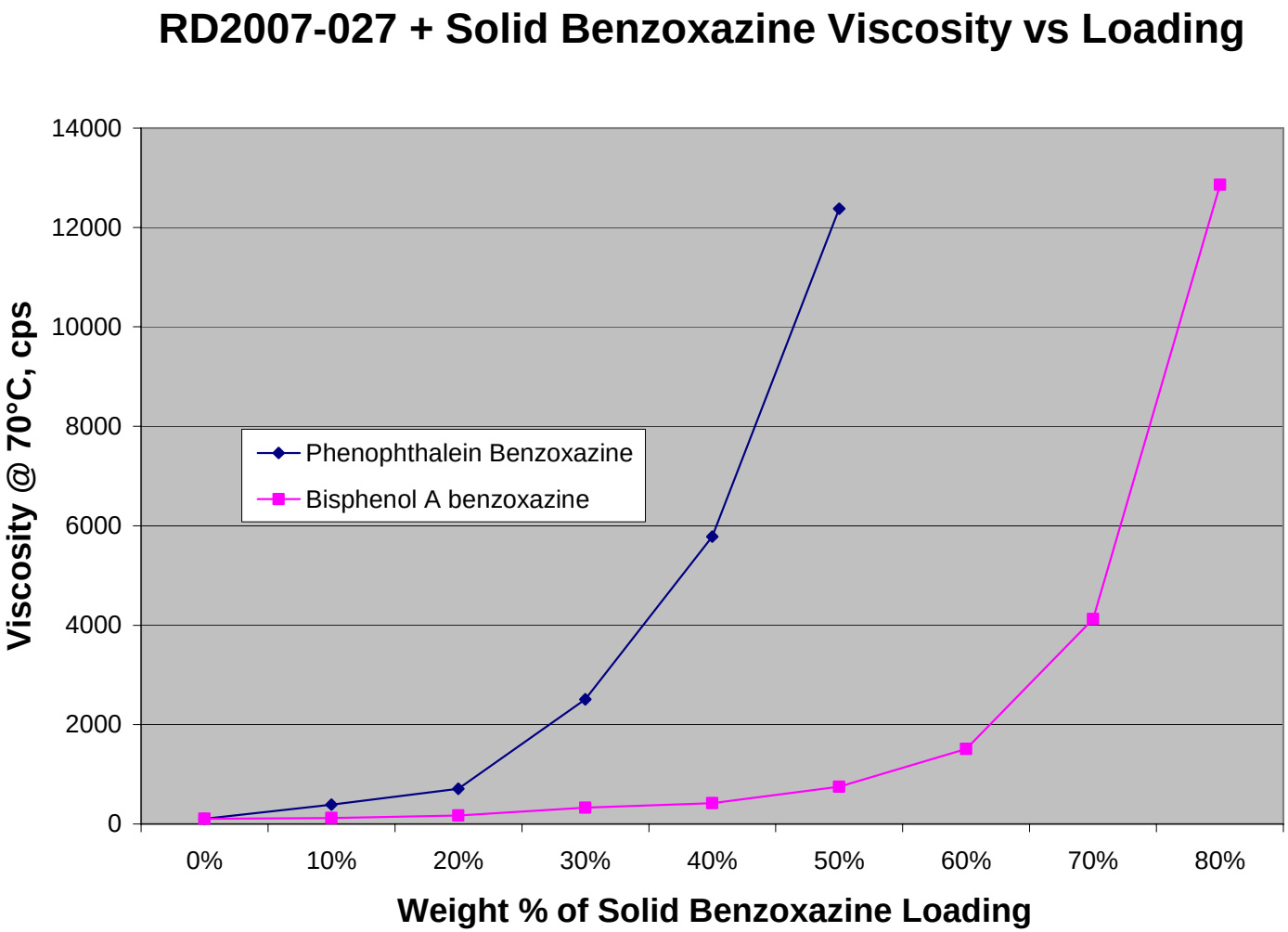
- Viscosity control or the ability to tailor the viscosity
- Expand the formulation capabilities with benzoxazine
- Make solvent free formulations

Acceleration of cure (lower onset of reaction)

Addition of tack and drape for composite applications
(Positive results have been seen)

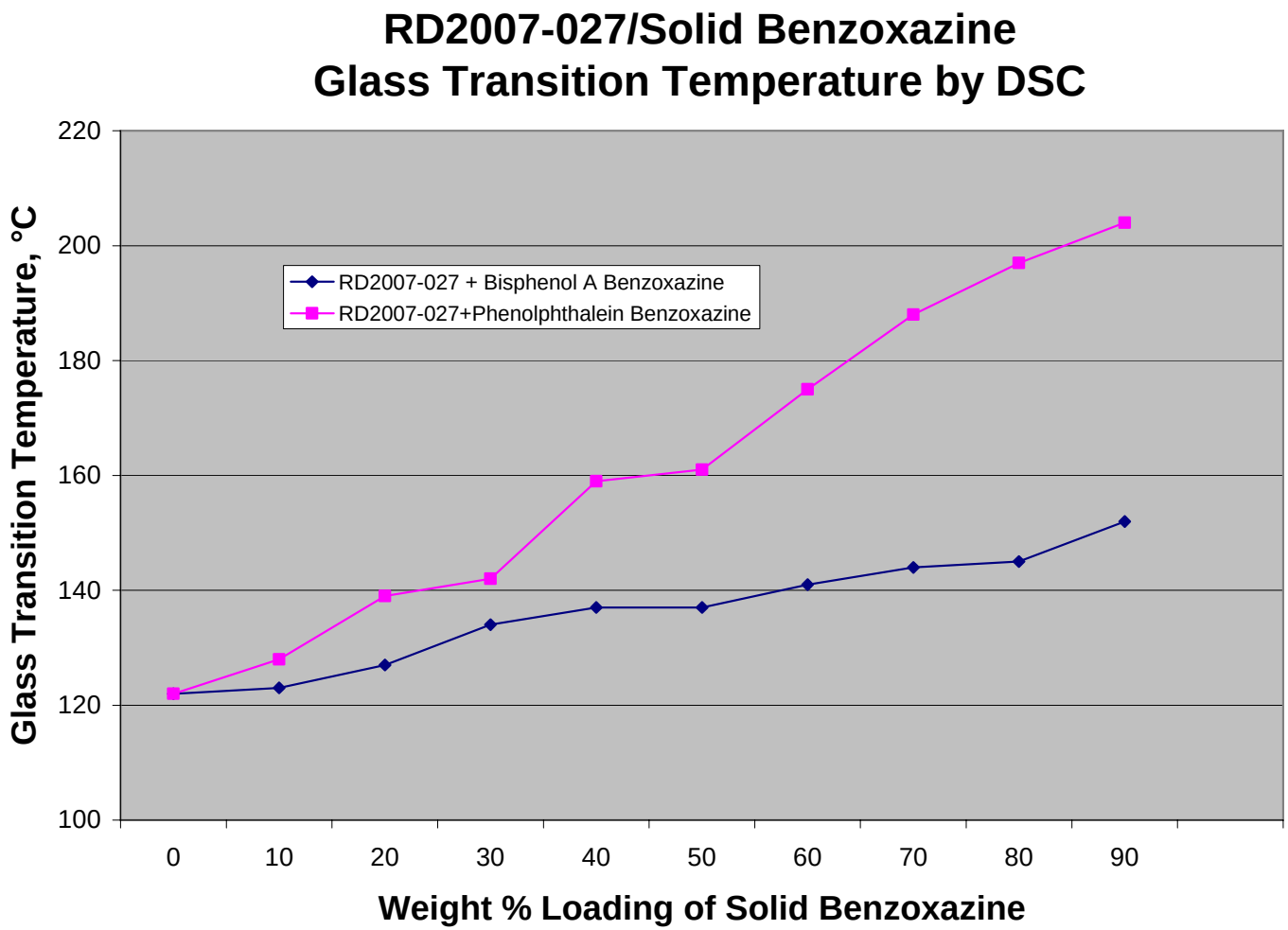
Liquid Benzoxazine Viscosity Modifier (RD 2007-027)

HUNTSMAN
Enriching lives through innovation



Liquid Benzoxazine Effect on Tg°C

HUNTSMAN
Enriching lives through innovation



Benzoxazines and blends

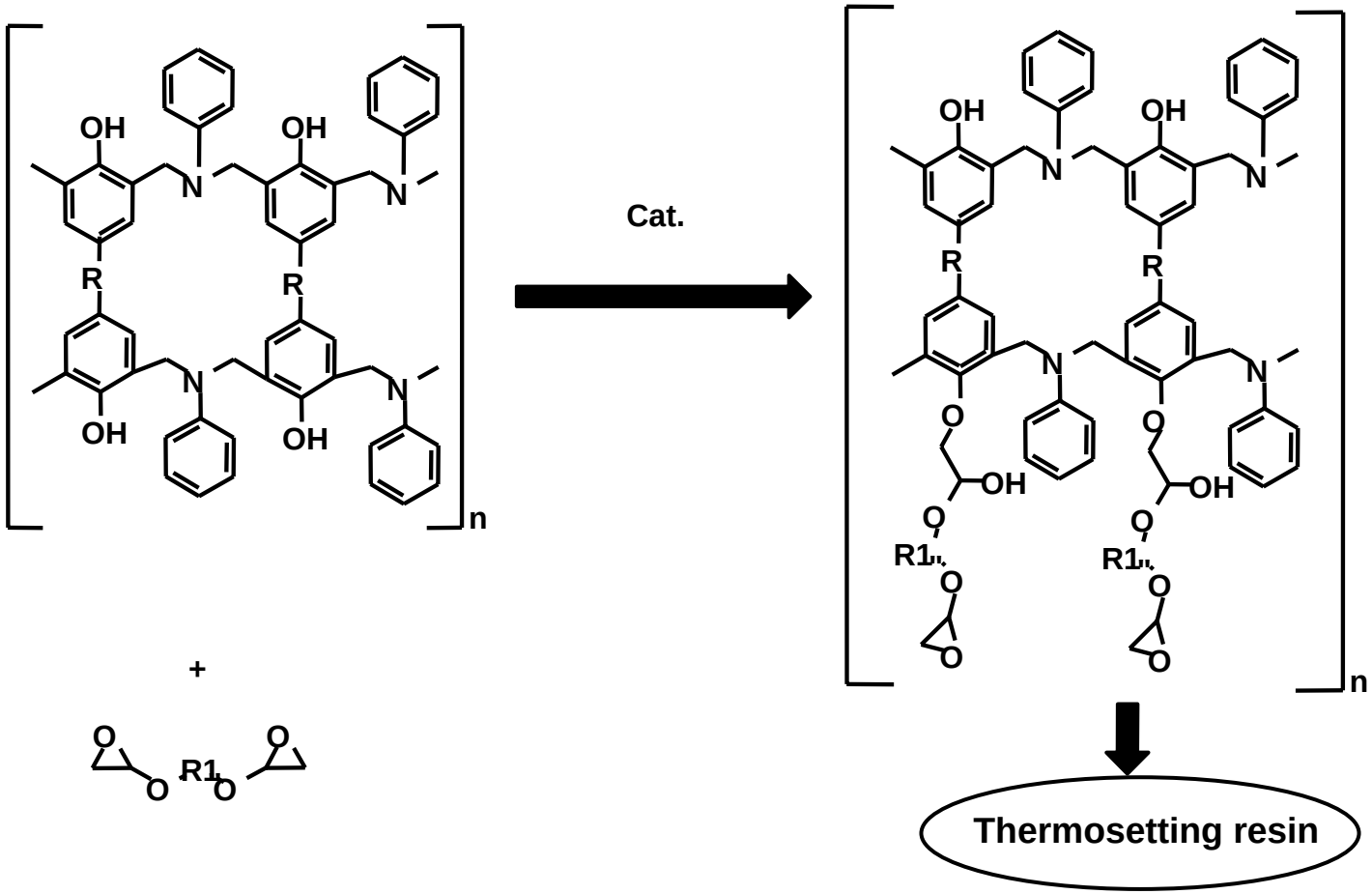
HUNTSMAN
Enriching lives through innovation

Polymeric materials based on the reaction of Benzoxazines with the following chemistries have been realized :

- Epoxy resins
- Cyanate Esters
- Maleimides / Bismaleimides
- Isocyanates
- Polyamides
- Phosphazenes
- Thermoplastics (PPO)
- Acrylates / Vinylmonomers
- Triazine compounds
- Anhydrides

Remark : Not exhaustive list …

Benzoxazines and Epoxies



Commercial System
Araldite® LZ 8282-1

HUNTSMAN
Enriching lives through innovation

- Commercial product
  - 70% solids in MEK solvent
  - Good shelf life at room temperature
  - Benzoxazine system
- Good FST properties
- High Tg system
- Primary application is for halogen free Printed Wiring Boards.
- Can be used as stand alone system or as an additive
- No phosphorous
- Room temperature stable prepreg
- Patented Propietary product

Solvent Based Formulations for Flame Retardant Prepreg for Aircraft Interiors

HUNTSMAN
Enriching lives through innovation

Formulation		LZ 8282-1	42-8743	49-8743	82-8743	50-8743
		Control				
Benzoxazine #1		X	X	X	X	X
Benzoxazine #2			X	X	X	
Catalyst #1			X	X	X	X
Catalyst #2			X	X	X	X
Epoxy				X	X	X
Toughener						X
Properties						
DSC Onset °C		217.1	152.8	151.2	164.3	160.5
DSC Peak °C		242.6	179.9	180.4	204.1	210
Viscosity @ 25°C Cps.		1200	57	200	2,500	1,825
1 Week. Viscosity @ 25°C Cps.		1200	64	290	2,750	2,650
DMA Tg - 1 hr. / 140°C Press Cure	E' Onset		85.1	90.4	95.6	70.1
Press Cure Plus 1 Hr./140°C			97.5	111.9	118.5	100.7
Press Cure Plus 1 Hr./160°C			110.5	133.2	143	111.6
Press Cure Plus 1 Hr./180°C			115.2	141.2	154	161.3
Press Cure Plus 1 Hr./200°C			122.7	144.6	161.4	171.2
Flame Testing (V-O)		V0	V0	VO	V0	VO
B-Staging		2 min./140°	2 min./140°C	1 min./140°C	2 min./150°C	5 min./150°C

Glass/Carbon Fiber Composite Physical Property Testing of 50-8743

HUNTSMAN
Enriching lives through innovation

- XU8282-1 system Has excellent FST properties.
- Initial 50-8743 glass composite property results for tensile, compressive, and 3-pt. flexural look comparable to phenolic when given a 1hr/300°F press cure.
- Initial 50-8743 glass composite property results for these properties after 1 hr./350°F cure greatly exceeded phenolic glass prepreg properties.
- Peel strength to nomex core after 1 hr./300°F cure was low in comparison to phenolic systems. Peel strength after 1 hr/350°F cure was equal or better than phenolic systems.

Aerospace Interiors Application: Preliminary Data

HUNTSMAN
Enriching lives through innovation

LZ 8282-1 / 7781 glass fabric :
Flamability of monolayer glass laminate 40% resin b.w.
Airbus Bremen Evaluation

Burning behaviour	**Test methods**	**Units**	**Phenolic Prepreg, 296 g/m² E-glass, 40% resin content** **Laminate** **1 layer**	**Benzoxazine LZ8282-1 prepreg E-glass 7781** 50% resin content **Laminate** **1 layer**
Flammability (12 sec.):	AITM 2.0002 B	mm/s/s	-	128/0/0
Flammability (60 sec.):	AITM 2.0002 A	mm/s/s	60/0/0	144/0/0
Smoke Density (Flaming):	AITM 2.0007	Ds	5	6
Toxicity (Flaming):	AITM 3.0005	ppm HCN	0	2
		ppm CO	50	113
		ppm NO_x	10	5
		ppm SO_2	0	1
		ppm HF	0	0
		ppm HCl	0	0
Heat Release/-Rate (HRR/HR):	AITM 2.0006	kw/m² kw*min/m²	65/40	58/34
Resin content (cured):		%	40	38.3
Curing conditions:				180°C, 120min, 1.0bar

FST Testing Results on Carbon Panels
Flame Retardant Epoxy vs. Formulated Benzoxazine
(10 Layer, 3K, 70 P Carbon Pressed @ 25 psi - 2 Hrs./170°C

HUNTSMAN
Enriching lives through innovation

Carbon Panel FST Properties	Test Method	Specification	RD 2009-010 Benzoxazine System	8533-91-2 Flame Retardant Epoxy/Anhydride
Flammability – 60 second vertical burn	FAR 25.853			
Extinquish Time –		**15 seconds max.**	**0.0**	**13.2**
Burn Length –		**6 inches max.**	**1.7**	**2.4**
Drip Extinquish Time -		**3 seconds max.**	**0.0**	**0.0**
Smoke Density	Title 14 CFR 25.853			
Specific Optical Density -	Boeing BSS 7238	**200 (Ds) Maximum average smoke density**	**32.5**	**147.8**
Heat release	Title 14 CFR 25.853 (d)			
Total Heat Release –	Amendment 25.83	**65 kW Min./m2 Max.**	**72.2**	**129.1**
Peak Heat Release-	Appendix F, part IV	**65 kW/m2 Max.**	**89.1**	**151.8**
Toxicity	BSS 7239 Boeing document # D6-51377 Rev. F	**HCN – 150 max.** **CO – Ref.** **NOx – 100 max.** **SO2 – 100 max.** **HF – 200 max.** **HCL – 500 max.**	**<5** **22** **10** **<20** **<25** **<5**	**<5** **143** **<5** **<20** **<25** **<5**

50-8743 FST Properties on glass - 39% Resin Content / 10 layer 7781 Glass / Press Cured @ 40 psi. 1 Hr/300°F & 1 Hr/350°F

HUNTSMAN
Enriching lives through innovation

Glass Panel FST Properties (1 hr./ 350°F press-cure)	Test Method	Specification	50-8743 1 hr/300°F	50-8743 1 hr./350F
Flammability – 60 second vertical burn	FAR 25.853			
Extinquish Time –		**15 seconds max.**	**0**	**0**
Burn Length –		**6 inches max.**	**2.0**	**1.8**
Drip Extinquish Time -		**3 seconds max.**	**0**	**0**
Smoke Density	Title 14 CFR 25.853			
Specific Optical Density -	Boeing BSS 7238	**200 (Ds) Maximum average smoke density**	**41.4**	**31**
Heat release	Title 14 CFR 25.853 (d)			
Total Heat Release –	Amendment 25.83	**65 kW Min./m2 max.**	**64.6**	**53**
Peak Heat Release-	Appendix F, part IV	**65 kW/m2 Max.**	**110.3**	**93**
Toxicity	BSS 7239 Boeing document # D6-51377 Rev. F	**HCN – 150 max.** **CO – 1000 max.** **NOx – 100 max.** **SO2 – 100 max.** **HF – 200 max.** **HCL – 500 max.**	**6** **194** **11** **<25** **<30** **<15**	**<5** **156** **<5** **<25** **<30** **<5**

82-8743 Composite Comparisons to H.T. Epoxy Laminating systems – Physical Properties

HUNTSMAN
Enriching lives through innovation

Glass Panel Properties	Test Method	4005/1500	4017/1510	82-8743
Flexural Strength @ R.T. Ksi	ASTM D790-03	35	36	41.6
Flexural Modulus @ R.T. Ksi	ASTM D790-03	1600	1600	3140
Tg DMA E' onset	ASTM D-4065	305°F	350°F	315°F
Lay-up Procedure		Vacuum Bagged	Vacuum Bagged	*Pressed @ 25 psi.
Cure		Stepcure+ 2 Hrs/300°F	Stepcure + 3 Hrs/350°F	*1 Hr/300°F + 1 Hr/350°F

Composites are 10 layer Volan A 7500 Glass / 90 ° Rotation

Summary and Conclusion

HUNTSMAN
Enriching lives through innovation

- **Flame Retardant Benzoxazine can Pass FST Requirements.**
  - Additives can lower Peak HRR.

- **Catalysts Can Greatly Lower Cure Onset on Benzoxazine Resins**

- **Liquid Benzoxazines are Shown to Reduce Viscosity, Accelerate Cure, and add Tack/Drape.**

- **Benzoxazine and Benzoxazine / Epoxy Blends can exceed Phenolic System Composite Properties (with given cures)**
  - Modulus , Ultimate Strength, Thermal Stability, Tg

- **Formulated System 50-8743 is promising.**

References

HUNTSMAN
Enriching lives through innovation

References

(1) Arkema Inc., King of Prussia, PA., Nanostrength® SBM E 20 Nano-Core Shell Toughener

(2) Roger Tietze, Technical Manager Composites Group Advanced Materials, Huntsman Corporation.

(3) Chantal Hubschmid, Formulation Chemist, Huntsman Corporation

(4) Testcorp, Mission Viejo, CA

(5) Patel, Neal & Mortimer, Steve - Hexcel Composites Limited, International patent “Improved Moulding Processes” International Patent #WO 2009/138749 A1, 19 November 2009.

HUNTSMAN

Enriching lives through innovation

Auxiliary Slides

(Auxiliary Slide#1) Bisphenol A Benzoxazine – 10% Toughener Loading

HUNTSMAN
Enriching lives through innovation

Toughener	SBM E 20	PY4122	LT1522	DY026	DY3601	DY-K
Cure cycle: 2h@180˚C + 2h@200˚C						
Flexural test (ISO 178/01)						
Flexural modulus (MPa)	4260	4917	4775	4674	4694	5008
Flexural strength (MPa)	157	118	165	114	108	107
Ultimate Elongation (%)	3.5	2.3	3.2	2.2	2.1	2.0
Tensile test (ISO 527T2/93)						
Tensile modulus (MPa)	4425	4906	4934	4824	4948	5171
Tensile strength (MPa)	63	51	79	37	44	40
Ultimate Elongation (%)	1.6	1.1	1.8	0.8	0.9	0.8
Bend Notch test (ISO 13586/03) of neat resin						
$K1_C$ (MPa√m)	0.975	0.686	0.943	0.679	0.725	0.682
$G1_C$ (J/m^2)	226	80.5	158.5	83.1	94.1	78.5
Cure cycle: 2h@180˚C + 4h@200˚C						
Flexural test (ISO 178/01)						
Flexural modulus (MPa)	4315	4893	4500	4862	4970	4896
Flexural strength (MPa)	141	155	183	121	127	129
Ultimate Elongation (%)	3.02	3.0	3.8	2.3	2.3	2.4
Bend Notch test (ISO 13586/03)						
$K1_C$ (MPa√m)	1.236	0.668	1.128	0.674	0.741	0.675
$G1_C$ (J/m^2)	298	76.9	237.5	79	94	79

(Auxiliary Slide#2)
Araldite® MY 0816 Epoxy

HUNTSMAN
Enriching lives through innovation

Attributes

- Lower flammability other epoxies
- High viscosity liquid
- High Tg epoxy
- Good chemical resistance
- Low smoke density
- Good adhesion characteristics
- High Modulus