Advanced Woven SiC/SiC Composites for High Temperature Applications

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The temperature, stress, and environmental conditions of many gas turbine, hypersonic, and even nuclear applications make the use of woven SiC/SiC composites an attractive enabling material system. The development in SiC/SiC composites over the past few years has resulted in significant advances in high temperature performance so that now these materials are being pursued for several turbine airfoil and reusable hypersonic applications. The keys to maximizing stress capability and maximizing temperature capability will be outlined for SiC/SiC. These include the type of SiC fiber, the fiber-architecture, and the matrix processing approach which leads to a variety of matrix compositions and structure. It will also be shown that a range of mechanical, thermal, and permeability properties can be attained and tailored depending on the needs of an application. Finally, some of the remaining challenges will be discussed in order for the use of these composite systems to be fully realized.

Composites at Lake Louise Canada
October 28th to November 2nd, 2007

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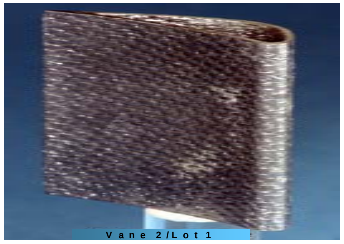
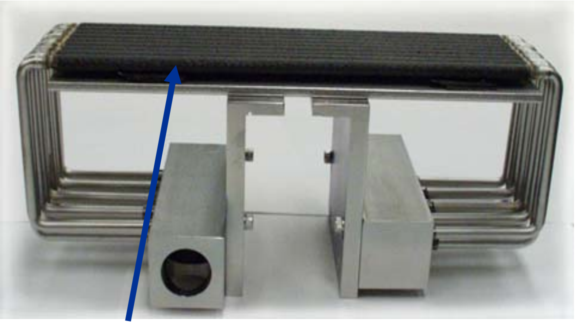
The Need for High Temperature ***Load-Bearing*** CMC

- Current SOA is Sylramic-iBN reinforced Melt (Si) -Infiltrated CMC → NASA N24A
  - 1315^{o}C use-temperature for ~ 1000 hours and 100 MPa – would like higher stress capability for turbine components
- Higher temperature applications for advanced turbine and scramjet engines, TPS structures, leading edge applications, and even nuclear applications *prohibit the use of free matrices with free Si*
- Therefore, need for *higher stress capability* (e.g., blades) and *higher temperature capability* CMC (e.g., leading edge and TPS structures)



Inlet Turbine Vane



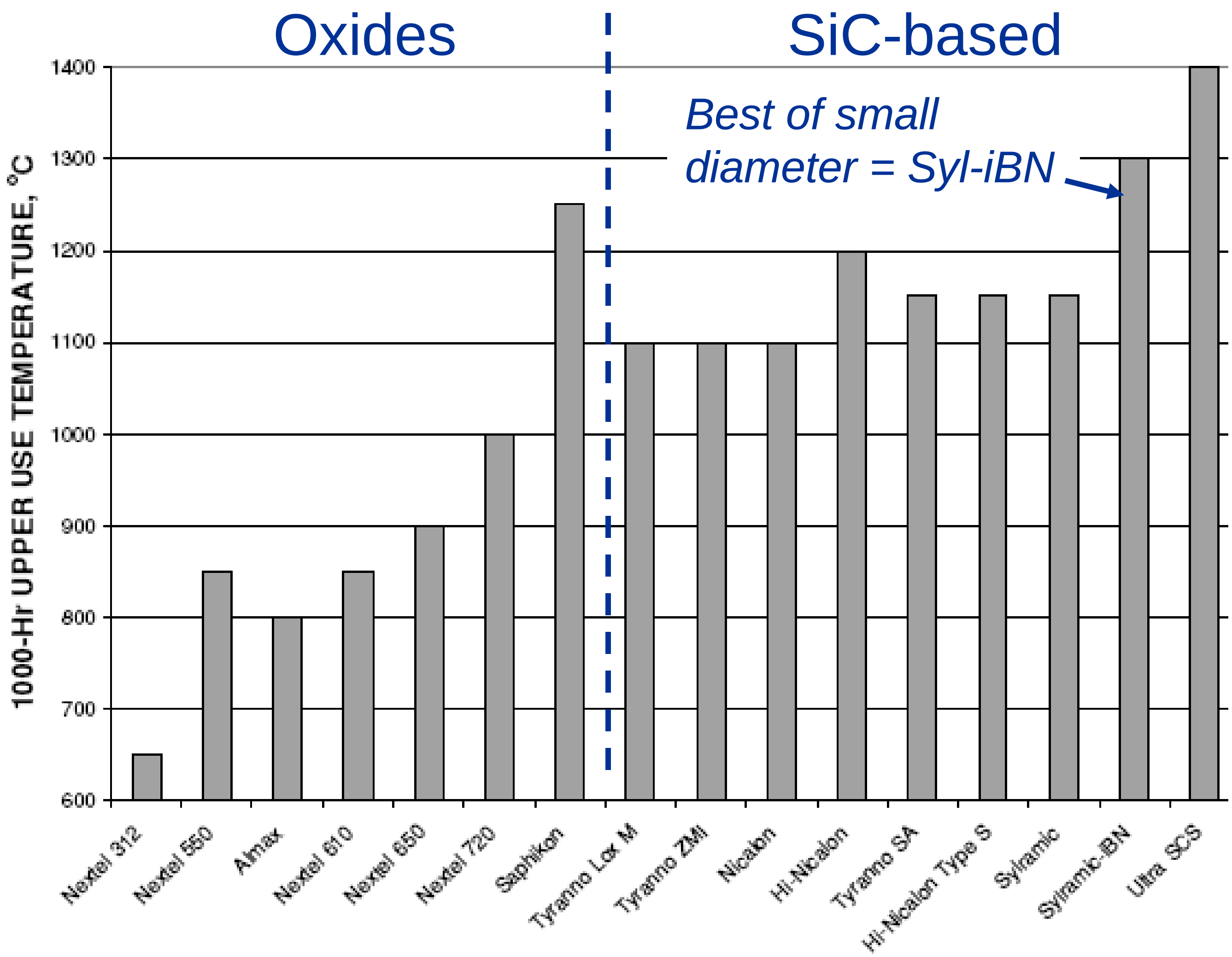
Thin-cooled structure

Outline

- The best fiber: Sylramic-iBN for $\geq$ 1300^{o}C applications
  – As the fiber goes, so goes the composite
- Fiber architectures that enable
  – Understanding the effect of fiber architecture in order to fabricate the best combination of composite properties
- SiC matrices for higher temperatures
  – Increasing temperature requirements prohibit free Si
- Implications and Conclusions

Fiber Comparison

1000 hr Use Temperature (σ_f = 500 MPa)



Sylramic-iBN:

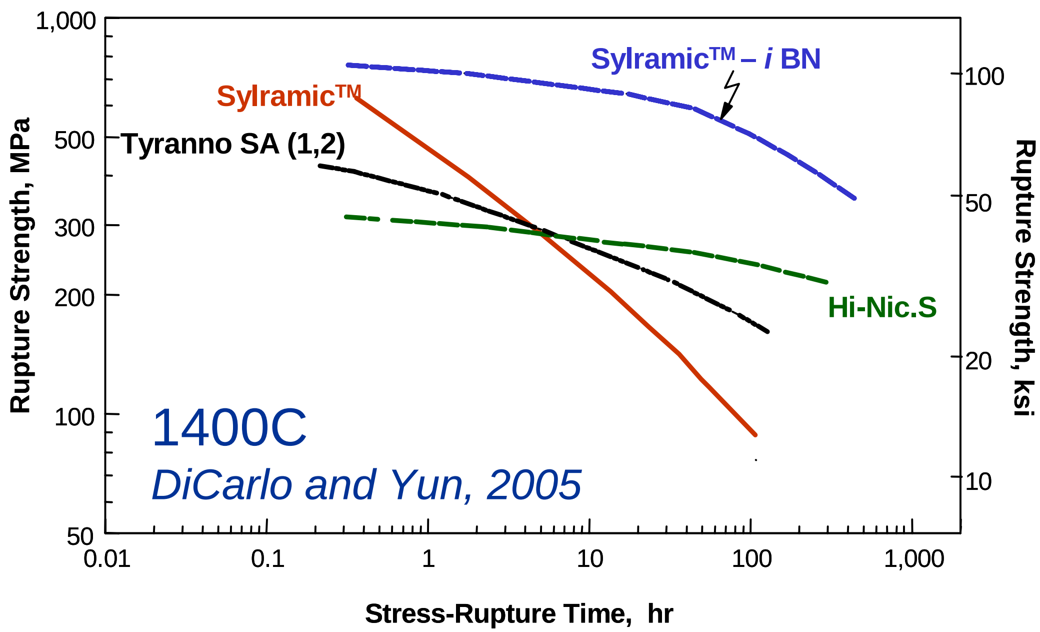
Polycrystalline B-containing SiC fiber (Sylramic, processed by COIC) subjected to post-process nitrogen containing heat treatment at high temperature (> 1700ºC).

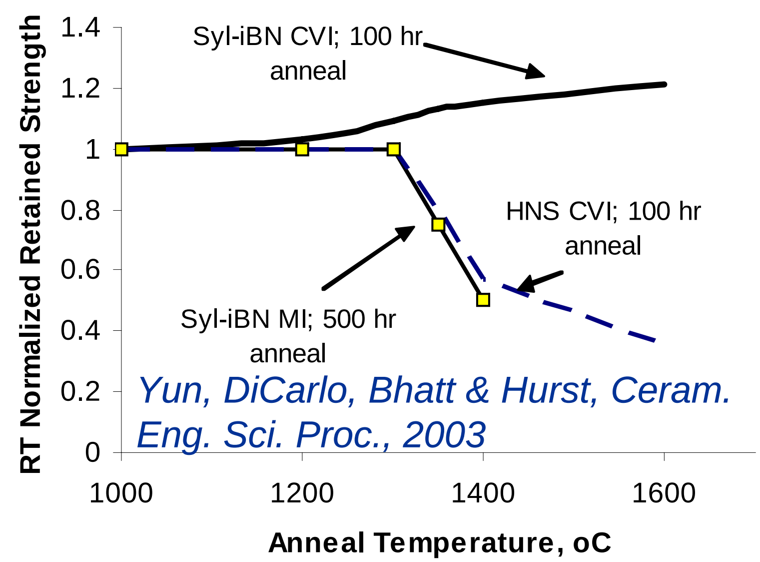
Removes B and improves creep-rupture properties

From, J.A. DiCarlo and H.M. Yun, Handbook of Ceramic Composites, Chapter 2 (Kluwer: NY, 2005)

Sylramic-iBN Based Composites for Applications ≥ 1300°C

- Sylramic-iBN = NASA derived heat treatments of Sylramic fiber
- Excellent creep resistance and thermal stability (up to 1800°C)
  - Best mechanical performance at high temperatures
  - In-situ grown (tailorable) BN-based interphase composition
  - Enables high temp processing routes not possible with other fiber-types, usually at temperatures well above the application use temperature!

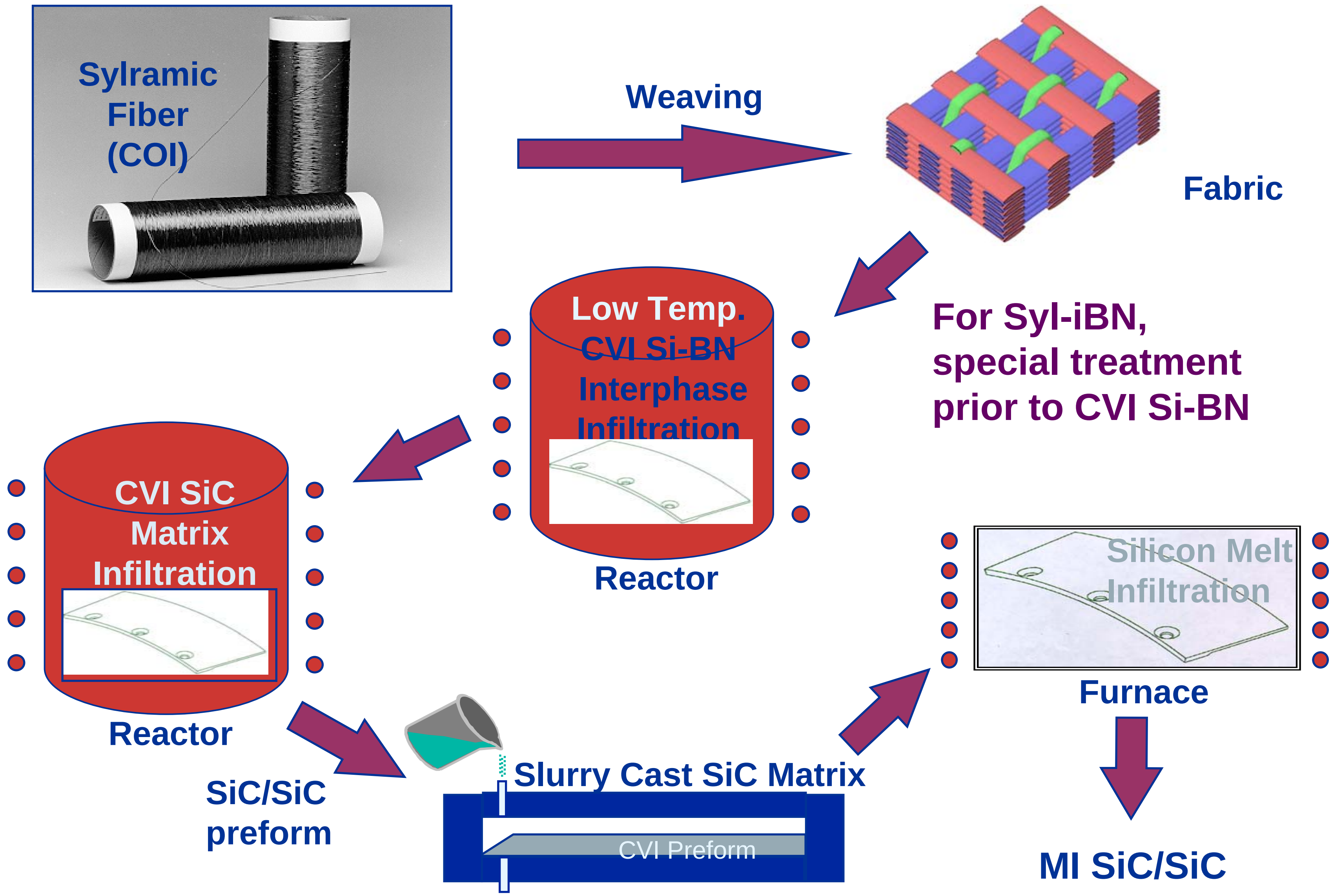




Fiber Architectures that Enable Processing and Properties for Desired Components

Approach → Process a wide variety of fiber-architectures in order to (1) determine the effect of architecture on composite properties for the purpose of tailoring properties in desired directions and (2) determine if these architectures could be successfully fabricated in order to anticipate processing further architecture modifications.

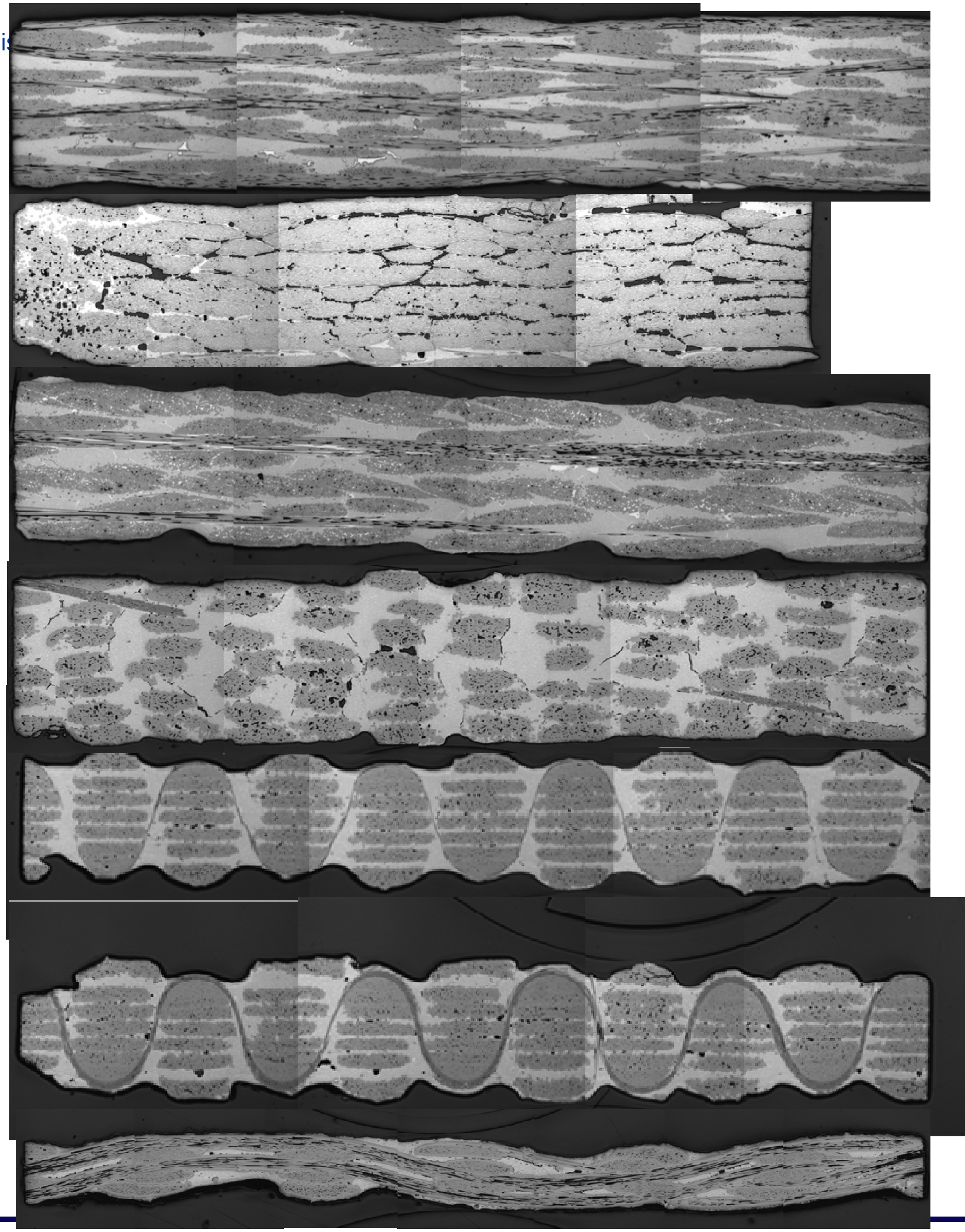
Standard Slurry Cast Melt-Infiltrated (MI) 2D&3D Woven Composites (GEPSC, Newark Delaware)



Tailoring Cracking Behavior with Fiber Architecture (Syl-BN MI Composites)

- A variety of architectures are being studied for the Syl-iBN MI system to determine effect of fiber architecture and fiber content on matrix cracking
  - 2D five harness satin with different tow ends per inch
    - Standard composite (N24A) = 8 layers of balanced 7.9 epcm (20 epi)
  - 2D five harness satin with different tow sizes
  - 3D orthogonal with different Z fibers – balanced and unbalanced in X and Y direction
  - Layer to layer angle interlock
  - Through the thickness angle interlock (with low Y fiber content) ≅ ***Unidirectional composite***
  - 2D five harness satin with high tow ends per inch in X direction and rayon in Y direction ≅ ***Unidirectional composite***

Some Cross-Sections



Determination of Fiber Volume Fraction

f_o = fraction of fibers that bridge a matrix crack (0 = loading direction), including fibers at an angle, e.g., a braided architecture

$$f_o = \frac{N_f A_f}{A_c} = \frac{N_{ply} N_{f/tow} N_{tows/ply} \pi R_f^2}{tw}$$

$$N_{tows/ply} = \frac{epcm}{10} w$$

$$f_o = \frac{N_{ply} N_{f/tow} epcm \pi R_f^2}{10t}$$

N_f = total number of fibers in the cross-section of the tensile specimen,

A_f = area of a fiber

A_c = cross-sectional area of the tensile specimen (tw)

N_{ply} = # of plys or layers through the thickness,

$N_{f/tow}$ = # of fibers per tow (800 for Syl-iBN),

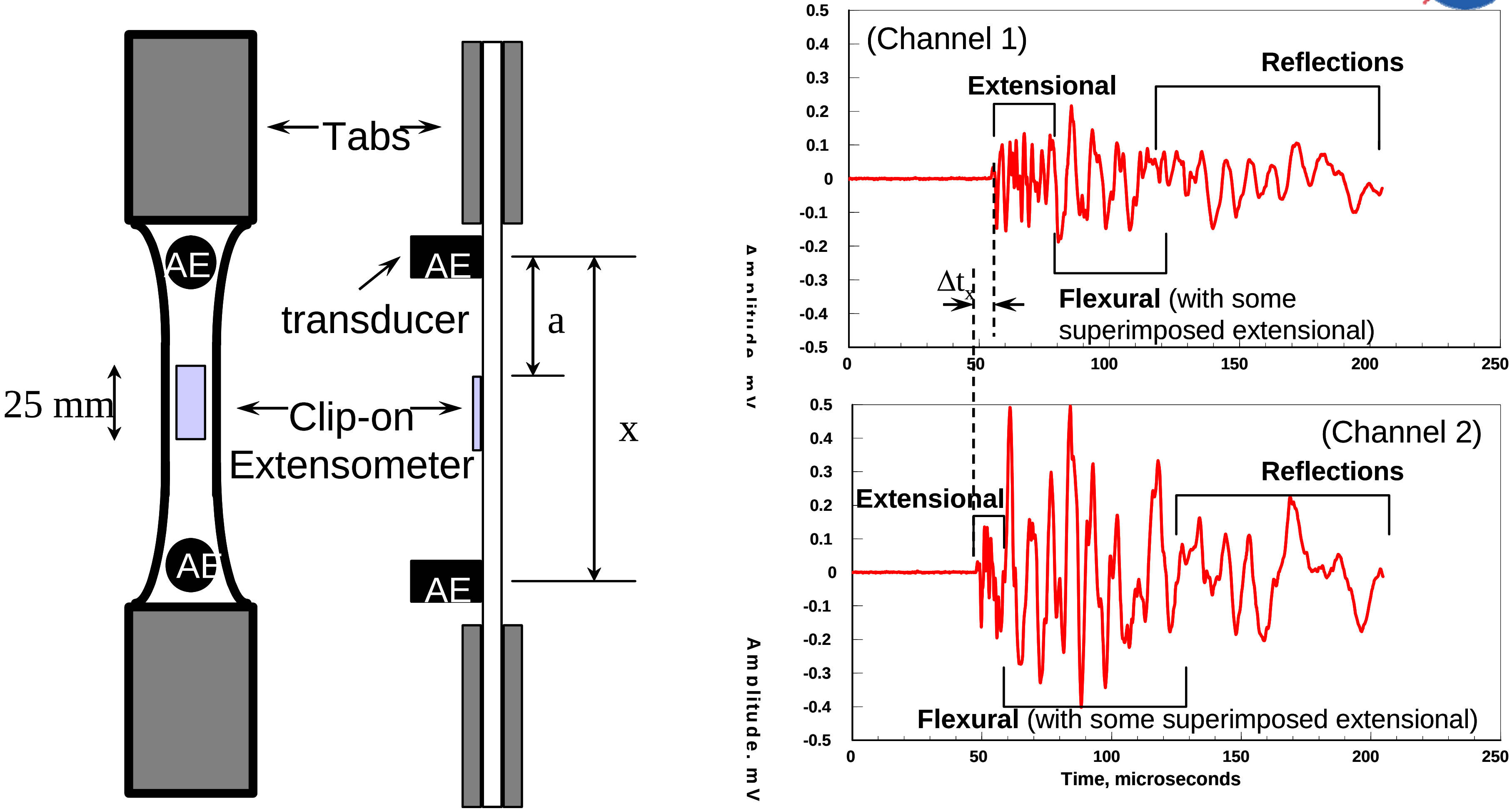
$N_{tows/ply}$ = number of tows per ply or layer

R_f is the fiber radius (5 mm or 0.005 mm for Syl-iBN).

epcm = tow ends per cm

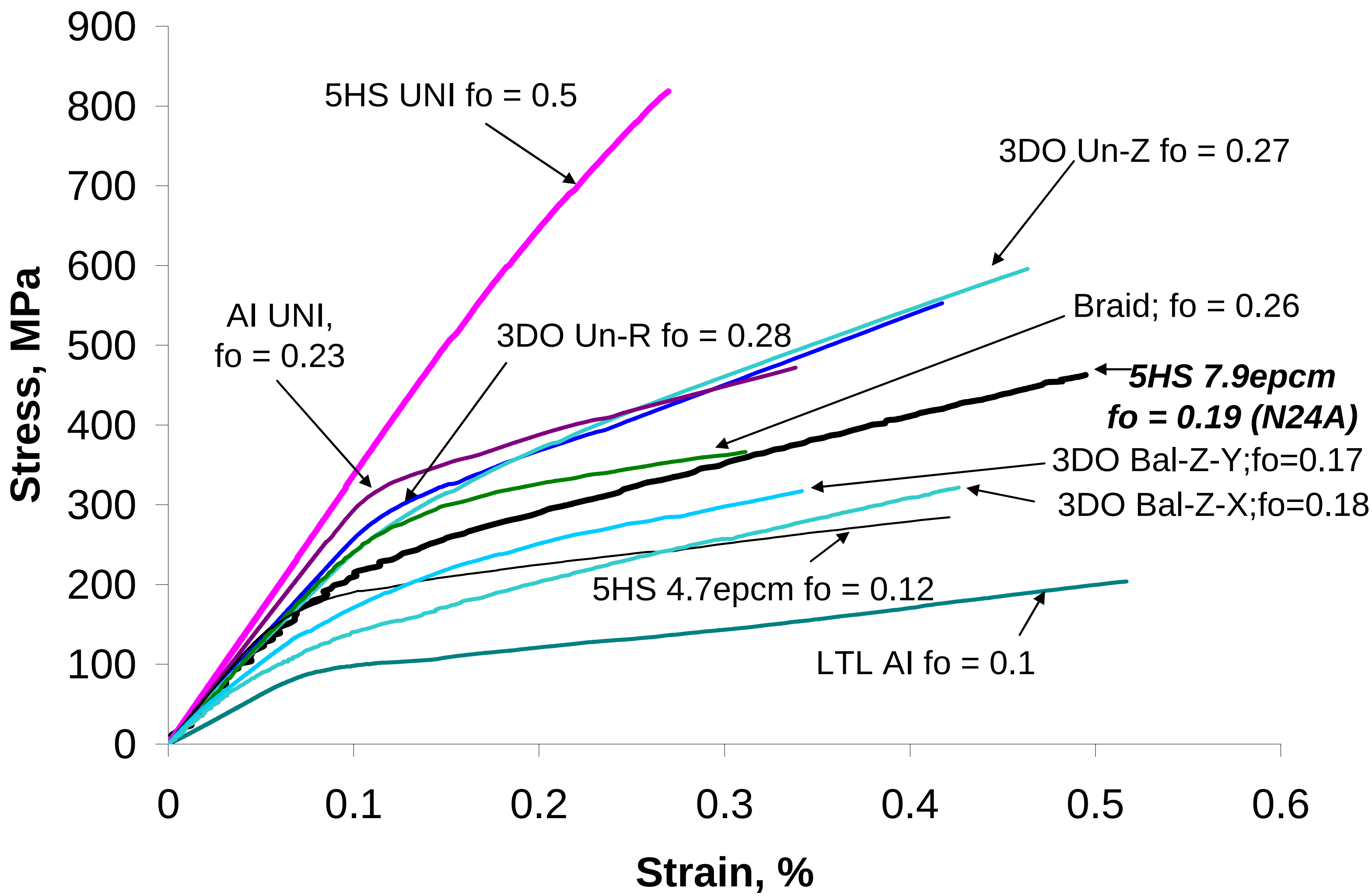
Composite	Description	Thickness (mm)	Fiber fraction, $f_{o,}$ in load direction	E (GPa)	UTS (MPa)
5HS UNI (1)	Unbalanced five-harness satin; fill direction = Sylramic at 17 epcm; warp direction = low epcm rayon	2.17	0.50	335	>818
AI UNI (2)	Unbalanced through-the-thickness angle interlock; fill direction = Sylramic at 11 epcm, 7 layers; warp direction = low epcm ZMI and rayon	2.0	0.23	305 $\pm$ 4	>472
3DO-Un-R (2)	Unbalanced 3D orthogonal; Y (loading) direction = Sylramic at 9.8 epcm, 7 layers; X direction = Sylramic at 3.9 epcm; Z direction = Rayon	1.53	0.28	275 $\pm$ 9	>575
3DO-Un-Z (2)	Unbalanced 3D orthogonal; Y (loading) direction = Sylramic at 9.8 epcm, 7 layers; X direction = Sylramic at 3.9 epcm; Z direction = ZMI	1.58	0.27	262 $\pm$ 9	596
LTLAI (1)	Layer-to-layer angle interlock; 5.5 epcm, 3 layers	0.96	0.10	125	204
2D 5HS [6]	Standard balanced 2D five-harness satin; ply lay up; number of plys varied from 4 to 8; epcm varied from 4.9 to 8.7.	1.5 to 2.2	0.12 to 0.2	220 to 290	See [6]
2D 5HS [6] (double tow)	Balanced 2D five-harness satin ply lay up; two tows woven together at 3.9 epcm, 8 plys.	2.1	0.19	197	480
Braid [8]	Triaxial braid; double tow; -67/0/67 – tested in hoop orientation so fibers are oriented $\pm$ 23^o to testing axis, 4 layers		0.26	250	352
3DO-Bal-R-Y [7]	Nearly balanced 3D orthogonal; Y (loading) direction = Sylramic single tow at 7.9 epcm,8 layer; X direction = Sylramic double tow at 3.9 epcm; Z fiber = Rayon	1.95	0.20	238	336
3DO-Bal-Z-Y [7]	Nearly balanced 3D orthogonal; Y (loading) direction = Sylramic single tow at 7.1 epcm,8 layer; X direction = Sylramic double tow at 3.9 epcm; Z fiber = ZMI	2.05	0.17	248	317
3DO-Bal-Z-X [7]	Same as 3DO-Bal-Z except oriented in the X (fill) direction (7 layer)	2	0.18	205	322

Modal Acoustic Emission of CMCs

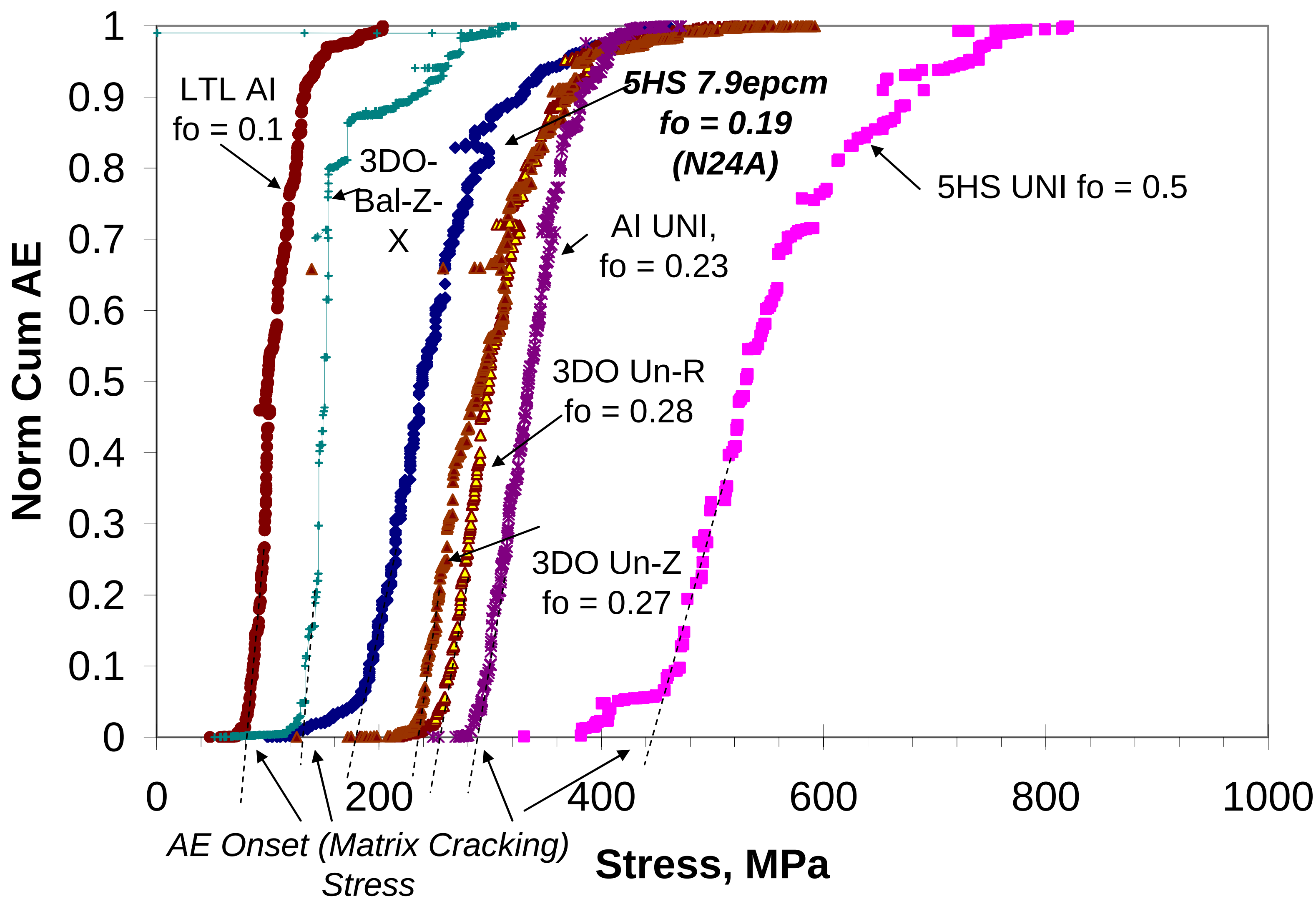


- ***Locate damage events and failure events → Δt***
- ***Monitor stress(or time)-dependent matrix cracking → Cumulative AE Energy***
- Identify damage sources, e.g. matrix cracks, fiber breaks → Frequency
- Measure stress(or time) dependent Elastic Modulus → Speed of sound

RT 0º σ/ε of Different Architecture Syl-iBN MI Composites

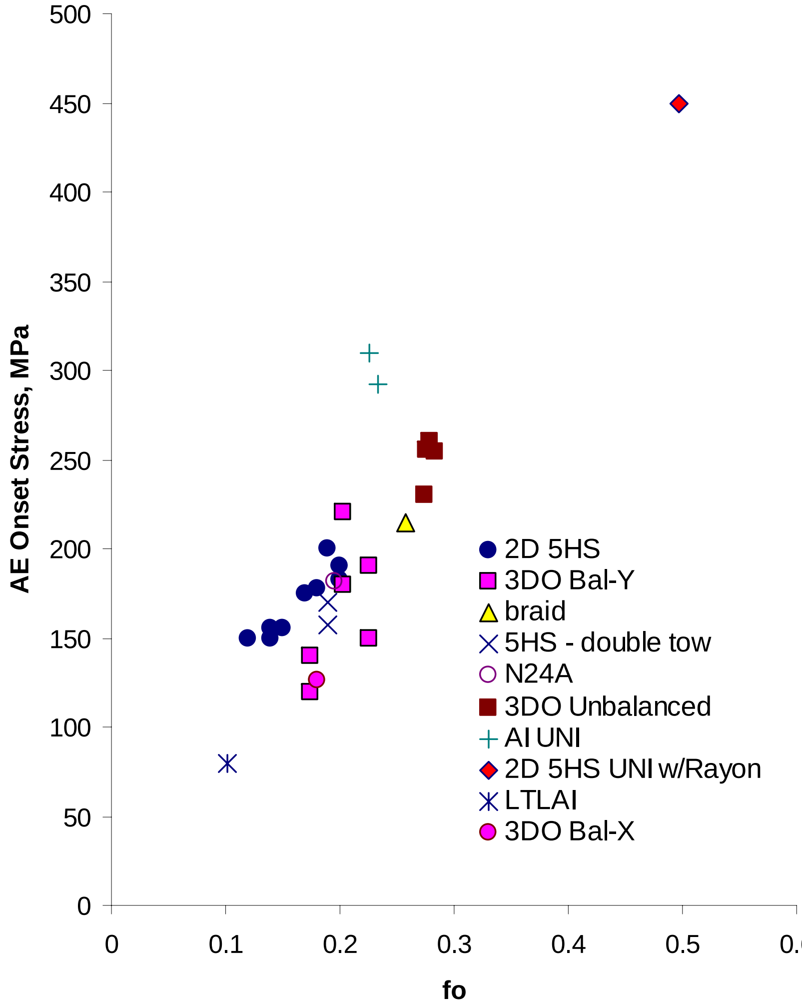


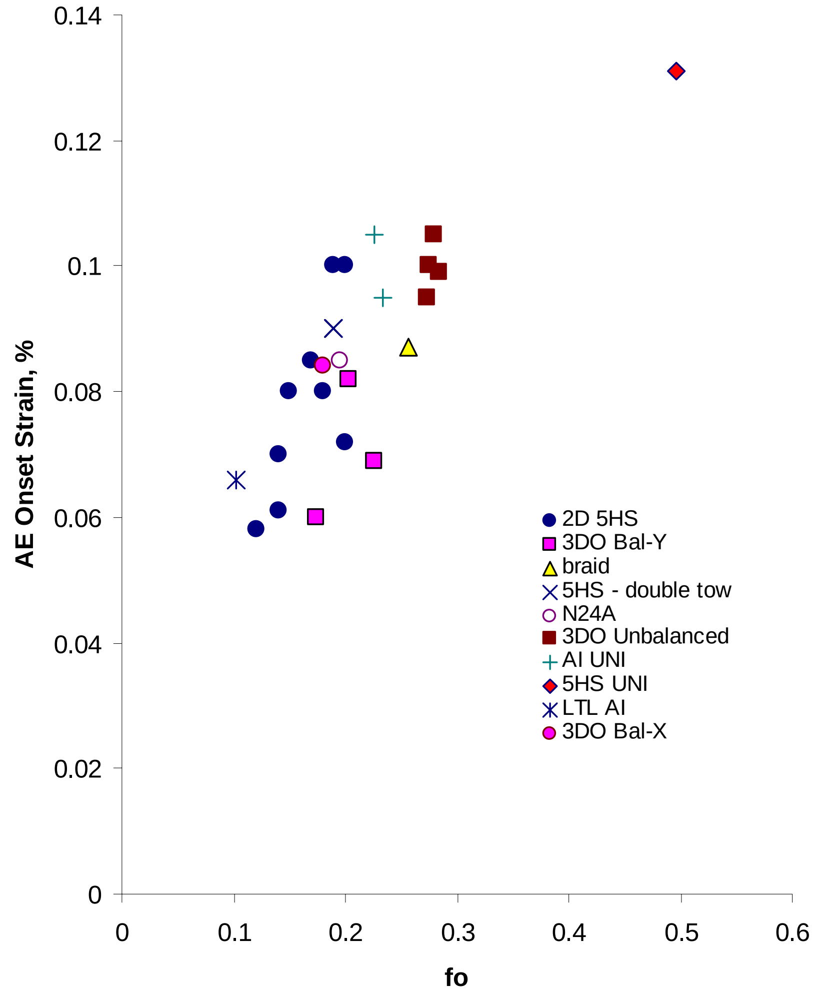
0º AE of Different Architecture Syl-iBN MI Composites



Effect of f_o on Matrix Cracking Stress

Primary factor affecting matrix cracking = fiber volume fraction





Calculating the unbridged ⊥ tow area

$$A_{\perp} = Length_{\perp Minicomposite} \cdot h_{\perp Minicomposite}$$

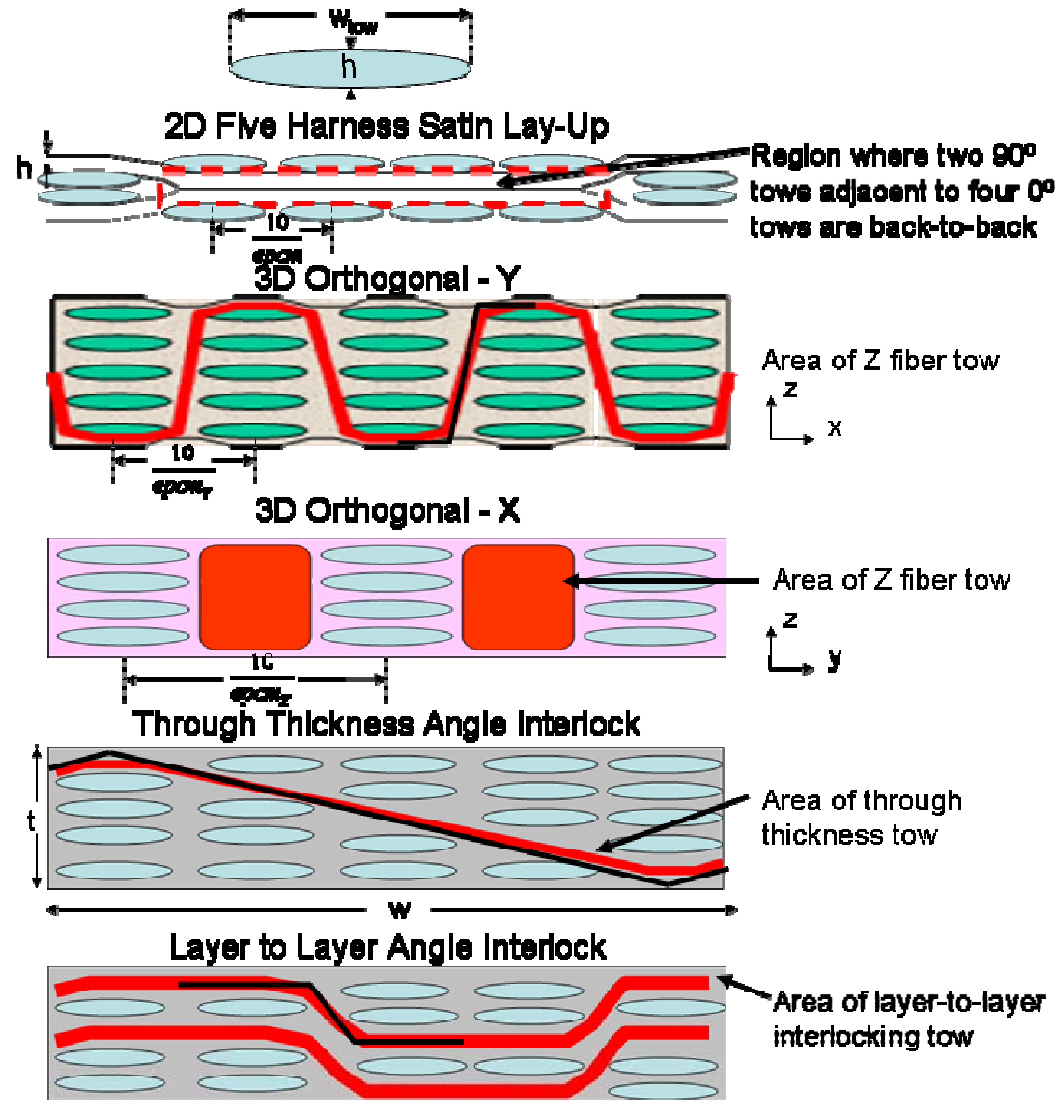
$$A_{\perp} = \frac{N_{hs} - 1}{epcm} 20 \cdot h_{90}$$

$$A_{\perp} = \frac{epcm \cdot w}{10}\left[\left\{\left(\frac{10}{epcm} - w_{tow-Y}\right)^{2} + \left(t - h_{z}\right)^{2}\right\}^{1/2} + w_{tow-Y}\right] \cdot h_{z}$$

$$A_{\perp} = \left(\frac{10}{epcm_{x}} - w_{tow-X}\right) \cdot t$$

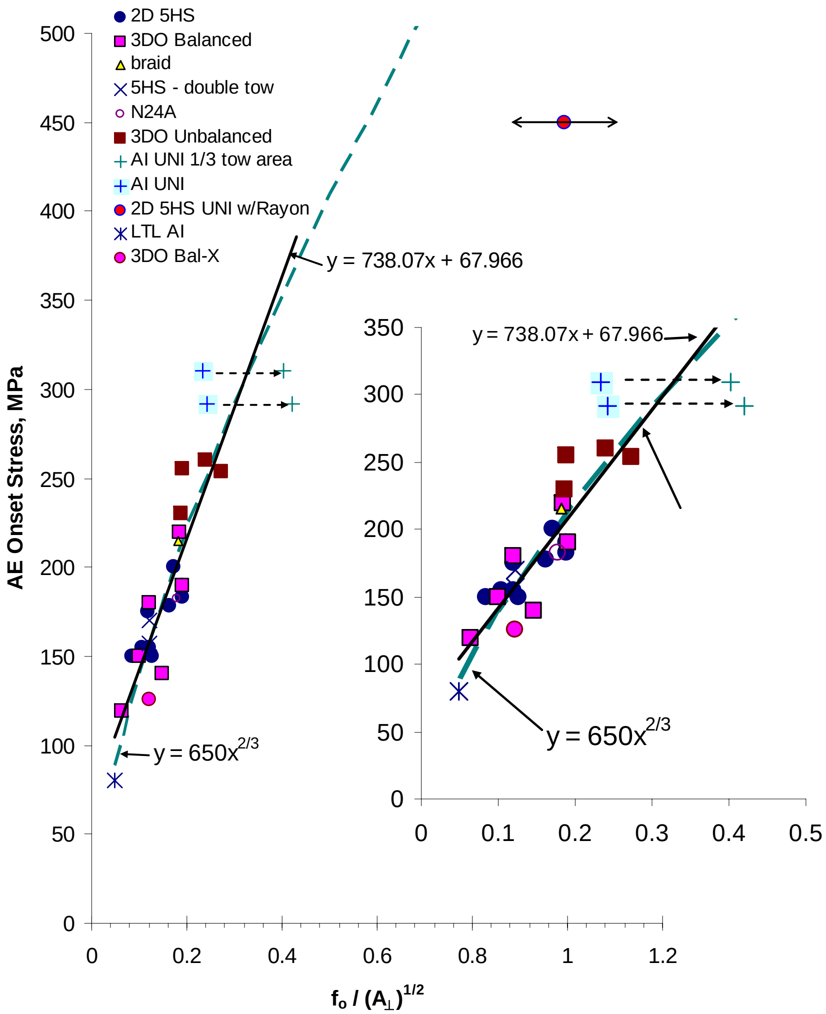
$$A_{\perp} = \frac{10 N_{ply}}{epcm} t \frac{epcm}{10} w \cdot h_{z} = N_{ply} t w \cdot h_{z}$$

$$A_{\perp} = \frac{epcm \cdot w}{10}\left[\frac{20}{epcm} + \frac{1}{2}\left\{t^{2} + \left(\frac{10}{epcm} - w_{tow-0}\right)^{2}\right\}^{1/2}\right] \cdot h_{z}$$

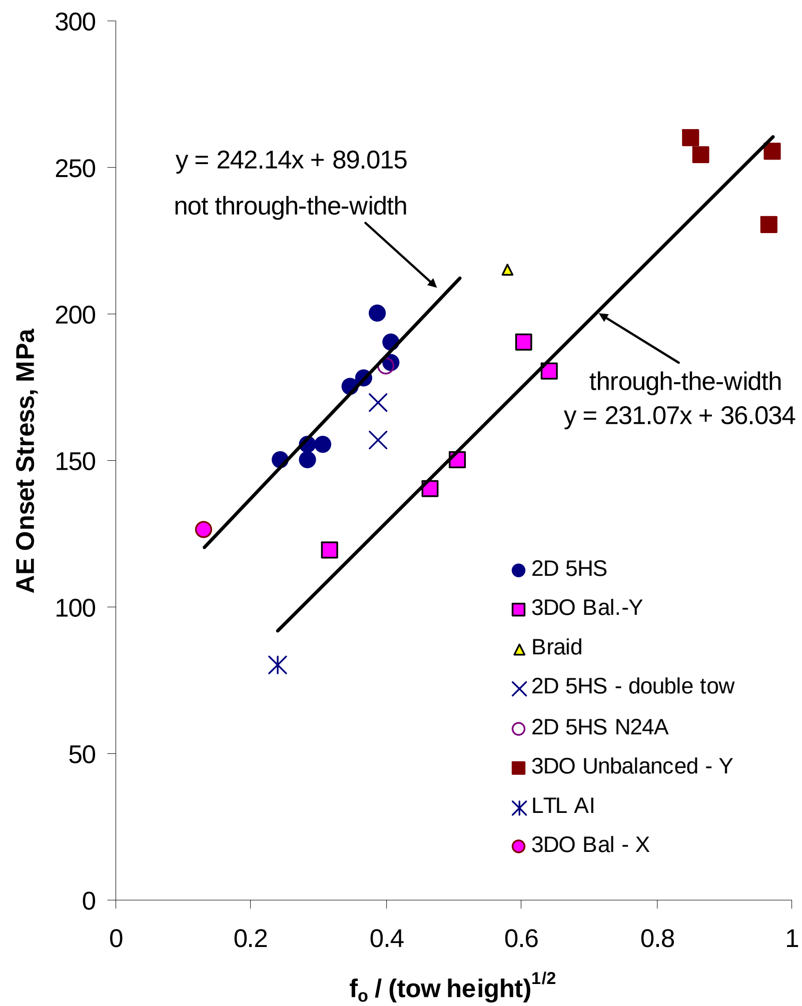


Effect of f_o and max ⊥ tow size on Matrix Cracking Stress

$f_o / (A_\perp)^{1/2}$

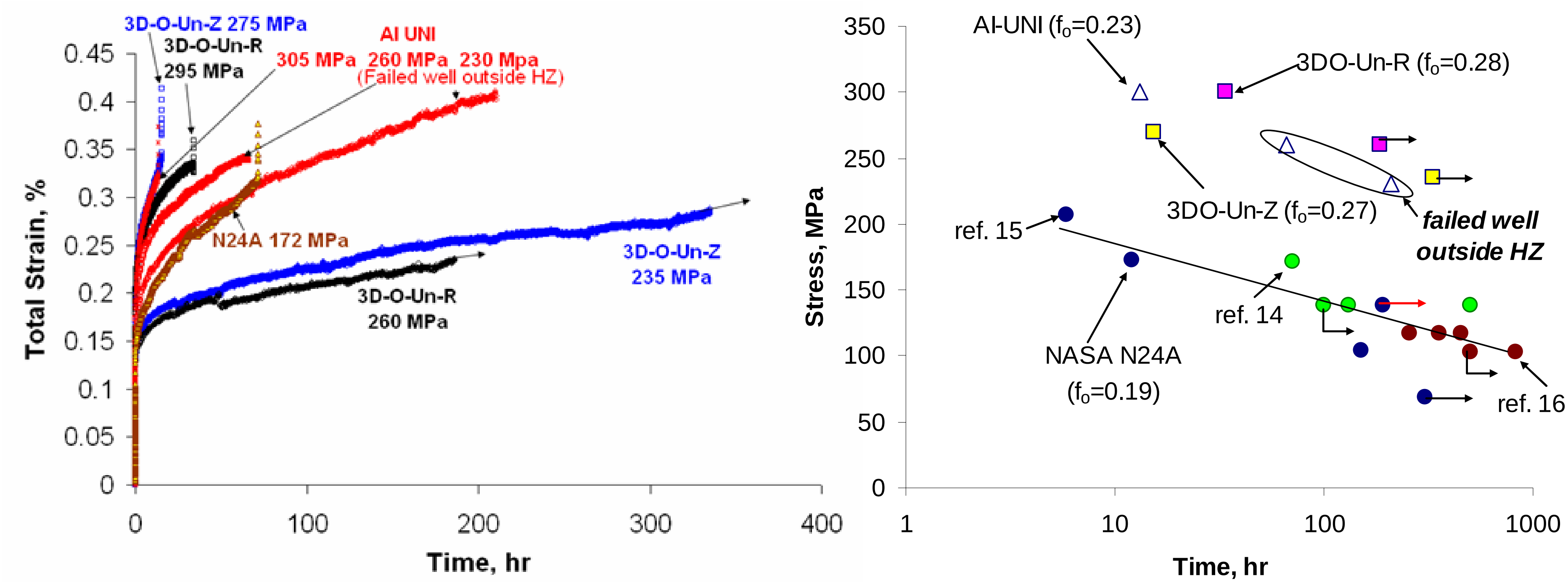


f_o / (tow height)$^{1/2}$



1315ºC Creep-Rupture of Different Architecture Composites

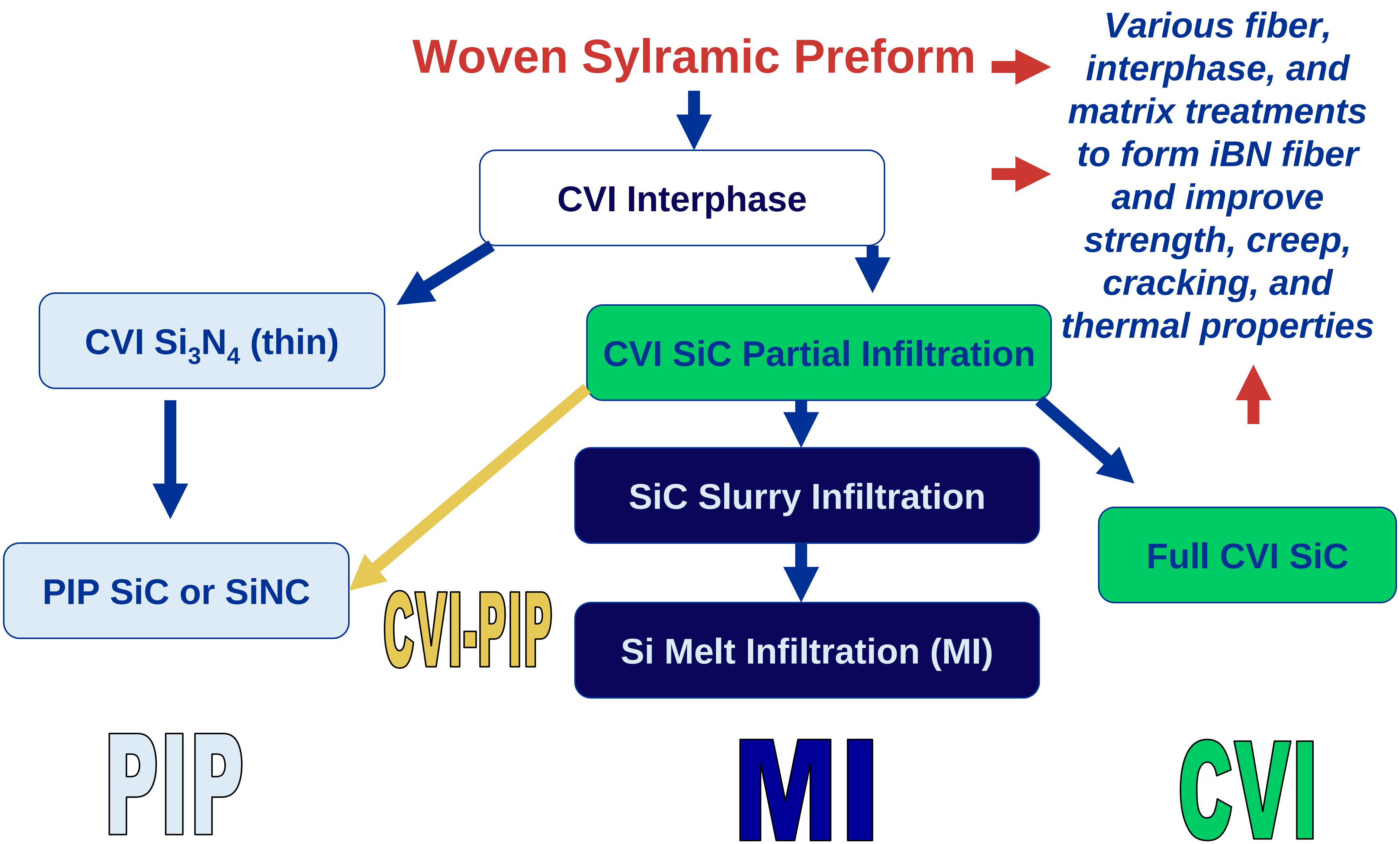
- Significant improvement (~ 100 MPa) in creep-rupture properties for unbalanced fiber architectures with high fiber fraction in loading direction over standard 2D five-harness composites

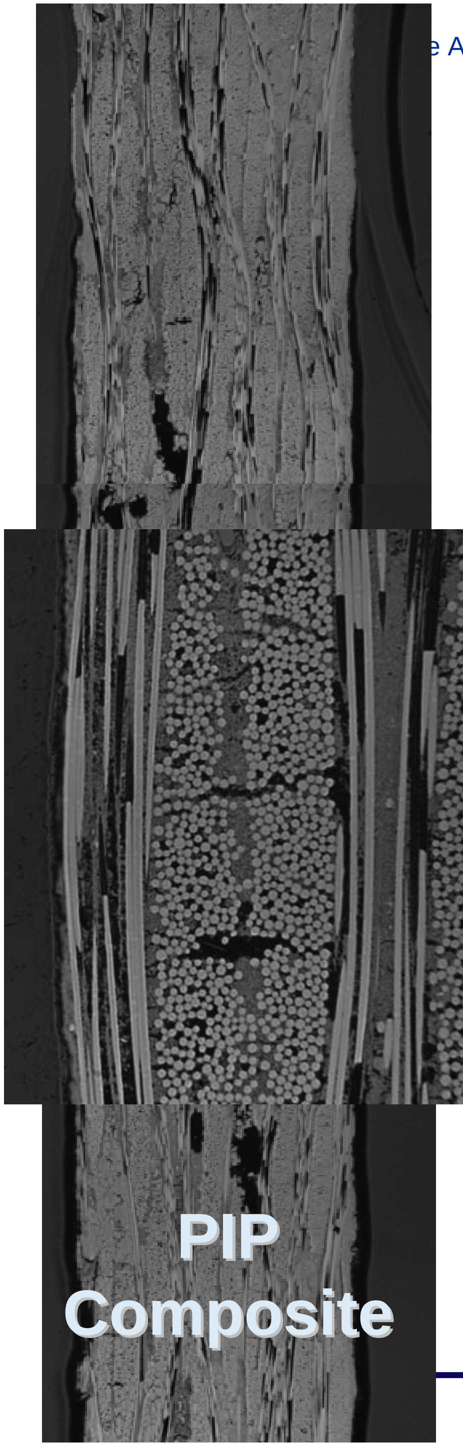


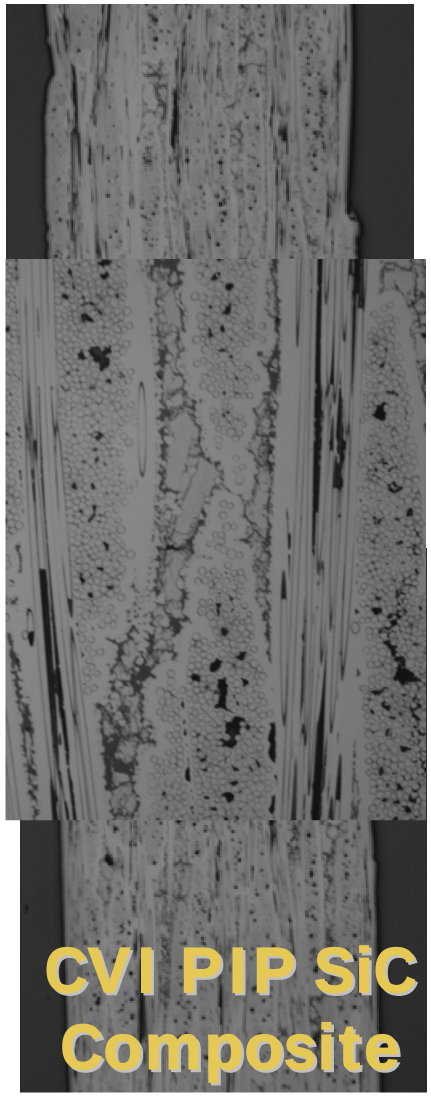
Sylramic-iBN Reinforced SiC-based Matrix Composites

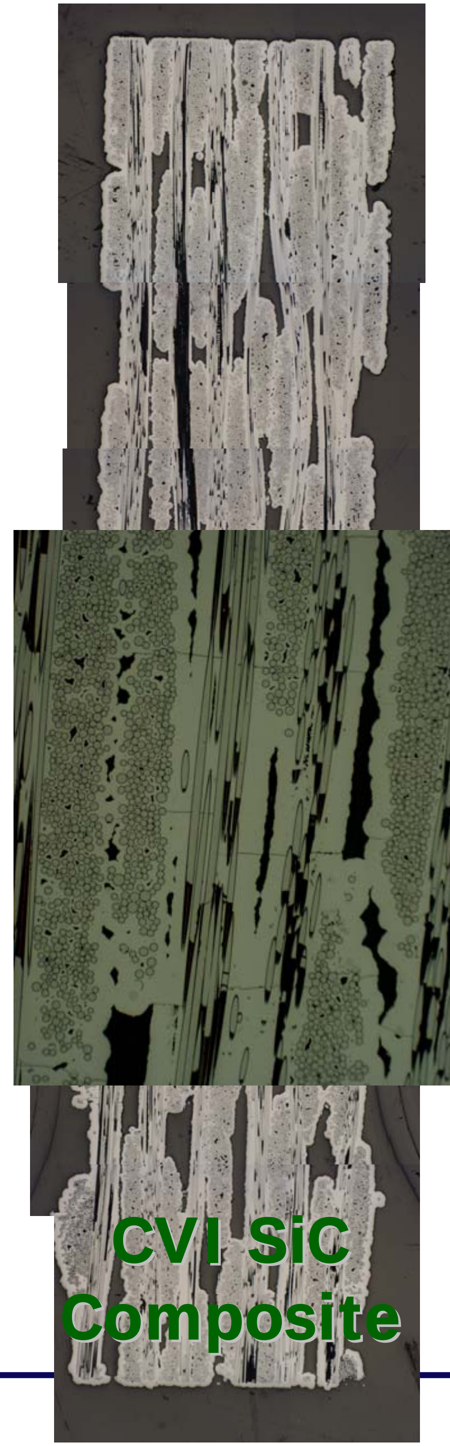
Fabricate different matrix composites with the same architecture: *8 ply, 7.9 epcm five-harness satin 2D weave composites*

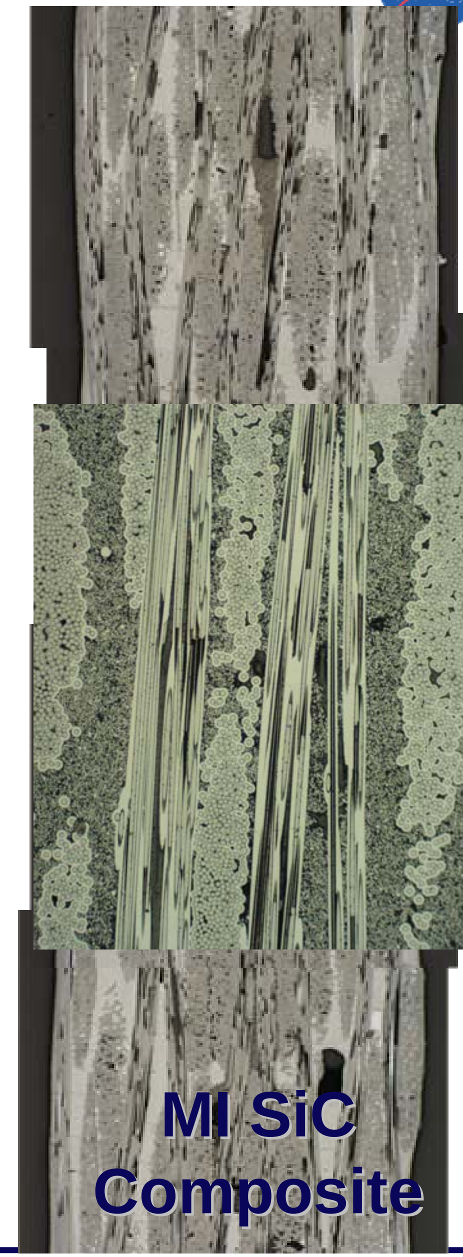
Sylramic-iBN Composites: Processing Approaches



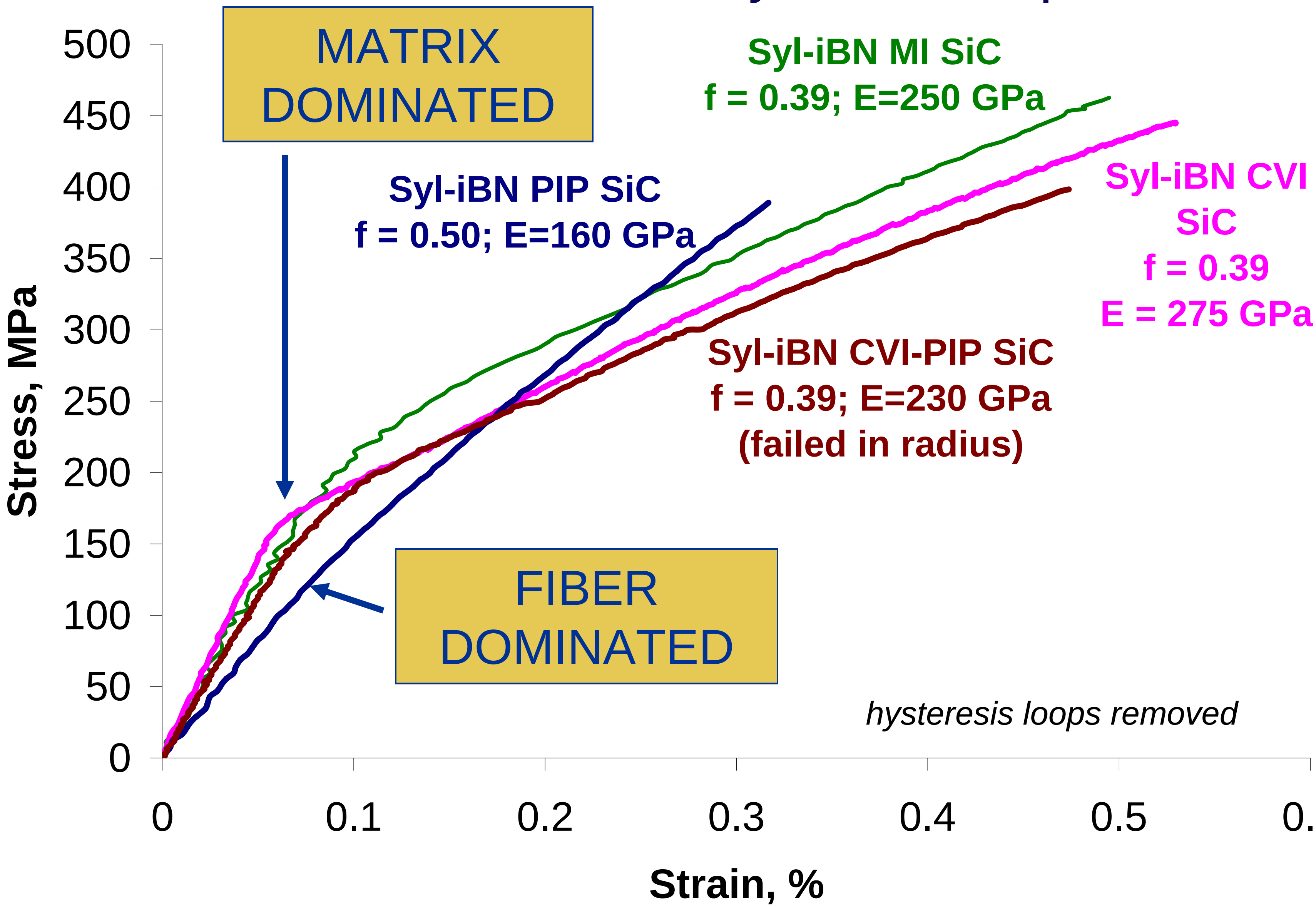

PIP
Composite


CVI PIP SiC
Composite


CVI SiC
Composite


MI SiC
Composite

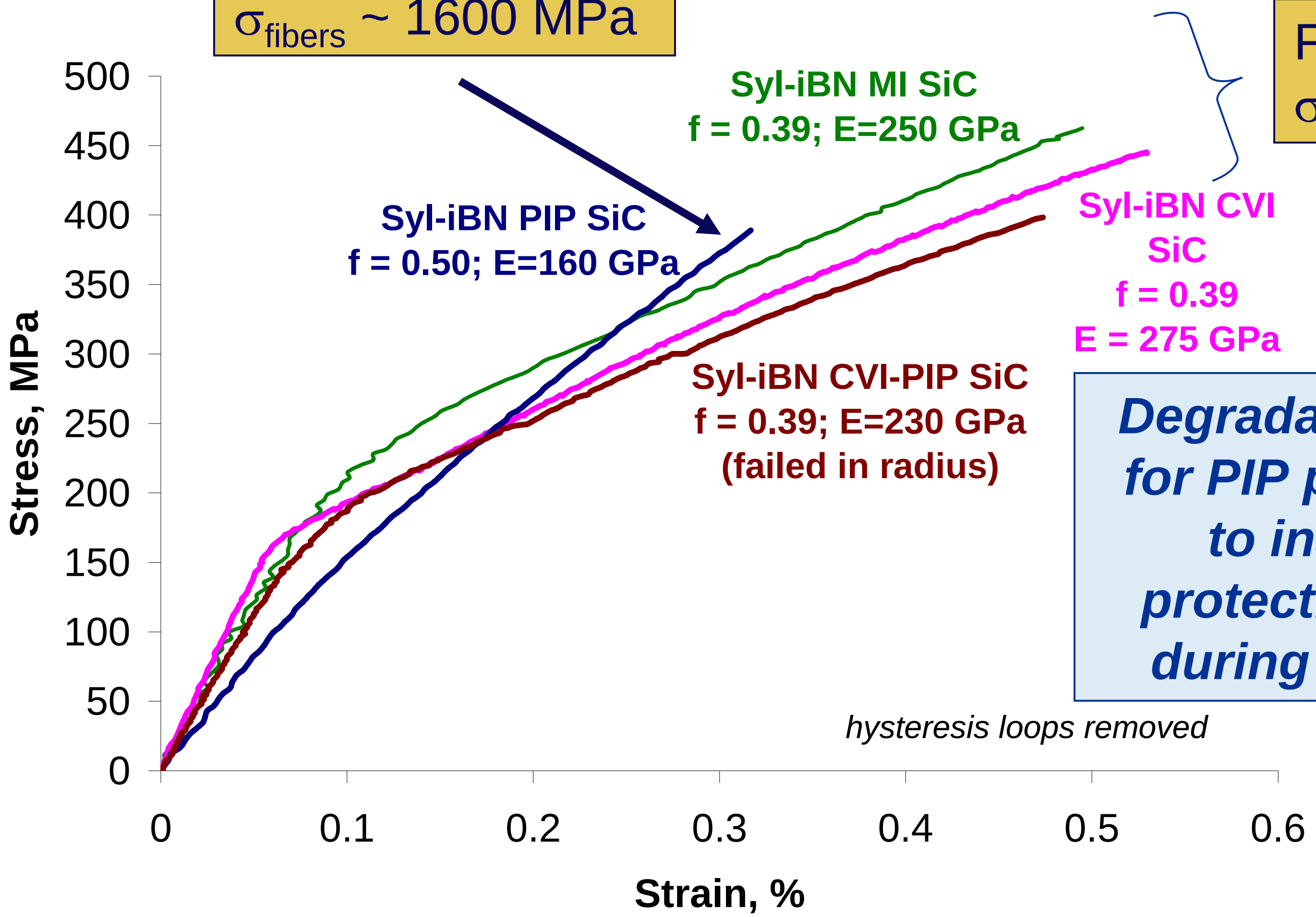
RT 0° σ/ε behavior of Syl-iBN Composites



Ultimate Properties: Fiber Strength After Processing
Degradation in PIP Composites

For the best PIP:
σ_{fibers} ~ 1600 MPa

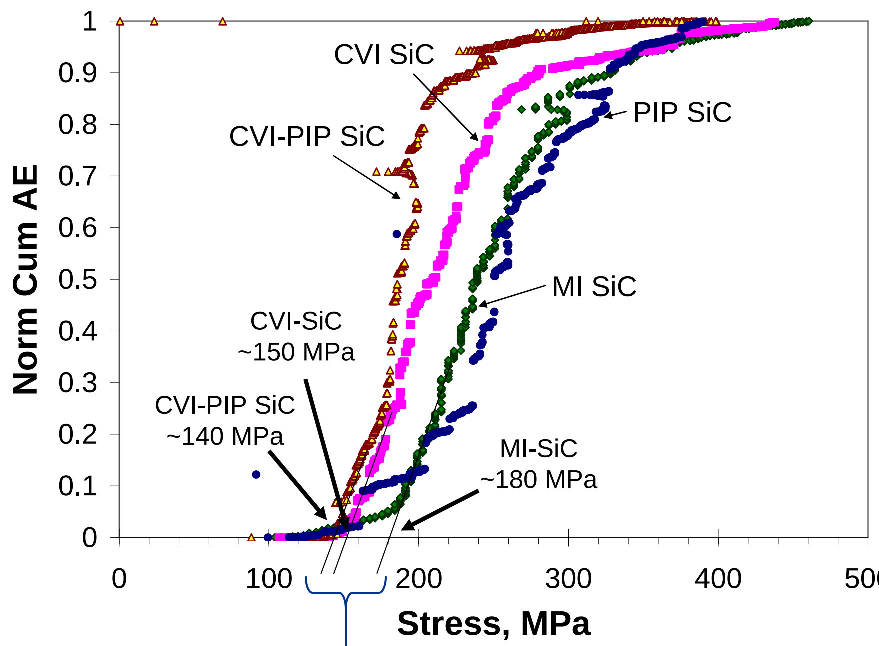
For CVI-based:
σ_{fibers}~2350 MPa

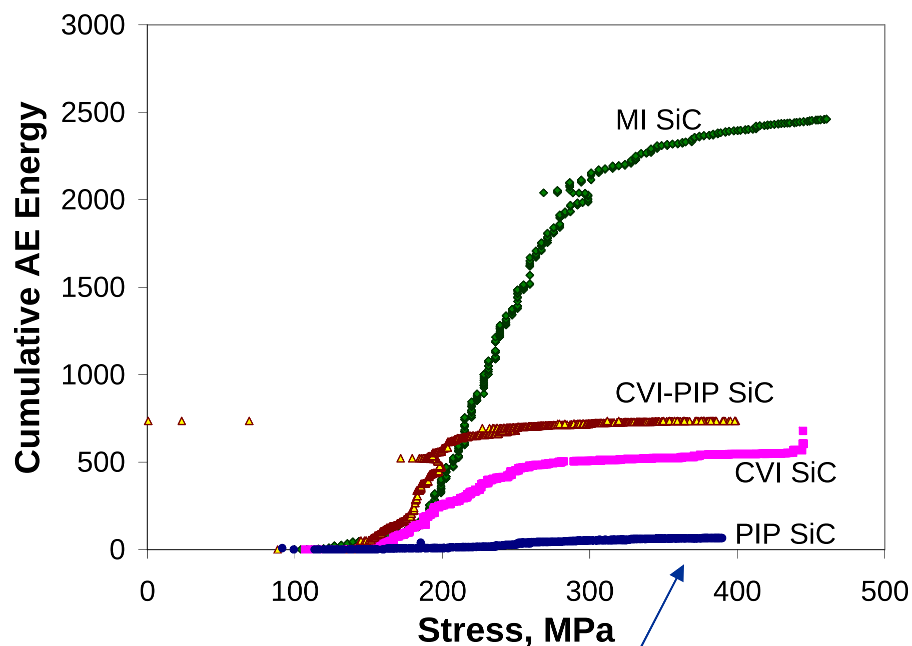


Degradation in fibers for PIP probably due to inadequate protection of fibers during processing

Matrix Cracking (Acoustic Emission) of Syl-iBN Composites

- For PIP (fiber dominated), very little AE activity and very little evidence of stress-induced cracks – significant processing induced shrinkage cracks
- For MI, CVI, and CVI-PIP (matrix dominated), significant matrix cracking → MI superior because pores are filled with silicon (removes stress concentrators at tow intersections and induces residual compressive stress in matrix)





Design criteria for long term use

PIP SiC has very little AE activity

Physical Properties of 2D-Woven Sylramic-iBN Panels

	Syl-iBN MI	Syl-iBN CVI	Syl-iBN CVI-PIP	Syl-iBN PIP
Density, g/cc	~2.75	~2.65	~2.70	~ 2.65
f	~0.38	~0.38	~0.38	~ 0.50
E, GPa	~ 250	~250	~ 210	~ 160
UTS, MPa	~ 450	~ 450	~ 400	Up to ~ 400
Stress on fibers at failure, MPa	~ 2400	~ 2400	2100 to 2400 (process)	800 to 1600 (process and filler)
Composite Vendors	GEPSC Goodrich	GEPSC Hyper-Therm	GEPSC + COIC (Starfire polymer)	COIC (Starfire polymer)

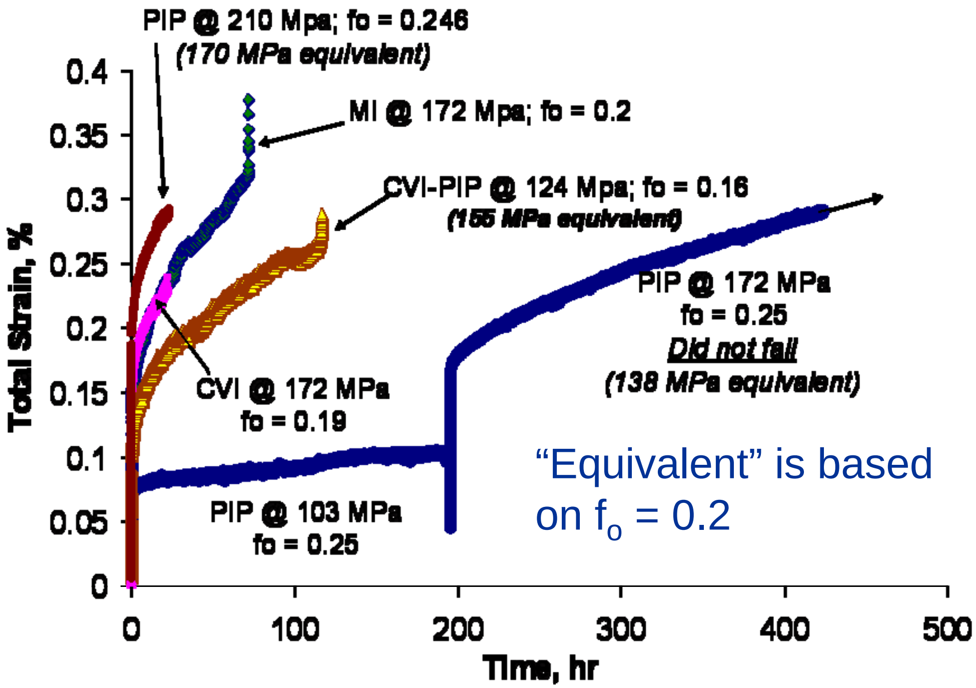
High Temperature 0^{o} Creep Rupture Behavior

-Si containing MI matrix composites begin to degrade due to Si diffusion and attack of CVI SiC and fibers above 1350^{o}C

-Therefore, tensile creep rupture tests were performed between 1315^{o}C and 1450^{o}C in air to show effects above and below Si melting point

Creep Rupture of Syl-iBN/SiC CMCs

-At 1315C, all composites survive 103 MPa (15ksi) for hundreds of hours
-At 1450C, CVI, PIP and CVI-PIP composites survive 69 MPa (10ksi) for hundreds of hours
-PIP composites rupture at the highest composite stresses because they have the highest volume fraction of fibers



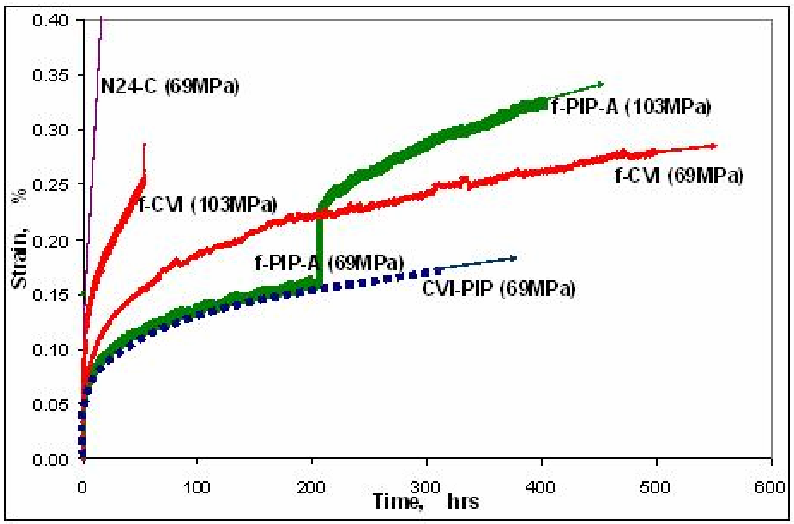


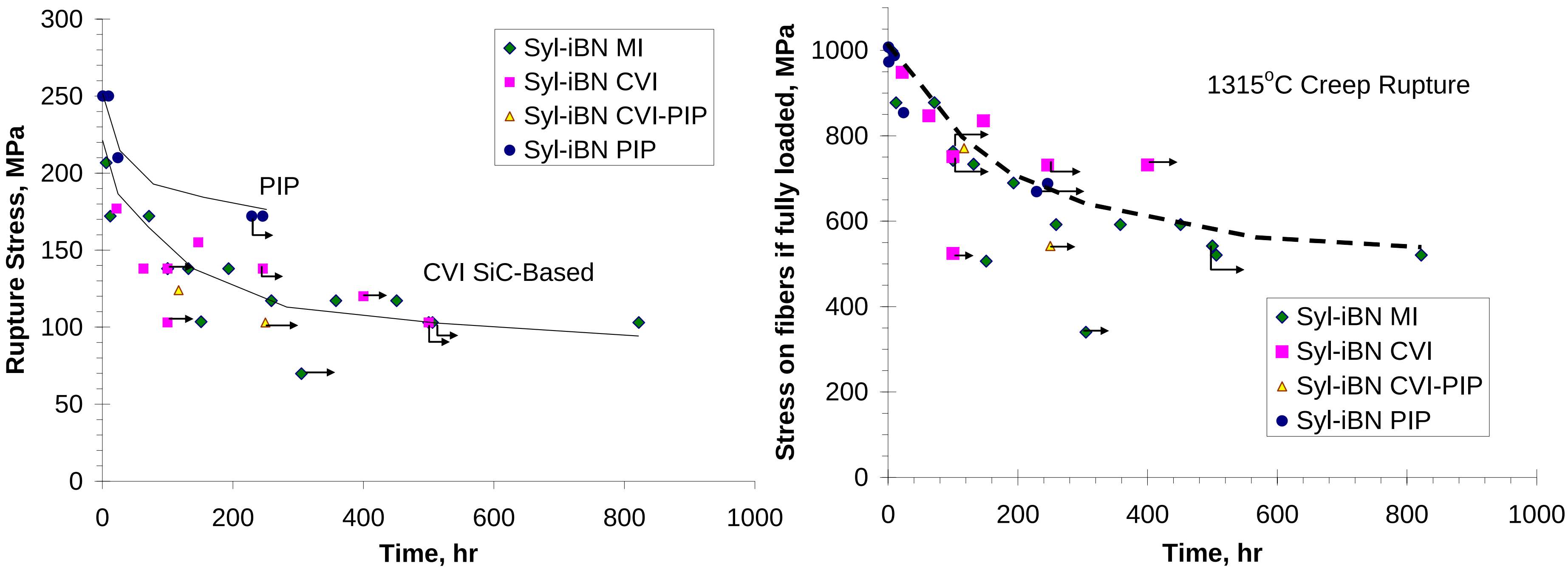
Fig. 4. Creep/Rupture Behavior of various NASA ASC 2D systems at 1450°C

1315°C Creep

1450°C Creep

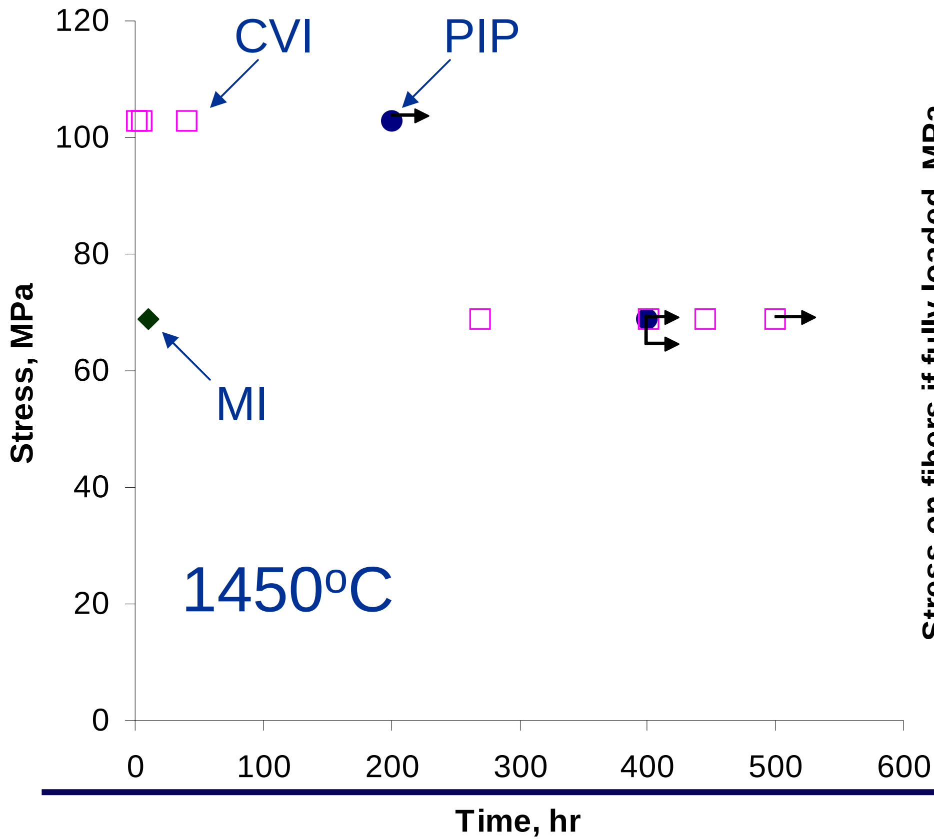
0º Creep Rupture Dictated by Fiber Rupture Properties at High Temperatures (1315ºC)

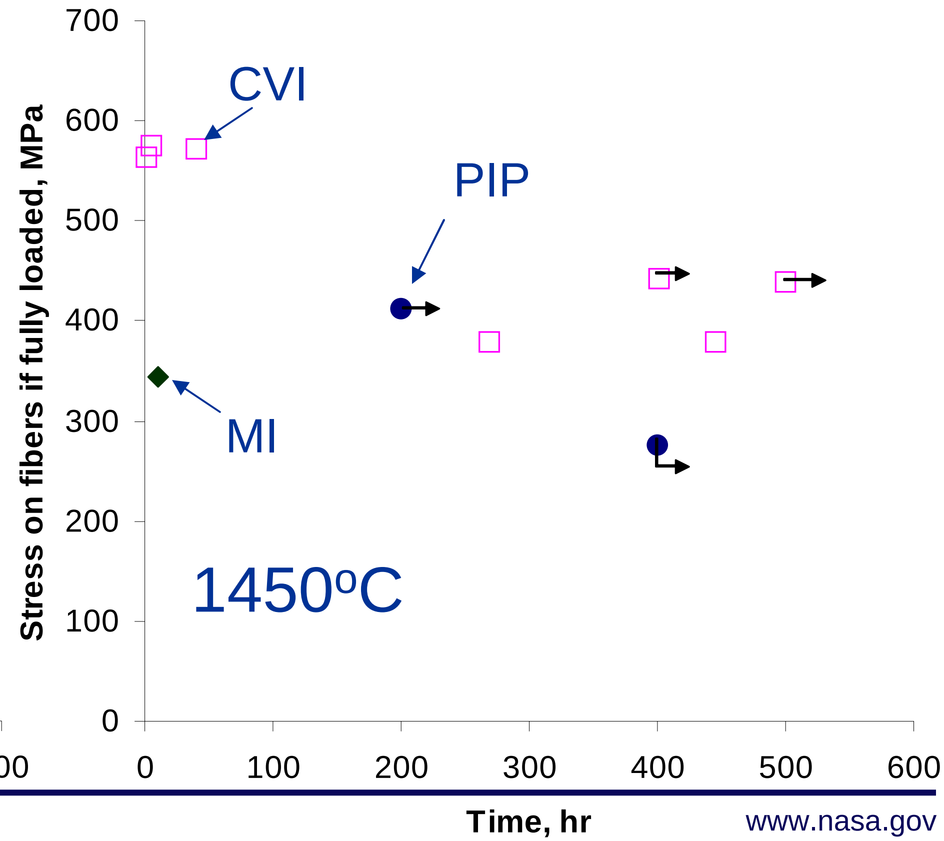
- ***Composite creep-rupture at 1315ºC appears to be dependent on stress on fibers for the three composite systems***
- ***Starting strength of fibers in PIP matrix ranged from 1300 to 1600 MPa compared to ~2400 MPa for other systems. → <u>Starting strength of fibers not a great factor for high temperature creep rupture</u>***



0º Creep Rupture Dictated by Fiber Rupture Properties at High Temperatures (1450ºC)

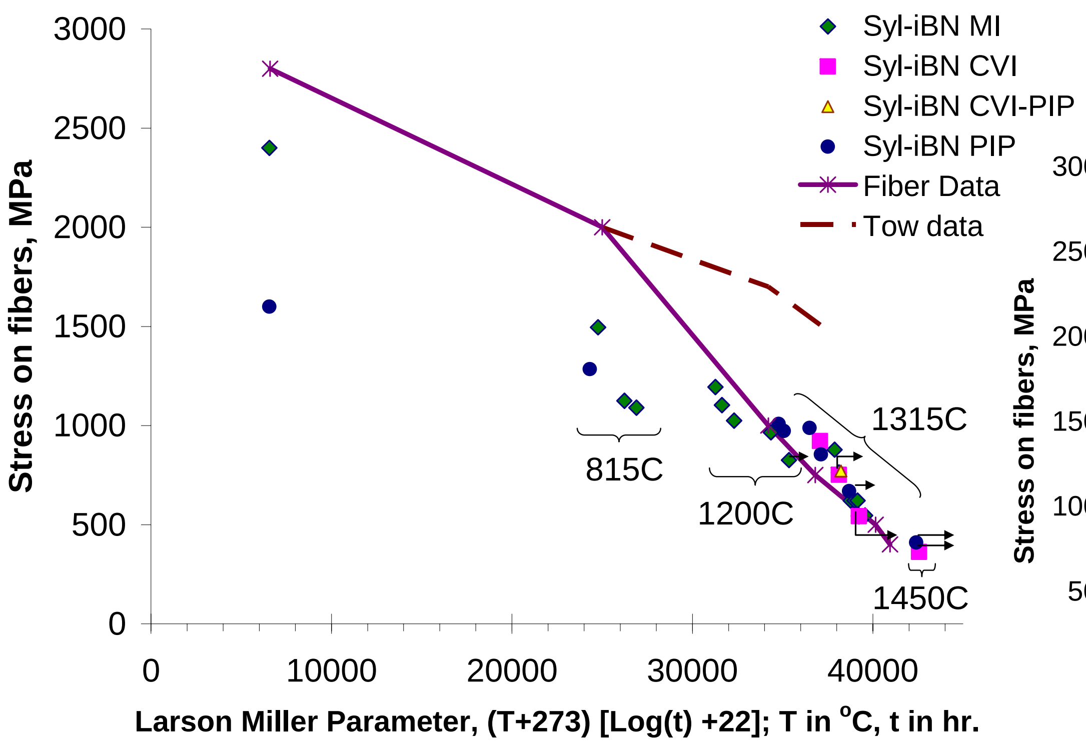
- ***Composite creep-rupture at 1450ºC appears to be dependent on stress on fibers for CVI and PIP composite systems; however, MI creep-rupture significantly lower***
- ***Starting strength of fibers in PIP matrix ranged from 1300 to 1600 MPa compared to ~2400 MPa for other systems. → <u>Starting strength of fibers not a great factor for high temperature creep rupture</u>***

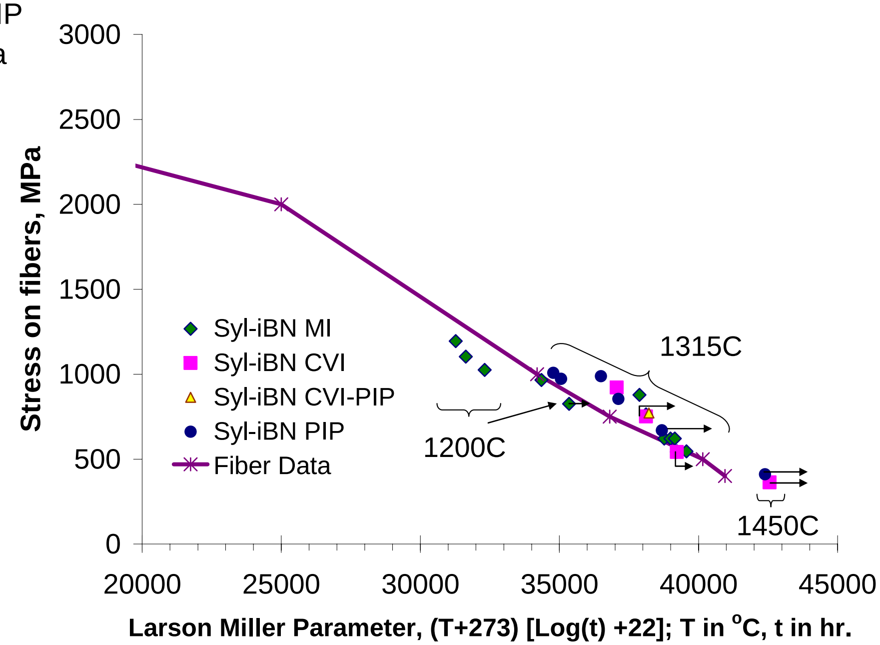




0º Creep Rupture of Composites are Comparable to Fiber Rupture Properties at High Temperatures

- Creep rupture life generally greater than comparable fiber-only data, but follow same general trend





Out of Plane Properties for 2D-Woven Panels

	Syl-iBN MI	Syl-iBN CVI	Syl-iBN CVI-PIP	Syl-iBN PIP
ILT strength, MPa	17	7 {5}*	10	23
K33 (25^{o}C), W/mK	25	18 {28}	28	8
K33 (1400^{o}C), W/mK	--	5 {8}	10	4
Permeability, mtorr/m**	25	2000	150	1200

*{ } indicates after a special annealing treatment

** Vacuum permeability measured using Veeco leak detector at 25^{o}C

Implications and Conclusions

- A plethora of properties (strength, thermal conductivity, permeability, etc…) can be tailored with the different SiC matrix processing routes available
  - Further refinement and optimization can be made with architectures and heat treatments (not discussed in this presentation)
- High temperature creep rupture properties appear to be controlled by fiber creep rupture properties
  - Starting strength of fibers not a factor at higher temperatures
  - Nature of crack growth and fiber creep-rupture properties needs to be better understood to quantify life-degrading mechanism(s)
- High temperature (1400C+), highest stress capability is with PIP matrix composites ***because higher fiber volume fractions are attainable***
  - *However, for high thermal conductivity, high off axis in-plane strength, and low permeability applications, CVI or CVI-PIP will be required –* ***Fiber fraction in desired directions could be increased with modified architectures to enhance properties***
  - The ability to better protect the fibers during PIP processing *may* result in higher use-stress capability or at least retained strengths
- Sylramic-iBN fiber-types are necessary to achieve maximum properties
  - Other fiber types degrade with advanced processing temperatures and/or lack creep resistance
  - Newer advances to Sylramic-iBN types (“Super Sylramic”) of fibers should increase high temperature performance