optimized resins & sizings for vinyl ester / carbon fiber composites

IACMI PA 16-0349-5.3-01

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project overview

- project title: optimized resins & sizings for vinyl ester/carbon fiber composites

- objectives:
  - design resins & sizings for vinyl ester / C fiber composites
  - develop technology suitable for **high speed production of automotive parts via prepregging**
  - demonstrate advantages relative to epoxy / carbon

Hood inner panel via compression molding

- motivation:
  - vinyl ester resins (VERs) offer potential processing and cost advantages relative to epoxies and other prepreg systems
    - elimination of refrigeration
    - improvement in cure speed
  - need for improvement in the resin-fiber interface

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project team

Partner	Responsibilities
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MICHELMAN	Sizing Development
ZOLTEK Toray Group	Sizing Application to PX35 Fiber
MICHIGAN STATE UNIVERSITY	Characterization of Resin-Fiber Interface
UDRI UNIVERSITY of DAYTON RESEARCH INSTITUTE	Fabrication & Molding of Prepreg Surrogates, Project Management

what we demonstrated

a vinyl ester / carbon fiber prepreg system with:

- no styrene
- long shelf life (> 23 months)
- no need for refrigeration
- fast cure (< 3 minutes)
- improved resin-fiber interface and mechanical properties
- reduction in the amount of process scrap that needs to go to a landfill
- reduction in embodied energy
- cost-effectiveness

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materials

- resins from Ashland:
  - monomer-free, styrene-free vinyl ester resins (VERs) designed for prepreg applications:
    - Arotran 901: BPA-based, T_g = 147°C
    - Arotran 902: More novolac character, T_g = 193°C

- sizings from Michelman and Zoltek:
  - aqueous resin dispersions based on multiple chemistries
  - designed for enhanced adhesion/interactions with vinyl ester resins

- fibers from Zoltek:
  - PX 35
    - 50K tow
    - E =242 GPa (35Msi)
    - σ = 4.14 GPa (600 ksi)
  - winding configurations
    - T grade ("ropes")
    - W grade ("ribbons")

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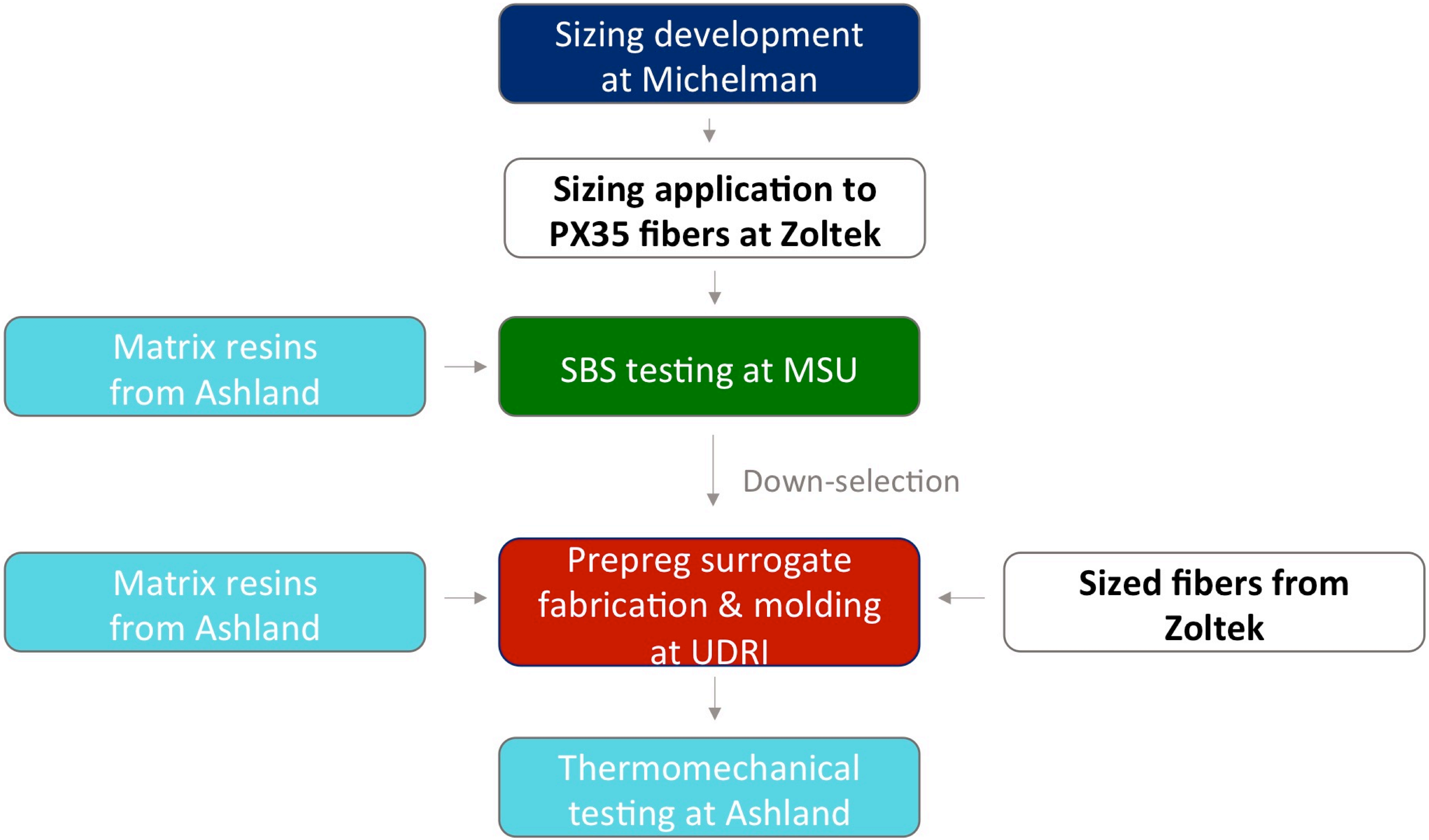
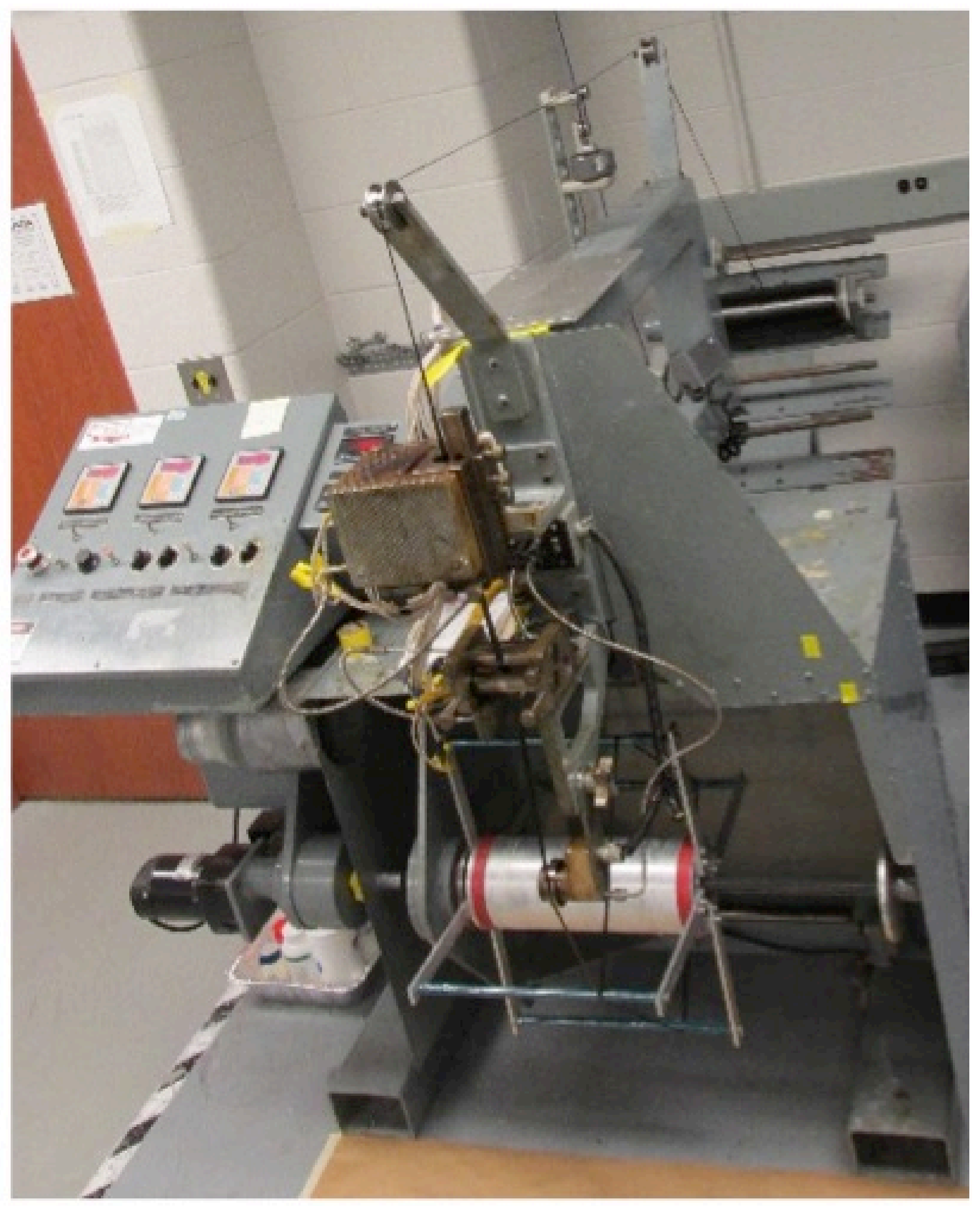
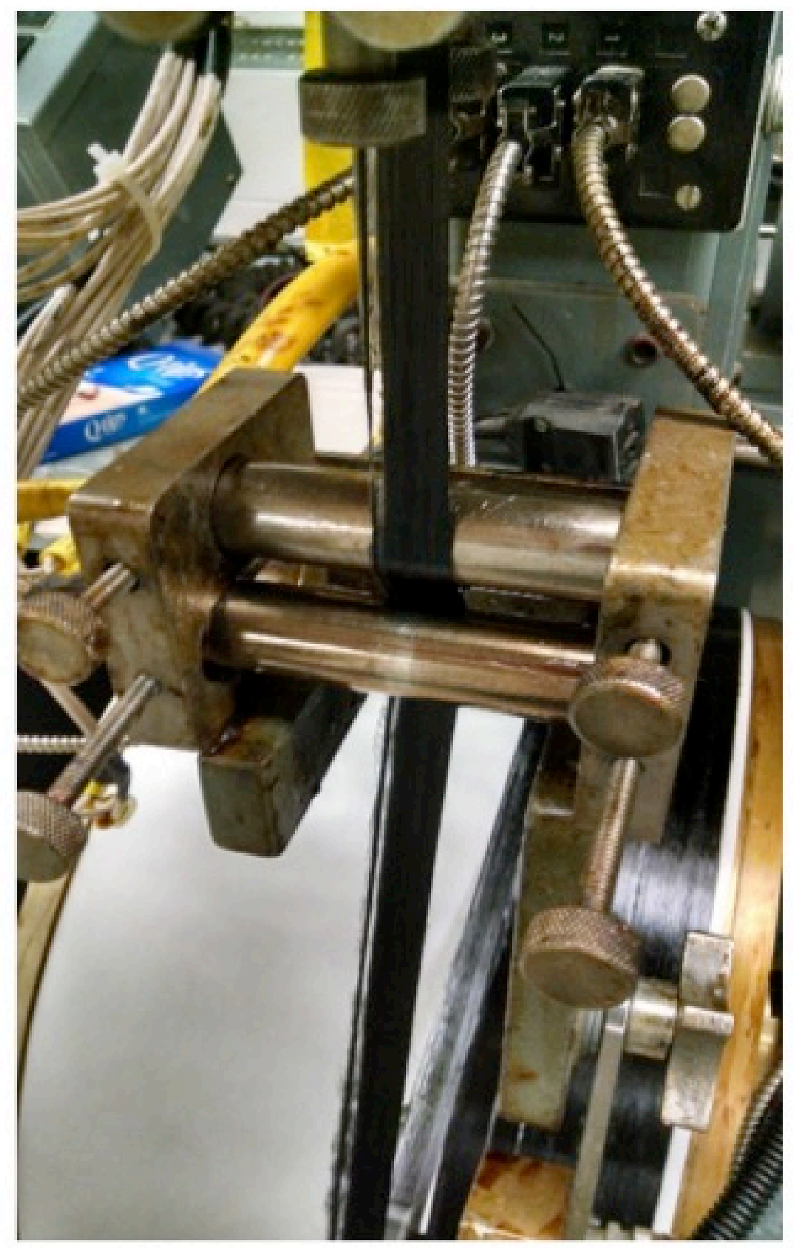
process flow diagram

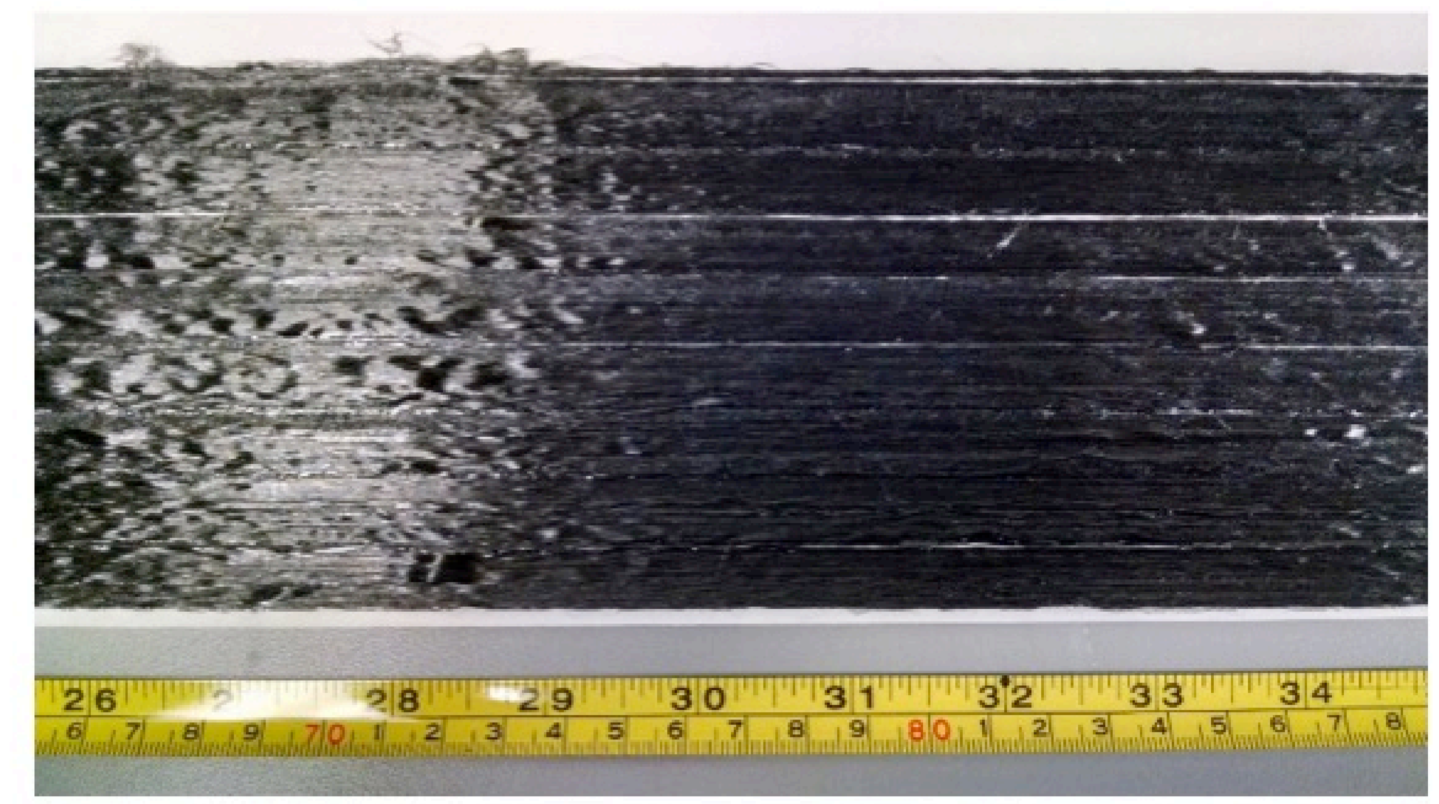


short beam shear (SBS) testing at Michigan State

- MSU prepared Short Beam Shear samples using matrix resins from Ashland and fibers sized at Zoltek
  - wet-winding process



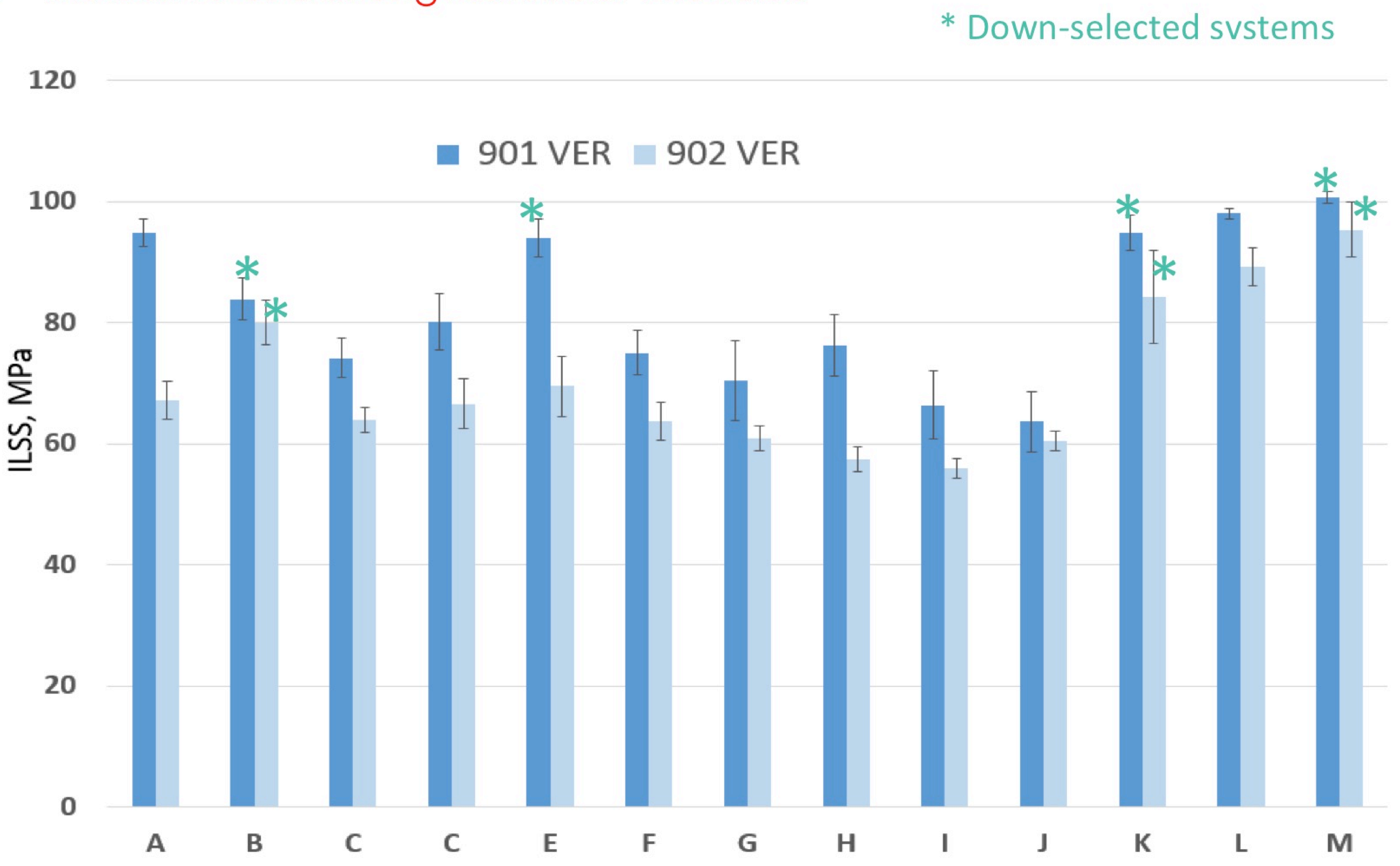




- interlaminar shear strength (ILSS) was measured
  - indicator of the strength of the resin-fiber interface
  - ILSS used to down-select systems for further testing at UDRI
  - epoxy benchmark also tested

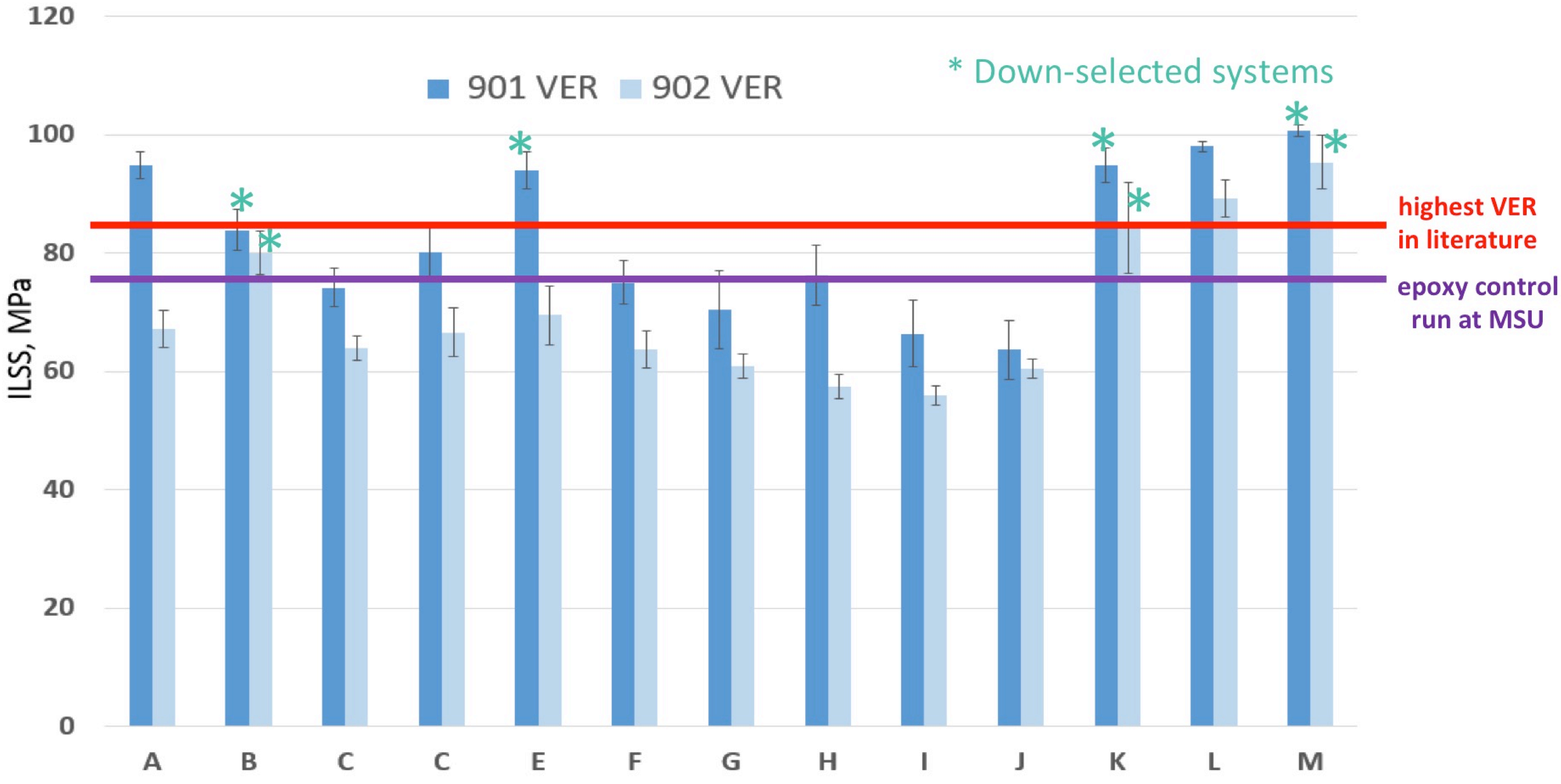
interlaminar shear strength (ILSS) results from Michigan State

- many of the down-selected systems had ILSS values near 100MPa
  - indicative of a strong resin-fiber interface



interlaminar shear strength (ILSS) results from Michigan State

- many of the down-selected VER systems had ILSS values that exceeded the epoxy control run at MSU and the highest value for VERs found in the literature
  - further support for a strong resin-fiber interface



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the down-selection process

26 resin/sizing combinations tested at MSU

↓

7 resin/sizing combinations tested at UDRI

↓

1 best-performing system

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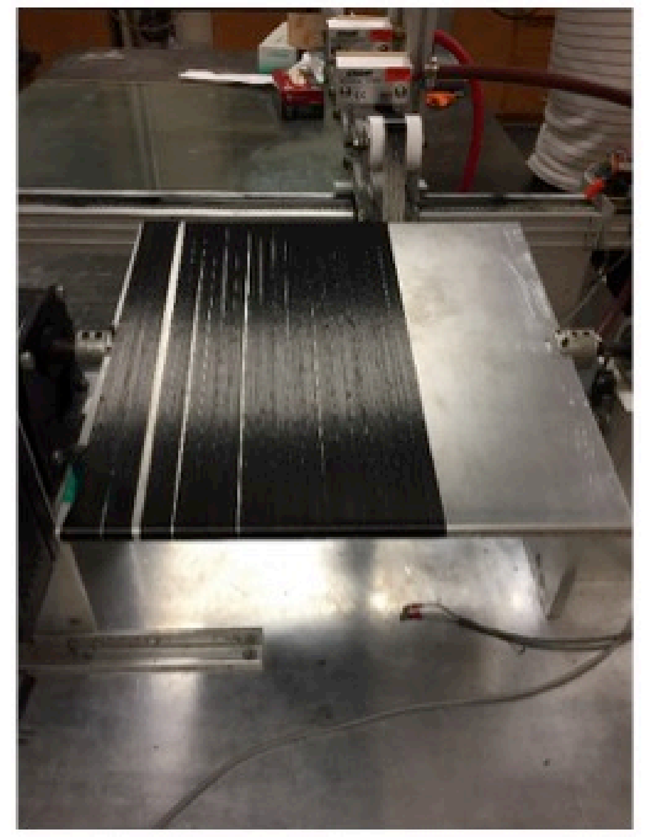
preparation, molding & characterization of prepreg surrogates

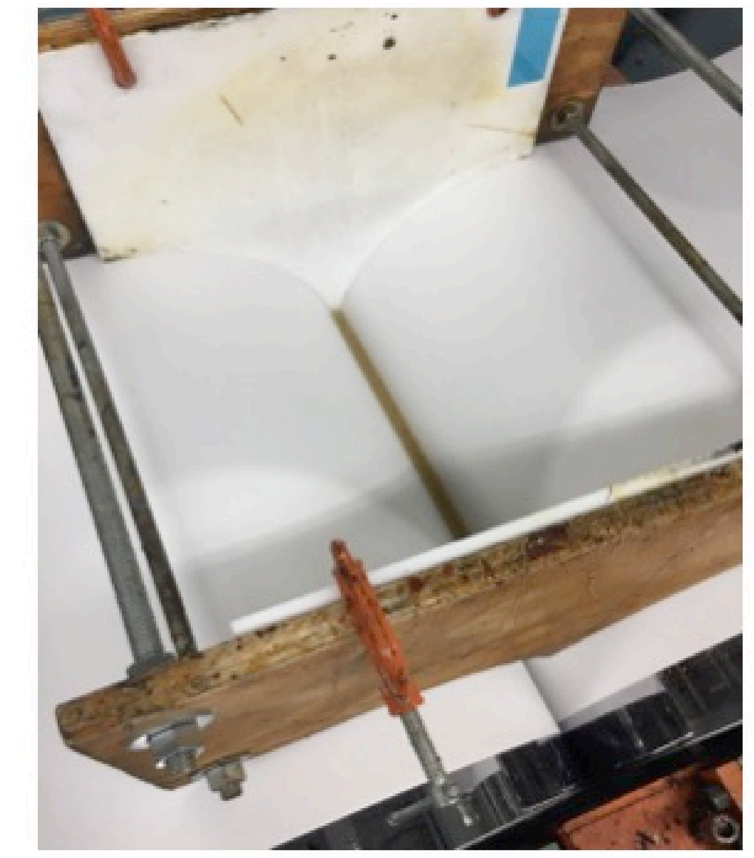
preparation & molding of prepreg surrogates at UDRI

Zoltek Panex35



Sized Fibers Dry-Wound on Mandrel

+



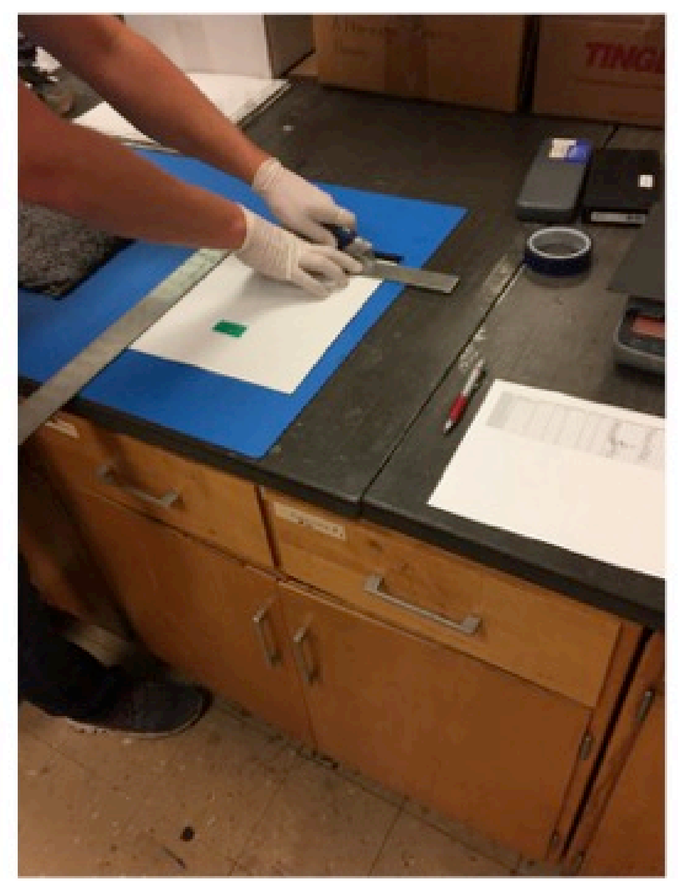
Hot-Melt Resin Films Cast at 170°F

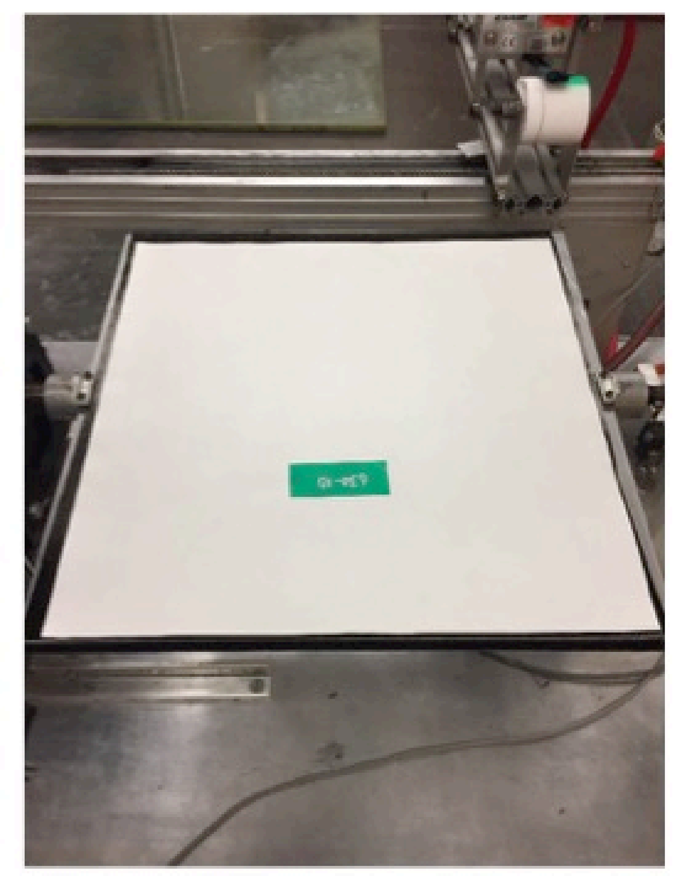
Lamination

these films and surrogates are very stable at room temperature

Resin + Carbon fiber
Resin + Carbon fiber
Resin + Carbon fiber
Resin + Carbon fiber
Resin + Carbon fiber
Resin + Carbon fiber
Resin + Carbon fiber
Resin + Carbon fiber

Debulking





Resin
Carbon fiber
Resin
Carbon fiber
Resin
Carbon fiber
Resin
Carbon fiber
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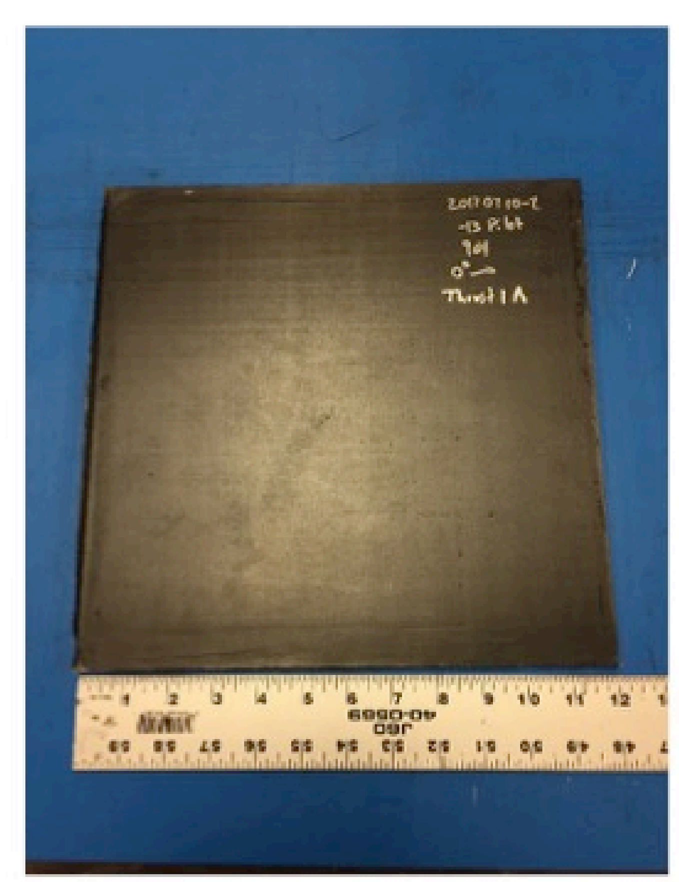
Resin
Carbon fiber

Prepreg "surrogate"

Compression Molding at 325 – 350°F, 100 psi, 3 min



Molded 12" x 12" plaque

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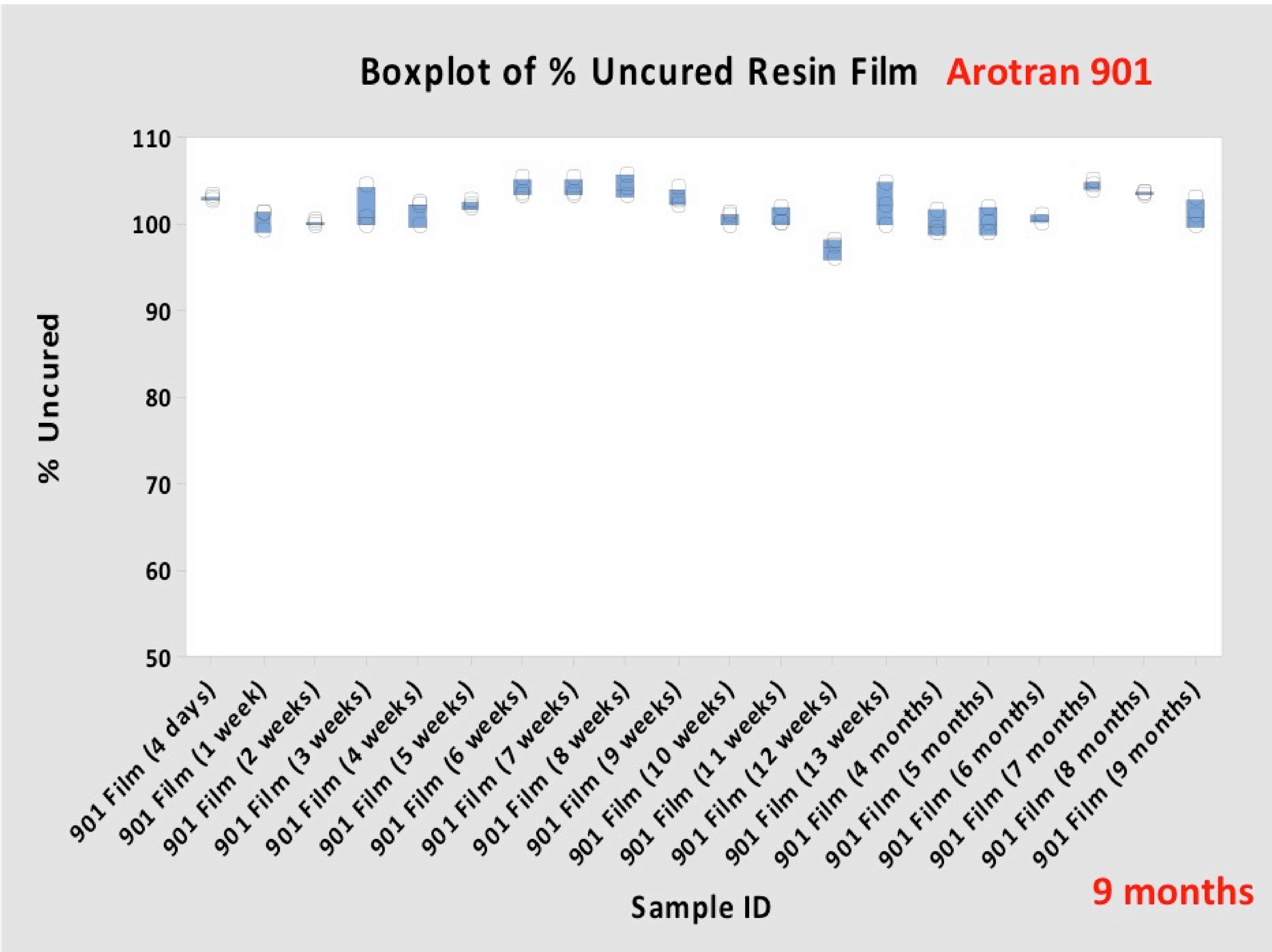
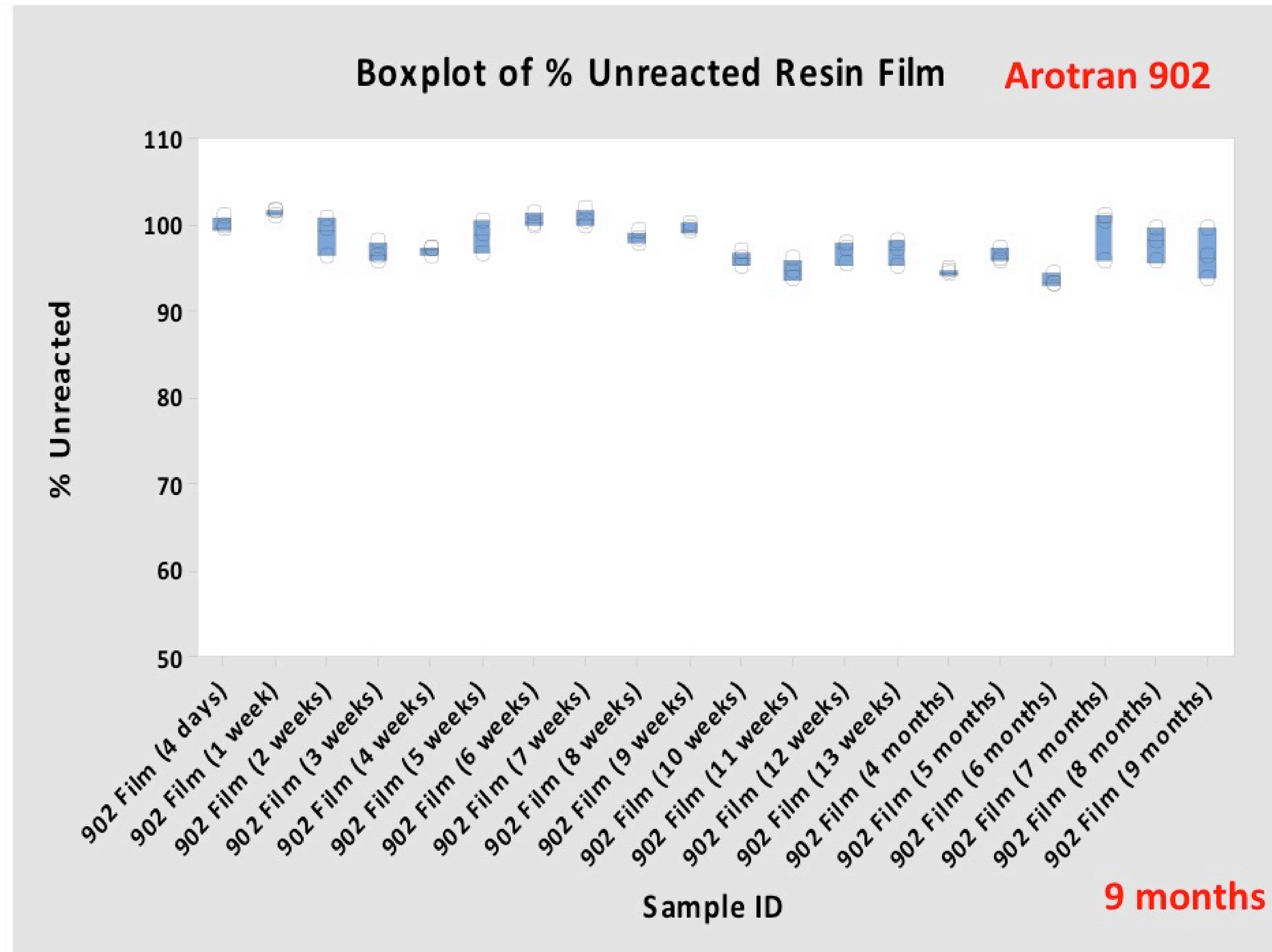
film stability:
DSC Results (901 & 902 Resin Films from UDRI)

- the VER films used to make prepreg surrogates have been stable at room temperature for **9 months**





We have demonstrated that VER resin films have very long shelf stability at RT.

Advantage over epoxies.

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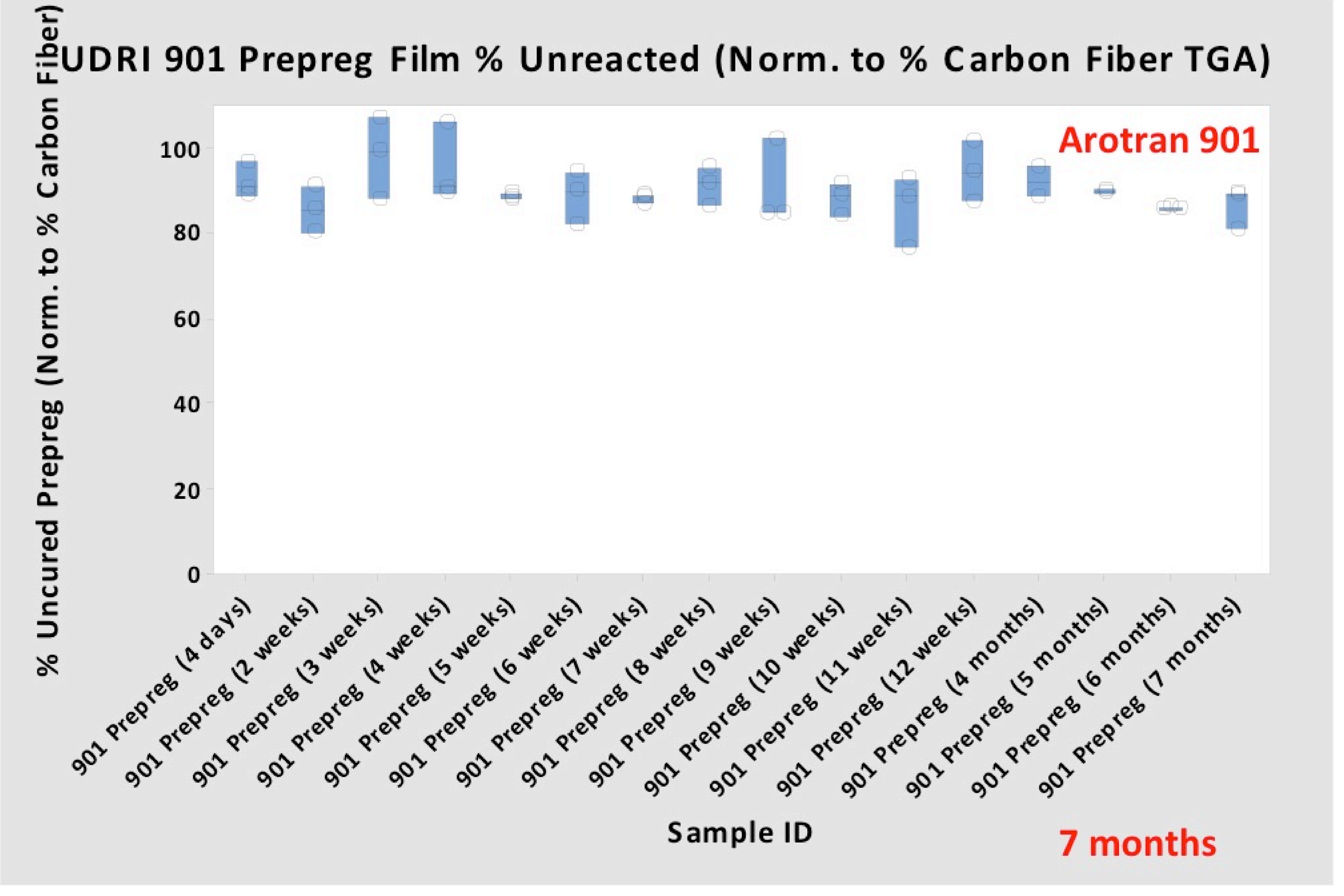
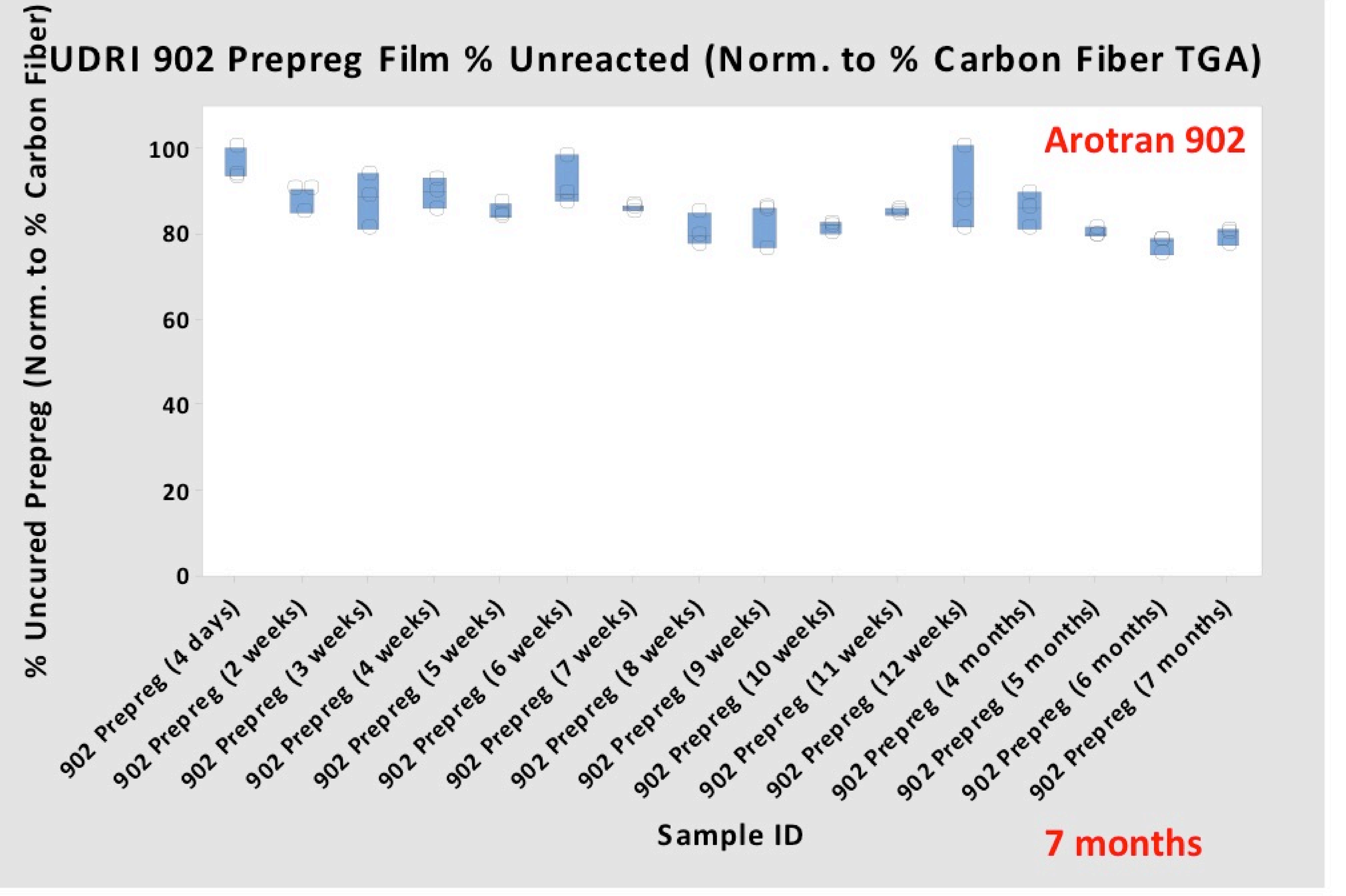
prepreg surrogate stability:
DSC Results (901 & 902 prepreg surrogates)

- the prepreg surrogates made at UDRI with VER films and sized, dry-wound Zoltek fibers have been stable at room temperature for **7 months**





We have demonstrated that VER prepreg surrogates have very long shelf stability at RT.

Advantage over epoxies.

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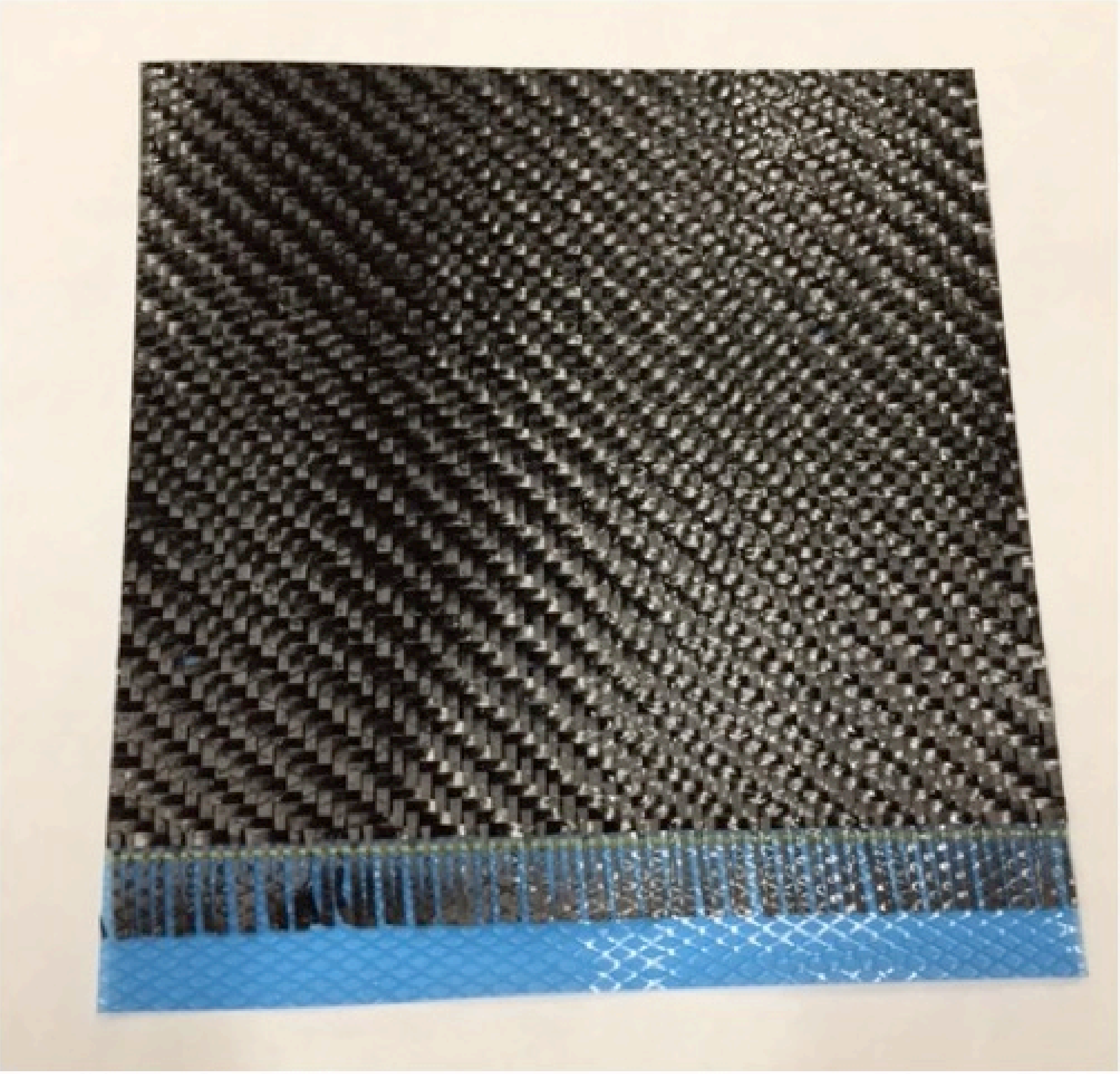
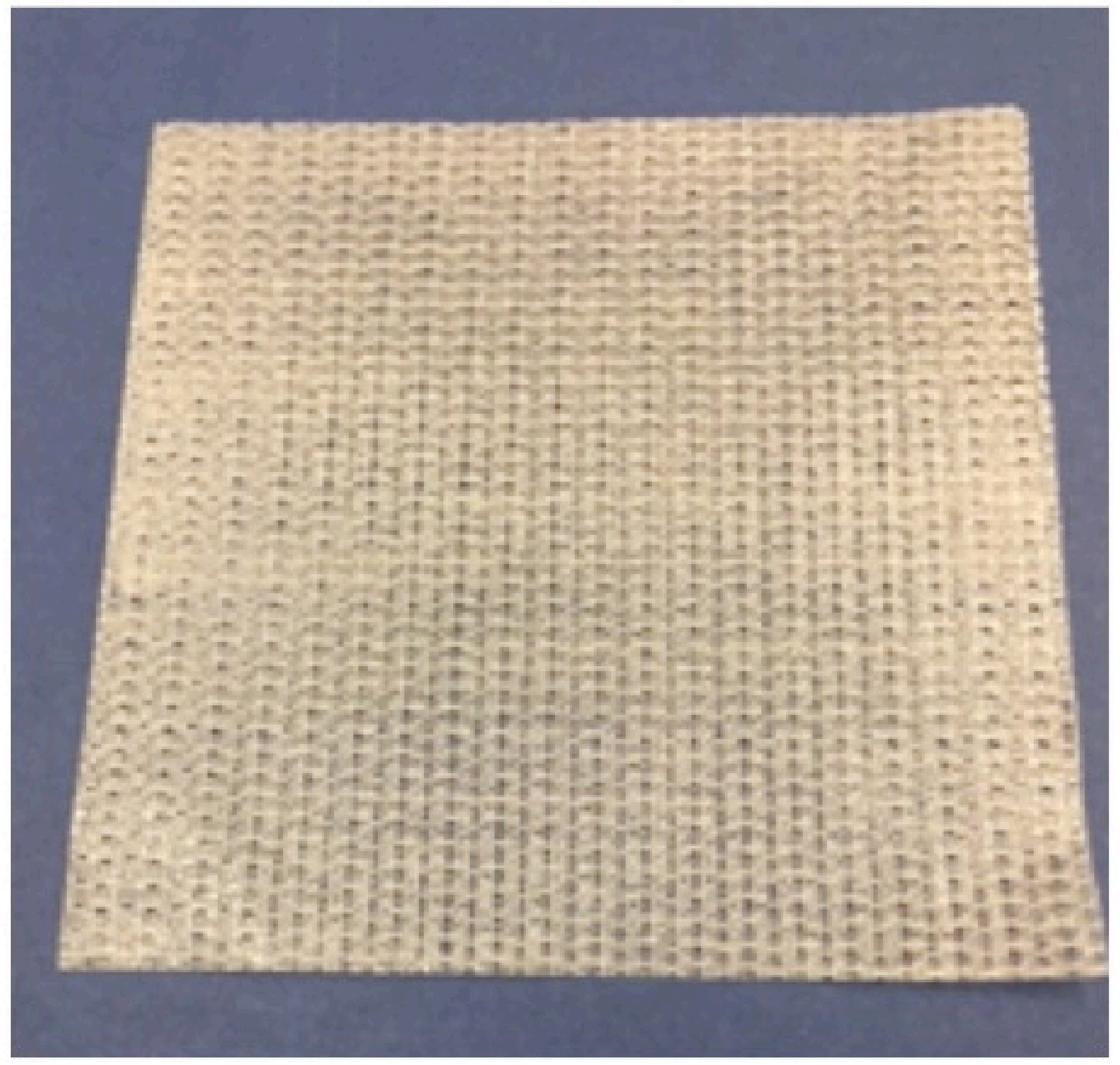
Ashland's vinyl ester resin technology for prepregs

- Arotran 901 has been successfully cast into prepregs at Renegade Materials
  - hot-melt method
  - with carbon and with glass fibers
  - acceptable processability & handling (tack)
  - long shelf life at room temp **(23 months)**

RENEGADE MATERIALS CORPORATION
UNBRIDLED INNOVATION





Carbon fiber and glass fiber prepregs
prepared at Renegade Materials in **Feb '16**

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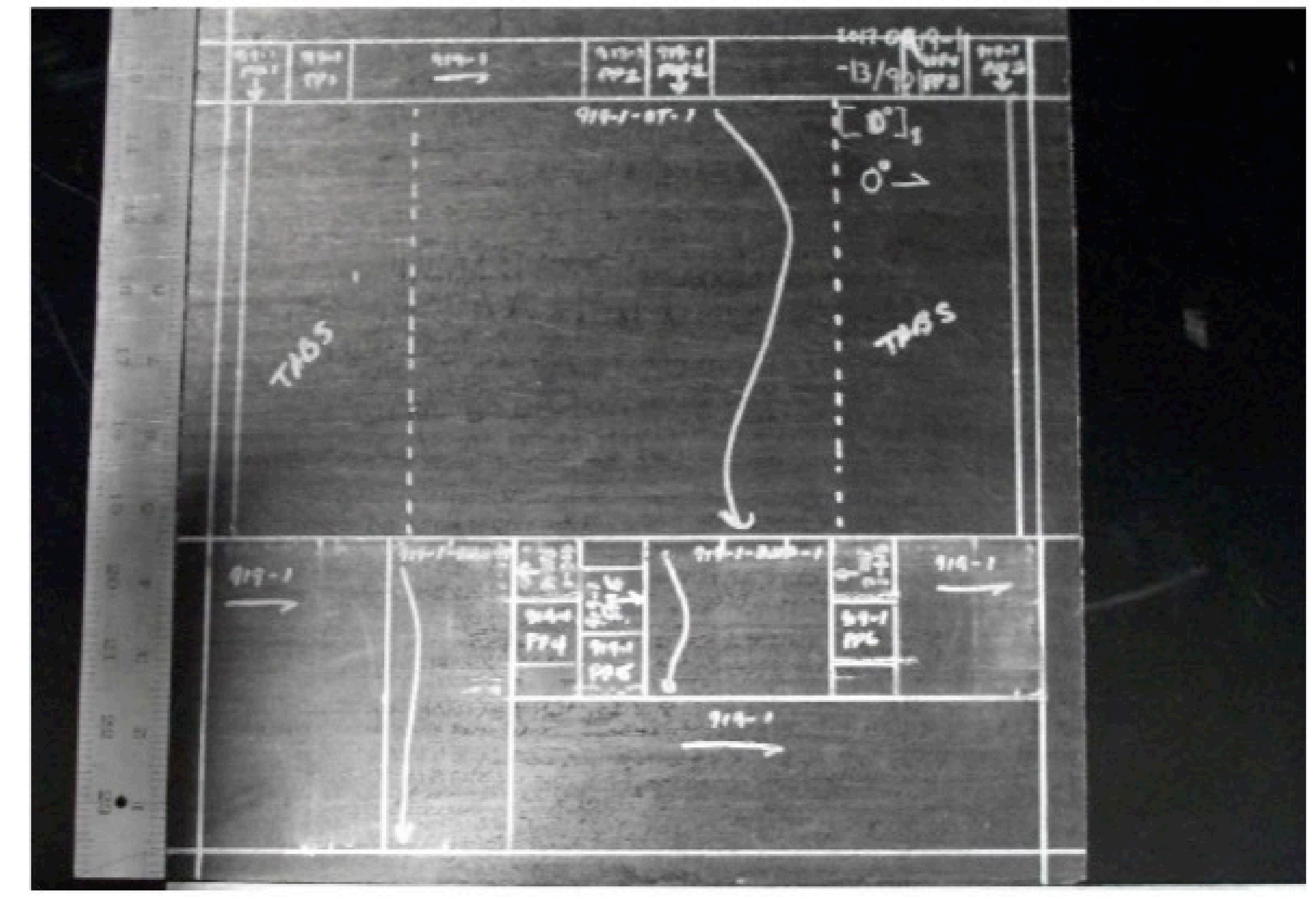
other processing considerations

- **fibers:** W grade fibers (ribbons) easier to process than T grade (ropes)

- **sizings:** processability & handleability of sized fibers were also taken into consideration when down-selecting systems for further work <u>and</u> selecting the best-performing system
  - spreadability
  - stiffness
  - ease of alignment

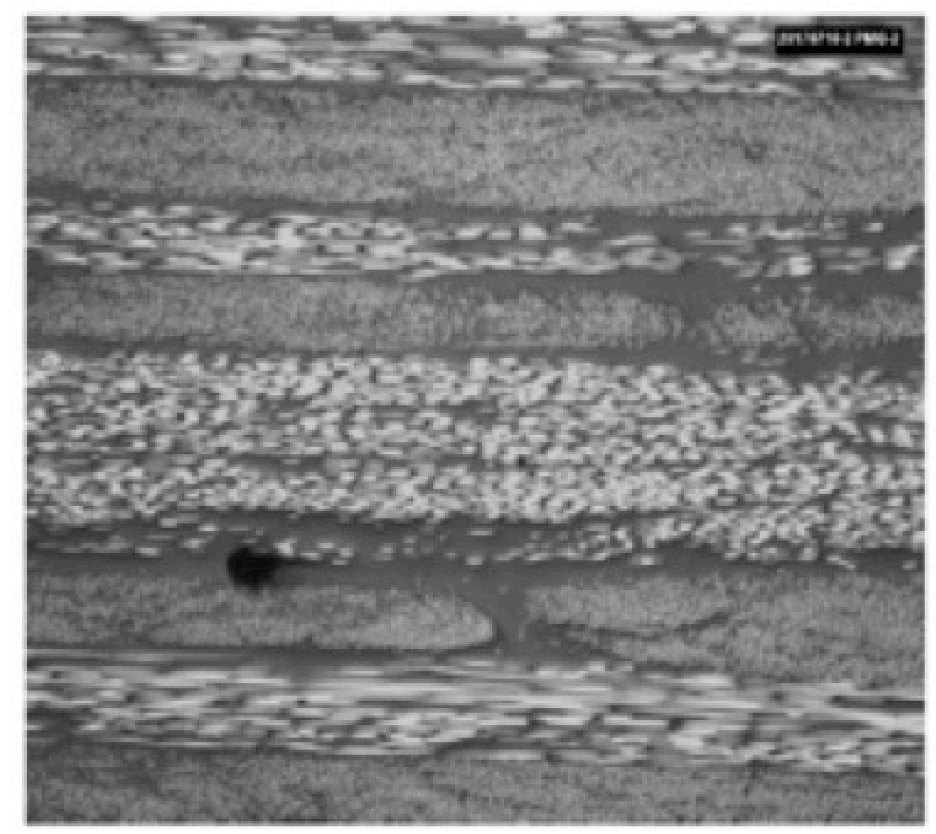
compression molding and mechanical testing

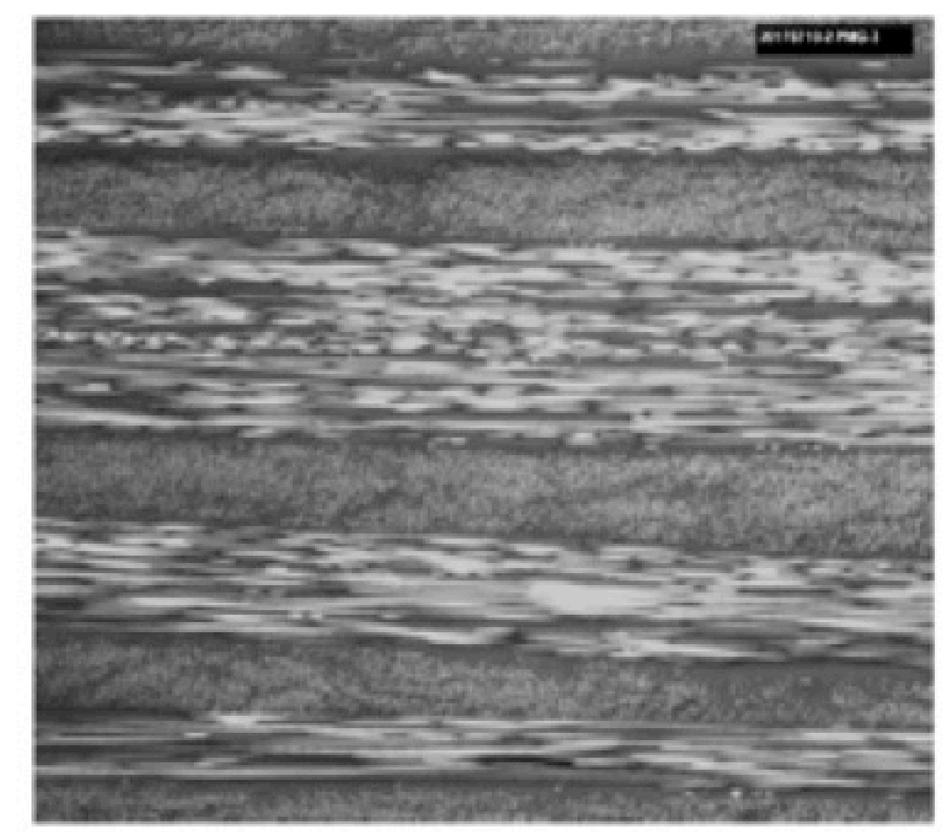
- 12" x 12" plaques were compression-molded at UDRI
  - 325 – 350°F (163 – 176°C)
  - 100 psi
  - 3 minutes

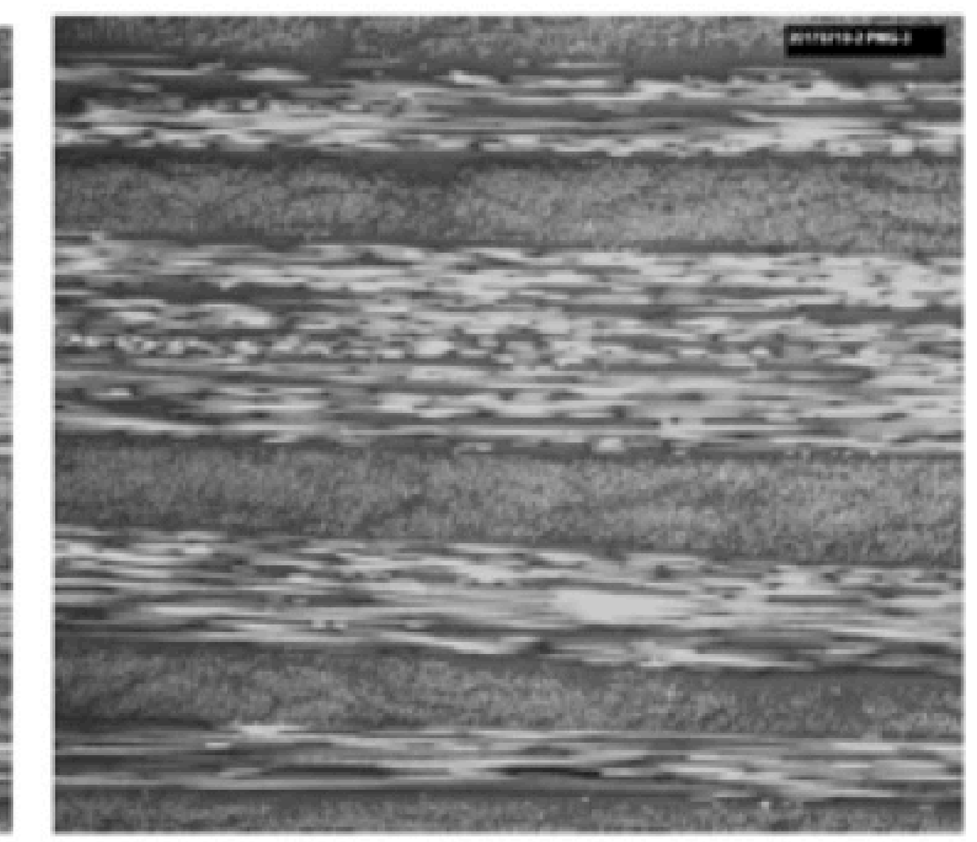


- two architectures
  - biaxial: $[0/90]_{4s}$
  - unidirectional $[0^{\circ}]_8$ & $[0^{\circ}]_{24}$

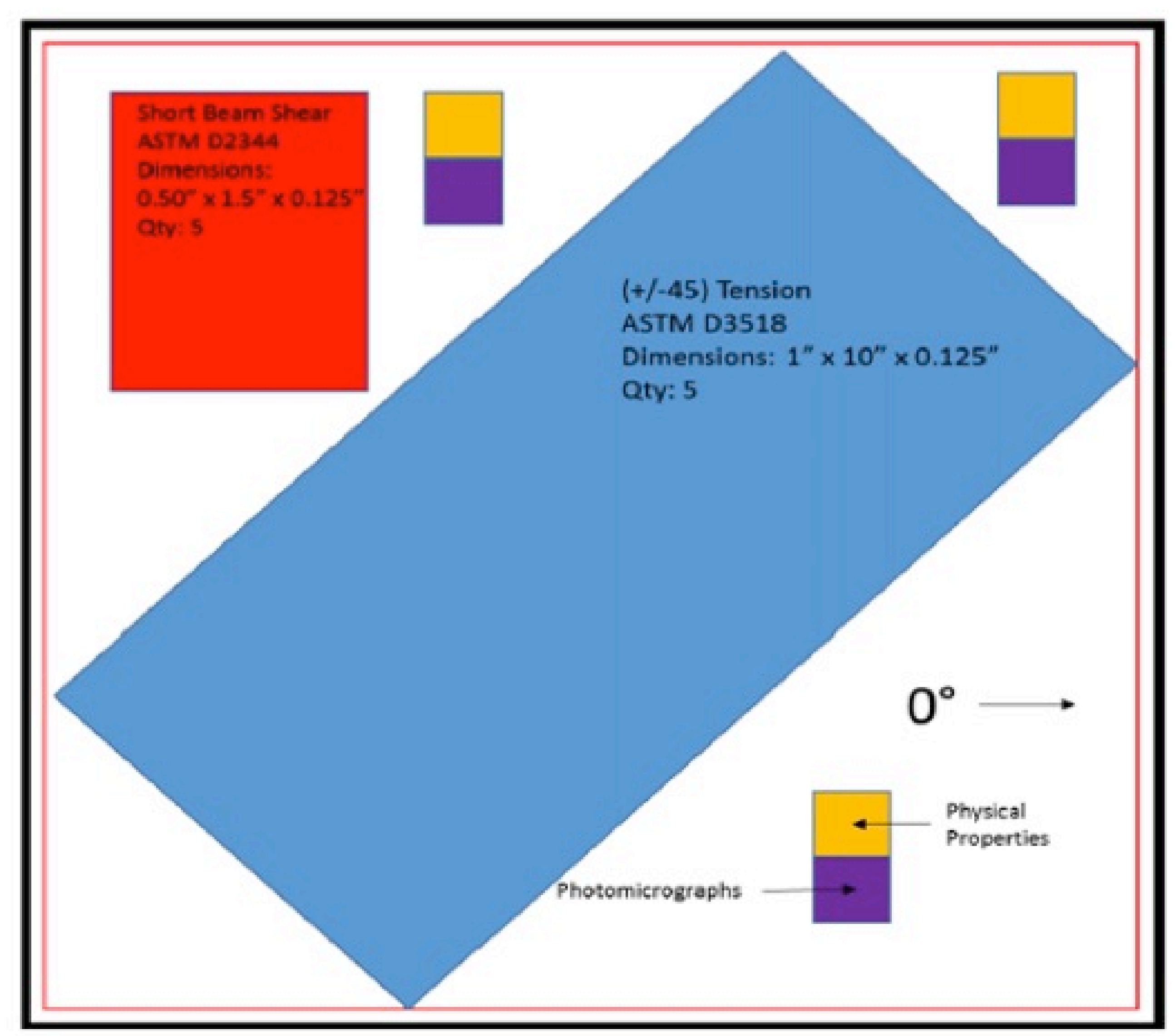
- "QC" of plaques
  - photomicrographs
  - low void content

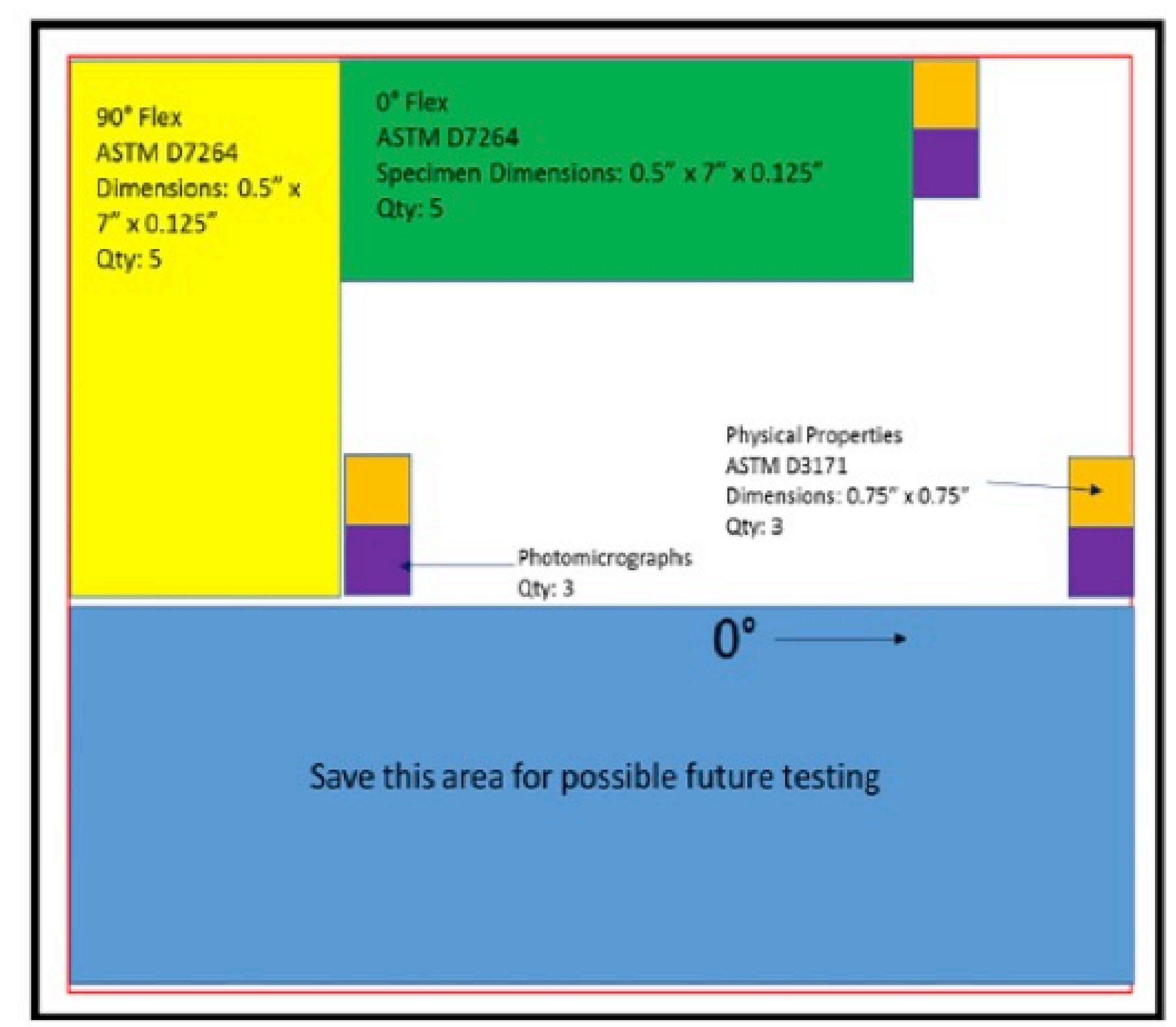






- samples shipped to Ashland for thermomechanical testing





mechanical testing protocol

Site	Scope	Tests	ASTM #	Architecture
MSU	Interlaminar Shear Strength (ILSS)	Short Beam Shear	D2344	$[0^{o}]_{11}$
UDRI	"QC" of Molded Prepreg Surrogates	Resin, Void & Fiber Content	D3171	$[0/90]_{4s}$, $[0^{o}]_{8}$, $[0^{o}]_{24}$
		Photomicrographs		
Ashland	In-plane Shear Strength	+/-45 Tension	D3518	$[0/90]_{4s}$
	Interlaminar Shear Strength (ILSS)	Short Beam Shear	D2344	$[0/90]_{4s}$
	Longitudinal (0^{o}) & Transverse (90^{o}) Flexural Strength & Modulus	3-Point Flex	D7264	$[0/90]_{4s}$
	Longitudinal (0^{o}) & Transverse (90^{o}) Tensile Strength & Modulus	0 and 90 Tension	D3039	$[0^{o}]_{8}$
	Fracture toughness	Mode I	D5528	$[0^{o}]_{24}$
		Mode II	D7905	$[0^{o}]_{24}$
	Glass Transition Temperature	DMA, tan δ	D4065	$[0/90]_{4s}$

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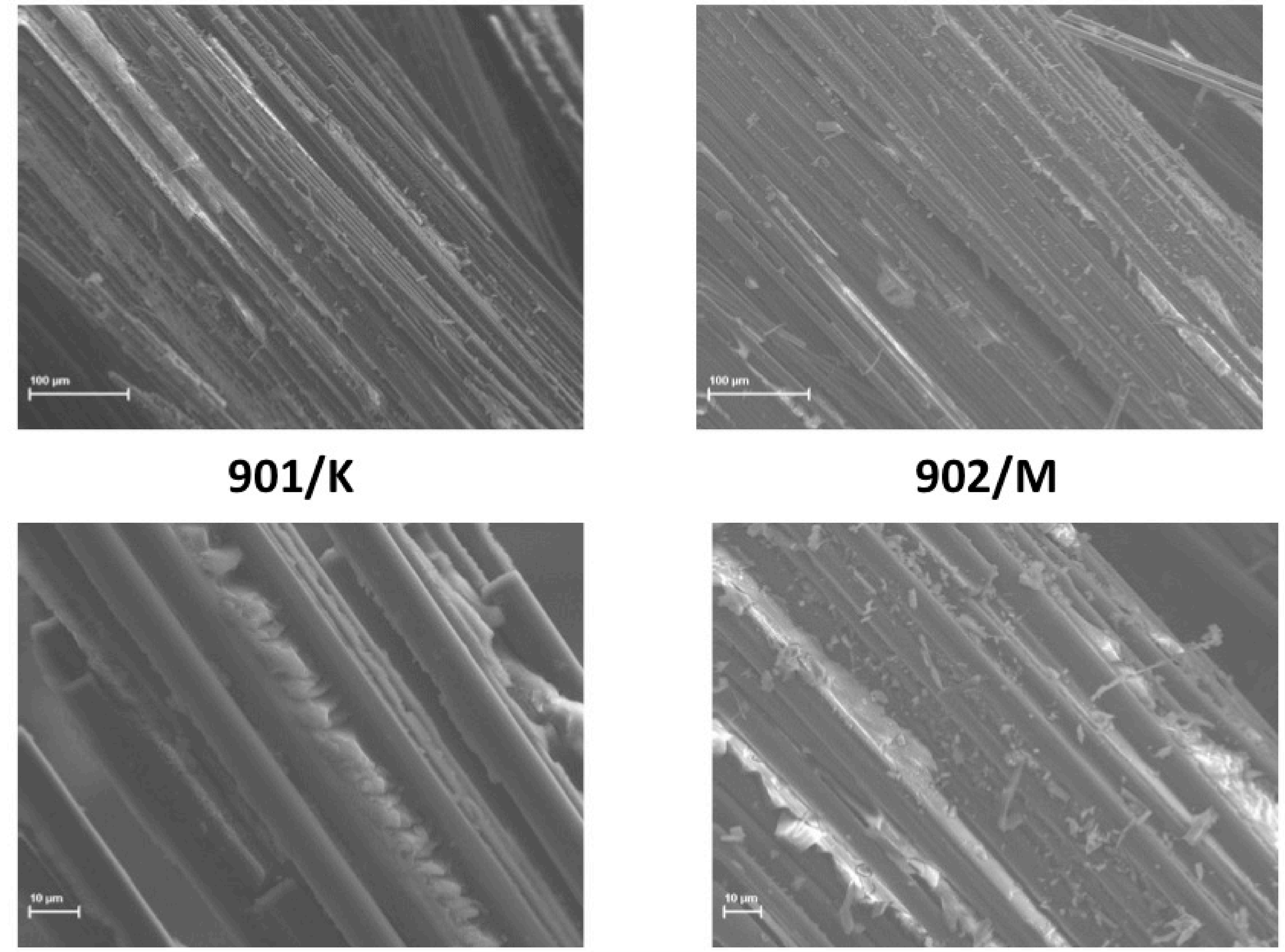
mechanical properties of best-performing system (901/K)

	Property	901/K
Resin-dominated	ILSS (MPa)	53
	In-Plane Shear Strength (MPa)	90
	Fracture toughness G_{Ic} (lbs-in/in^2)	2.6
	Fracture toughness G_{IIc} (lbs-in/in^2)	3.24
Fiber-dominated	Flexural strength (MPa)	1032
	Flexural modulus (GPa)	70
	Tensile strength (MPa)	1501
	Tensile modulus (GPa)	122



Fracture surfaces of in-plane shear specimens

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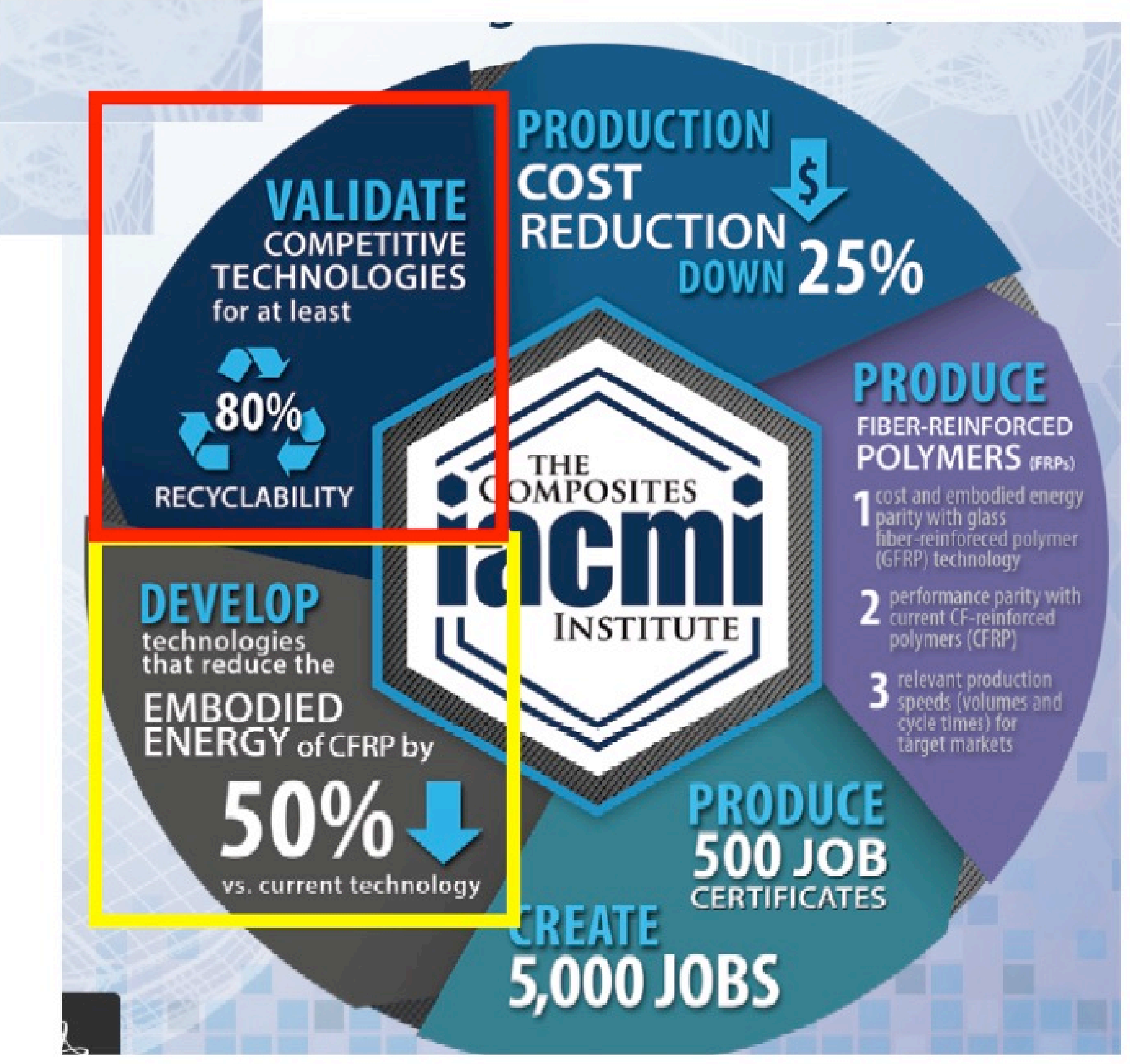
recycling & embodied energy considerations

IACMI's recycling and embodied energy objectives

- IACMI has these stated goals:
  - increase the recyclability of composites into useful products **by 80%** by 2020
  - reduce embodied energy **by 50%** vs. current technology



- key finding: the use of vinyl ester prepregs can help achieve these goals !

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exploiting vinyl ester chemistry

- unlike epoxies, which are cured with an amine or an anhydride co-reactant, vinyl esters do not undergo crosslinking reactions during the production and storage of a prepreg

- vinyl esters prepregs are produced at a temperature much lower than they are cured.
  - production using hot melt resins at 170°F
  - curing with peroxide initiator at 300-350°F
  - very stable at room temperature

- the absence of crosslinking leads to advantages over epoxies in
  - shelf-life stability / no need to store in a freezer
  - recycling and re-use of prepreg scrap

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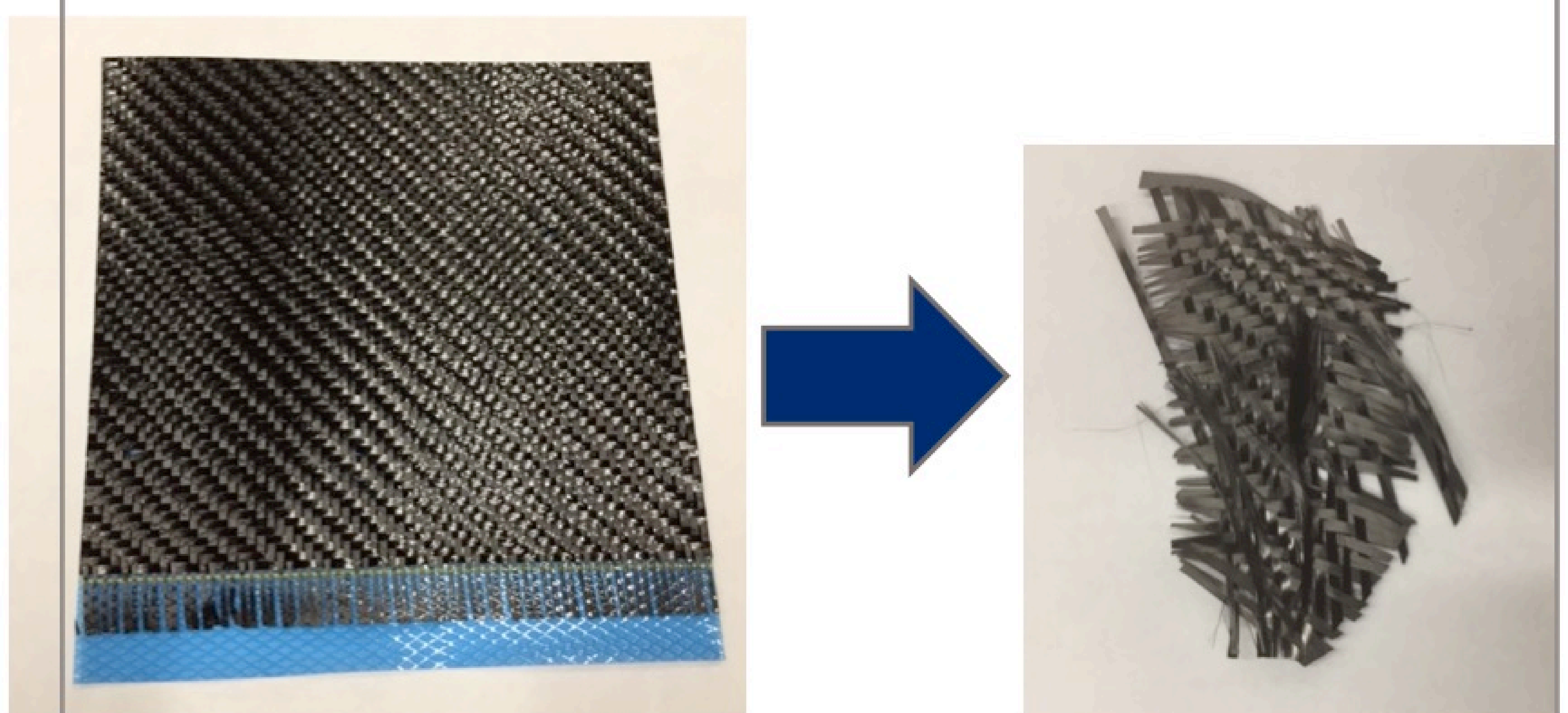
recovering the carbon fibers from prepreg scrap

vartega

- Vartega's focus: recovery & recycling of carbon fibers from prepreg scrap
- technology: multi-step extraction
- Vartega's process readily removes resin from Renegade prepregs



Renegade prepreg
(33-40 wt % resin)

After
(1-3 wt % resin)

recycling VERs
is easier than epoxies

- it should also be possible to recover the resin in a usable form (future work)

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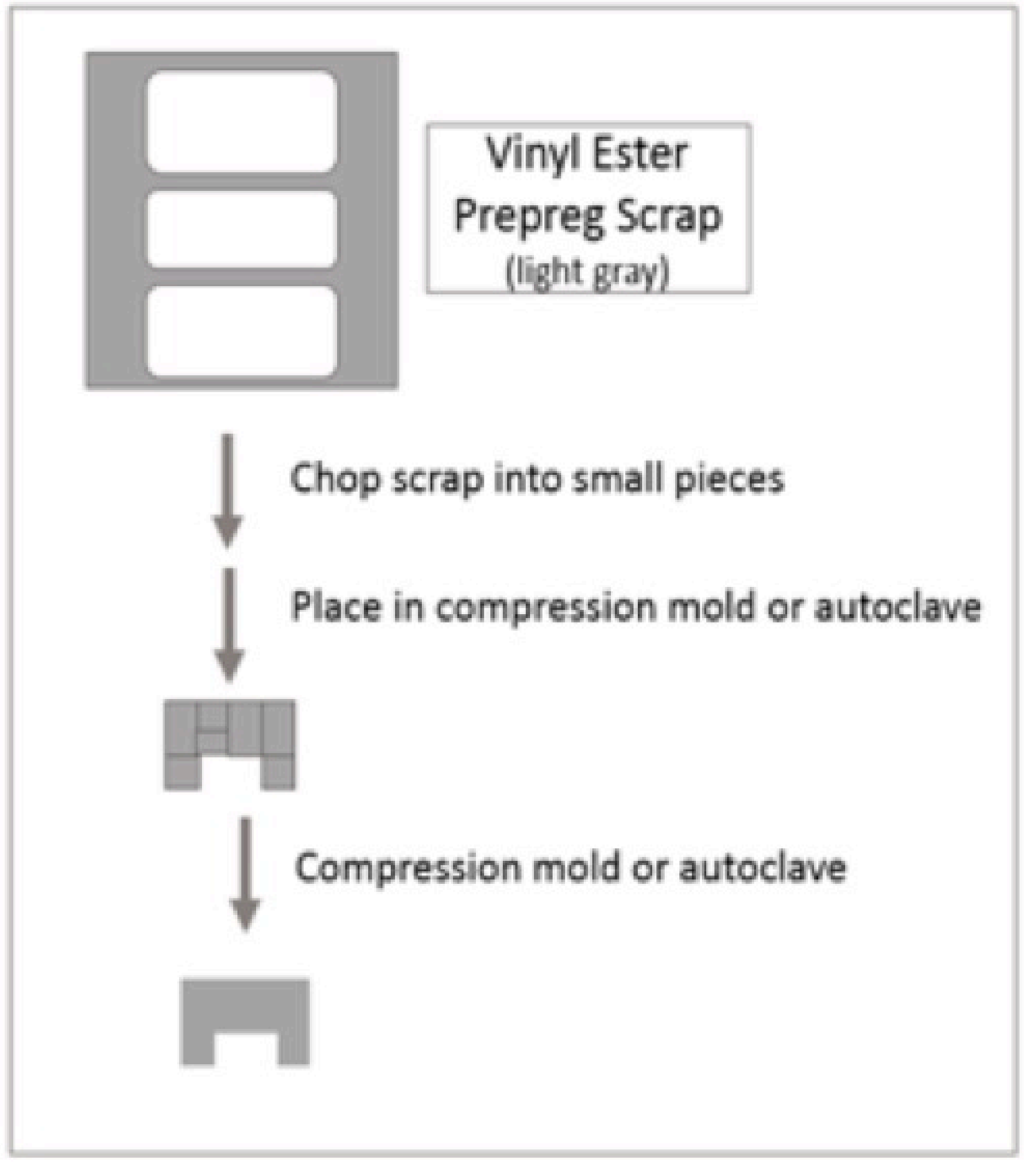
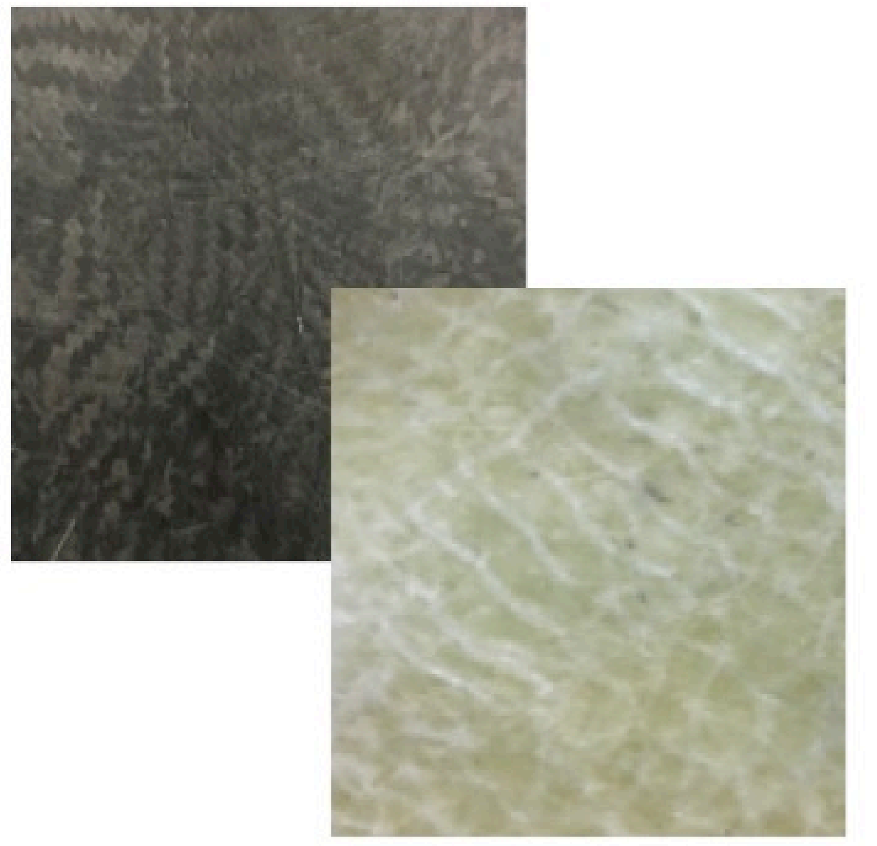
re-use of vinyl ester prepreg scrap

- re-use of prepreg scrap is possible
  - compression molding of scrap
  - possible due to the absence of crosslinking

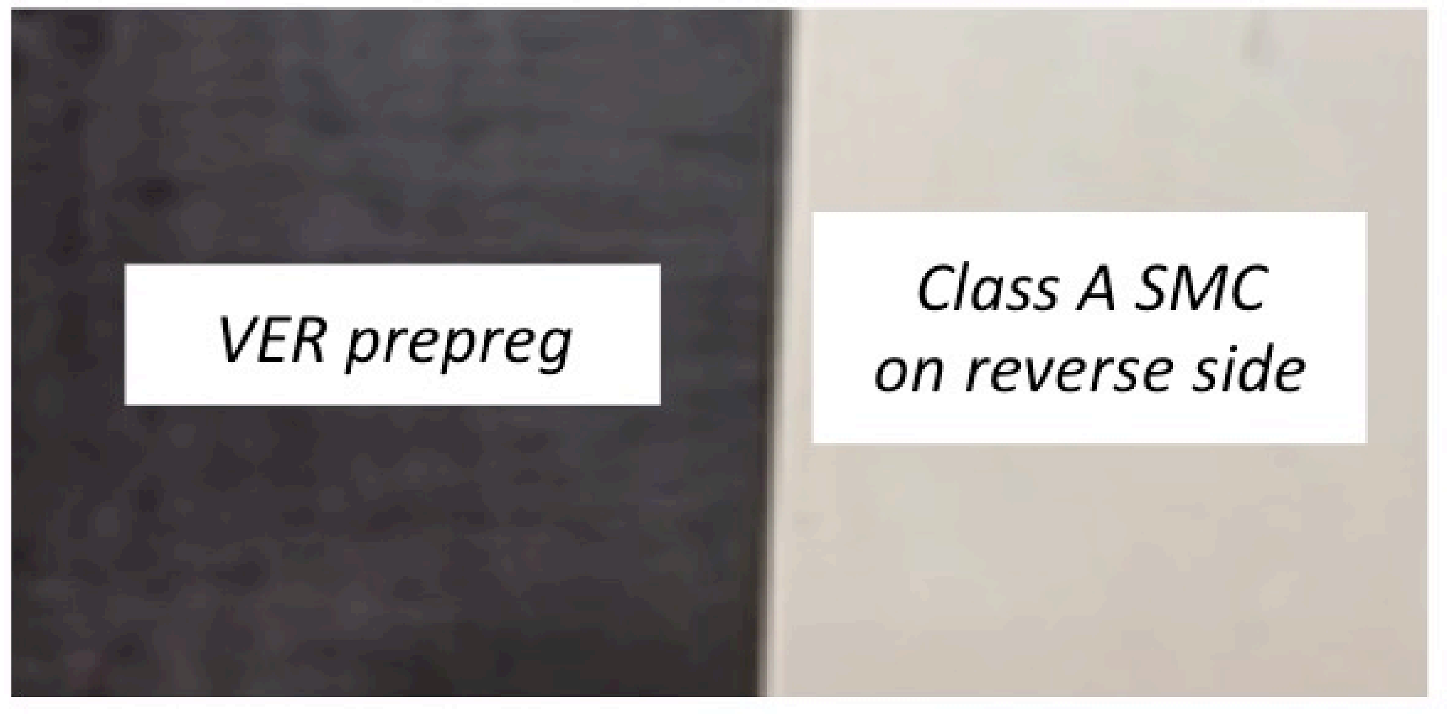
Compression molding of prepreg scrap





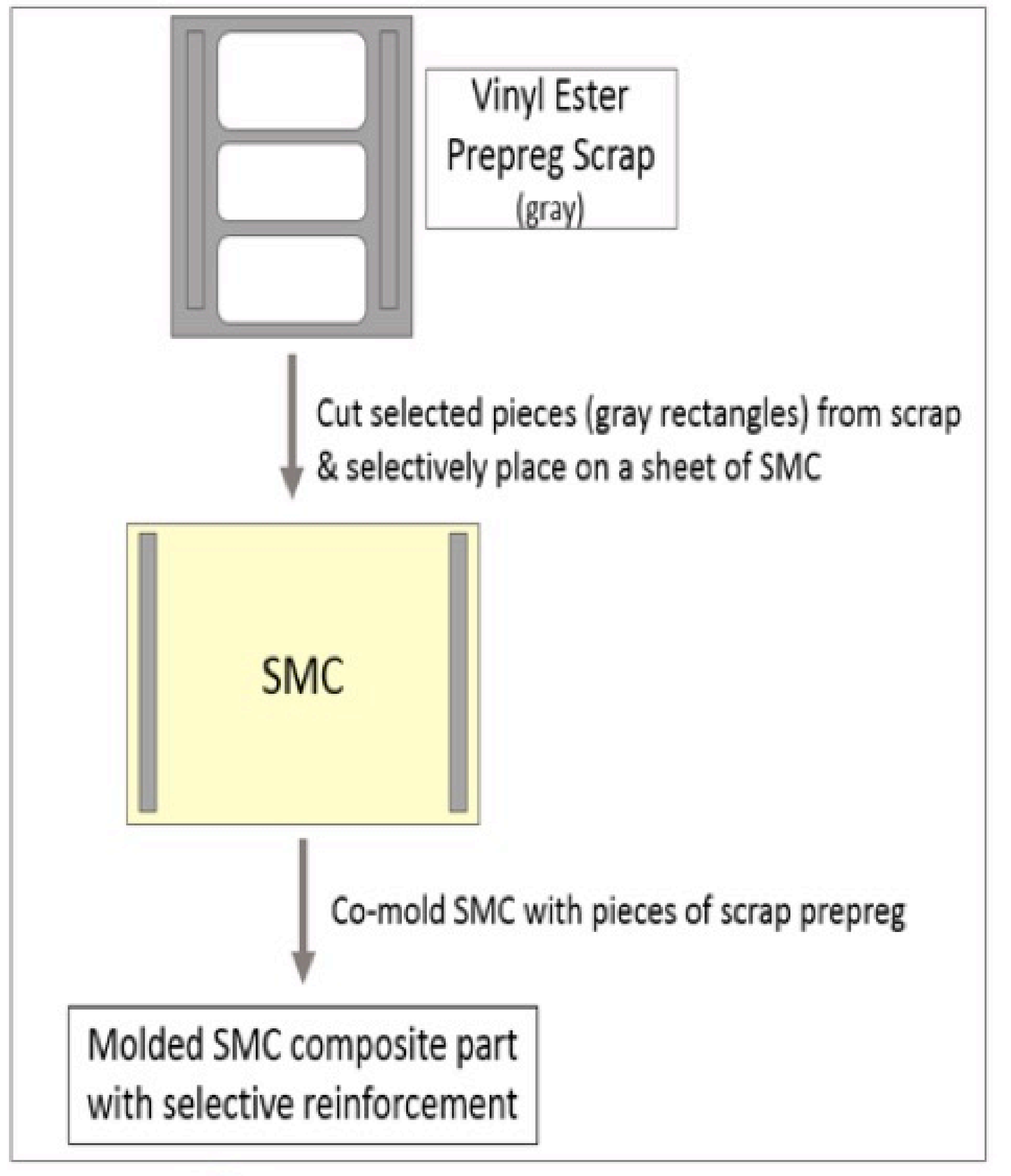
chopped pieces of Renegade prepregs molded after 23 months

- co-molding with SMC is also possible
  - virgin prepreg or prepreg scrap
  - molding conditions virtually the same



both sides of a co-molded prepreg / SMC part

Selective Reinforcement of SMC



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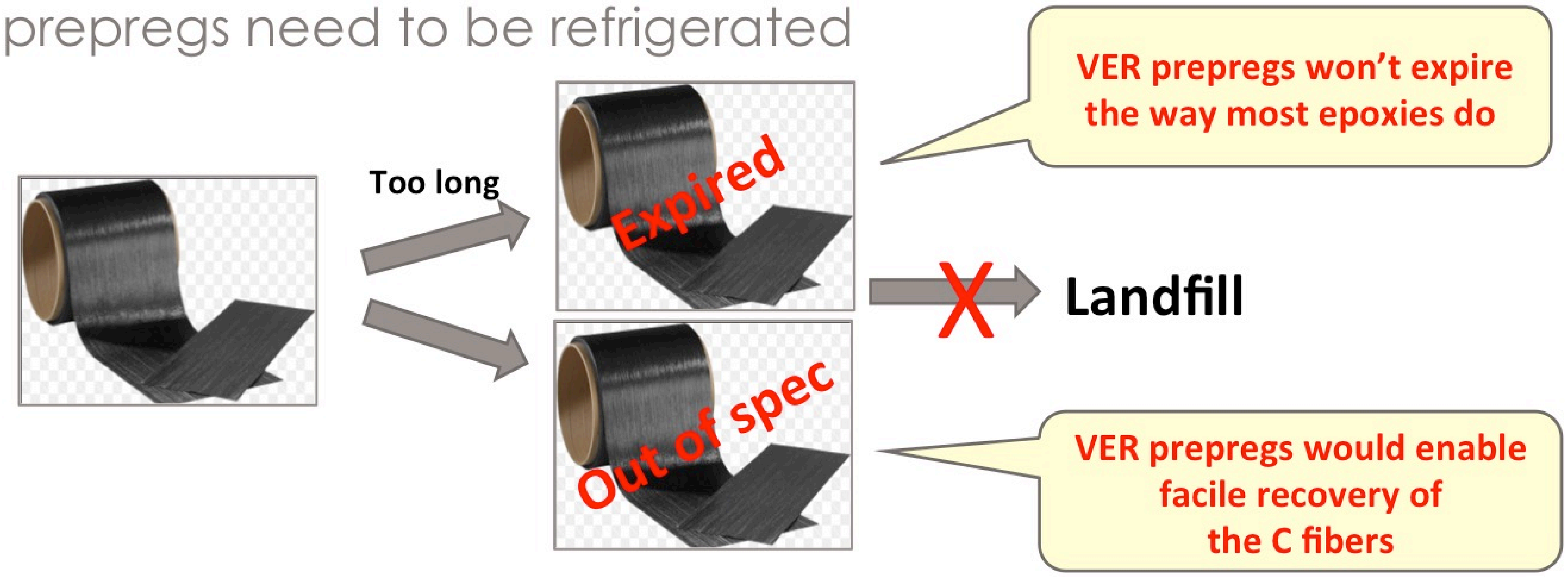
how vinyl ester prepregs can reduce process scrap

- expired prepreg:
  - created when prepreg is kept beyond its recommended shelf life & becomes unusable
  - most epoxy prepregs need to be refrigerated



- cutting scrap:
  - the pieces of prepreg not used to make a part

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embodied energy calculations

Embodied energy =

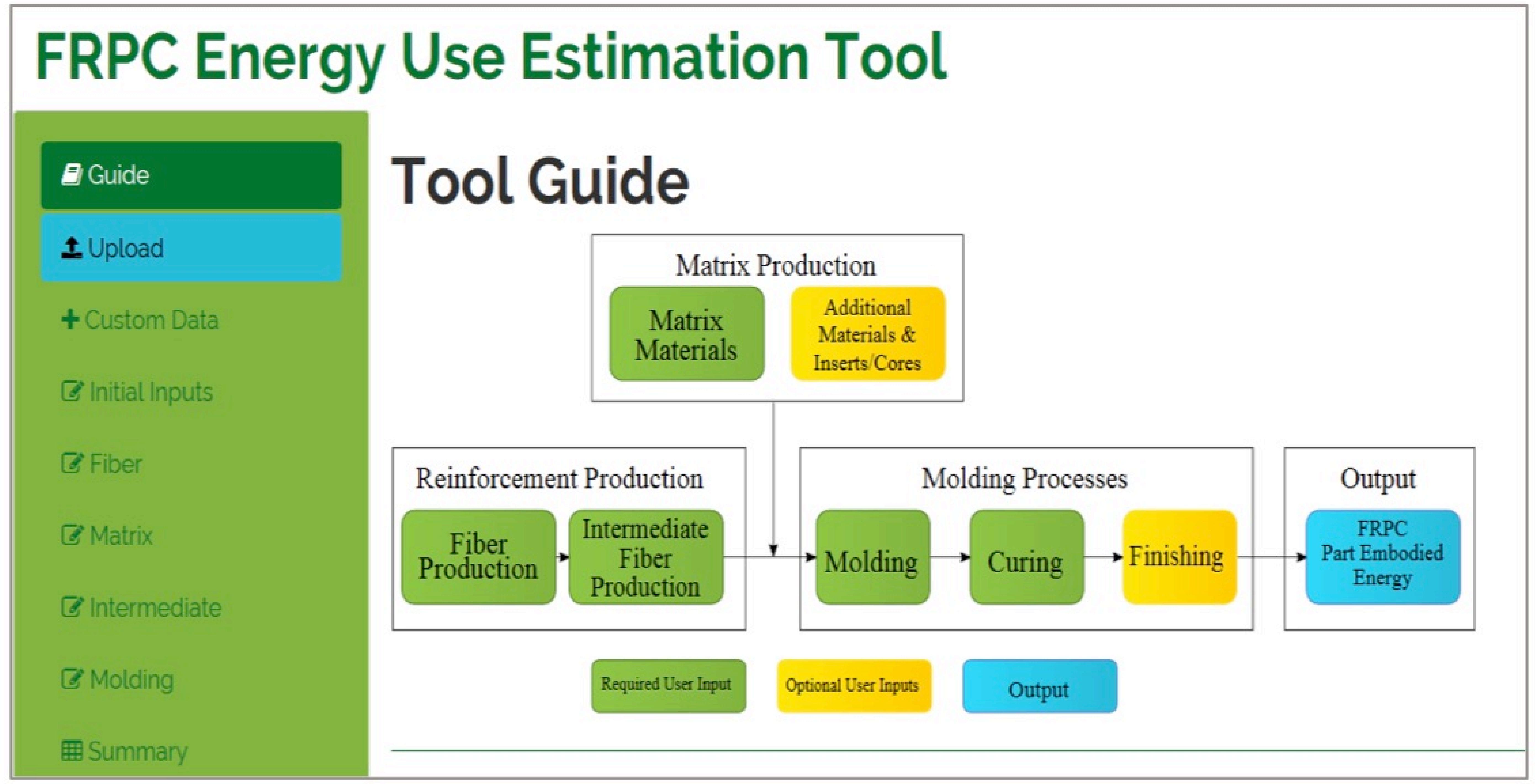
[Energy to make the resin & the fiber]

+

[Energy to make the part]

+

[Energy to make the energy]



- FRPC is an easy-to-use tool developed by Sujit Das & Kristina Armstrong at ORNL
- we have used it to compare:
  - styrene-free vinyl esters (customized input)
  - epoxies (default values)

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https://ornlenergyestimatortools.shinyapps.io/frpc-energy-estimator2/

potential embodied energy savings with vinyl ester prepregs

- 30% is the most commonly-heard value quoted for prepreg scrap
- the FRPC calculator uses 40% scrap as a default value for "Manual Prepregs"

% Process Scrap	% Reclaim VER	% Reclaim Epoxy	% Reduction in Embodied Energy
30	50	0	9
	100	50	6
		25	14
		0	22
40	50	0	17
	100	50	11
		25	22
		0	33

Some very significant reductions in embodied energy should be possible with VERs

- key assumptions:
  - calculations are based on the "average primary energy" in the US
  - vinyl ester parts are 10% heavier than epoxy parts due to lower mechanicals (very conservative)
  - there are refrigeration energy savings with VER prepregs
    - no need for freezer storage
  - the energy required for recycling is not included in the analysis
    - but it should be low for an extraction process

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in summary .....

- vinyl ester / carbon fiber prepregs have an attractive value proposition
  - no styrene
  - long shelf life (> 23 months)
  - no need for refrigeration
  - fast cure
  - reduction in the amount of process scrap that needs to go to a landfill
  - reduction in embodied energy
  - cost-effective

looking ahead …..

motivation for a stage 2 project

- vinyl ester prepregs have an attractive value proposition
- stage 1 work has been done with prepreg surrogates, not prepregs
- we want to demonstrate utility in an actual part
- we want to explore recycling and re-use in greater depth
- everyone leverages everyone else's $ and resources

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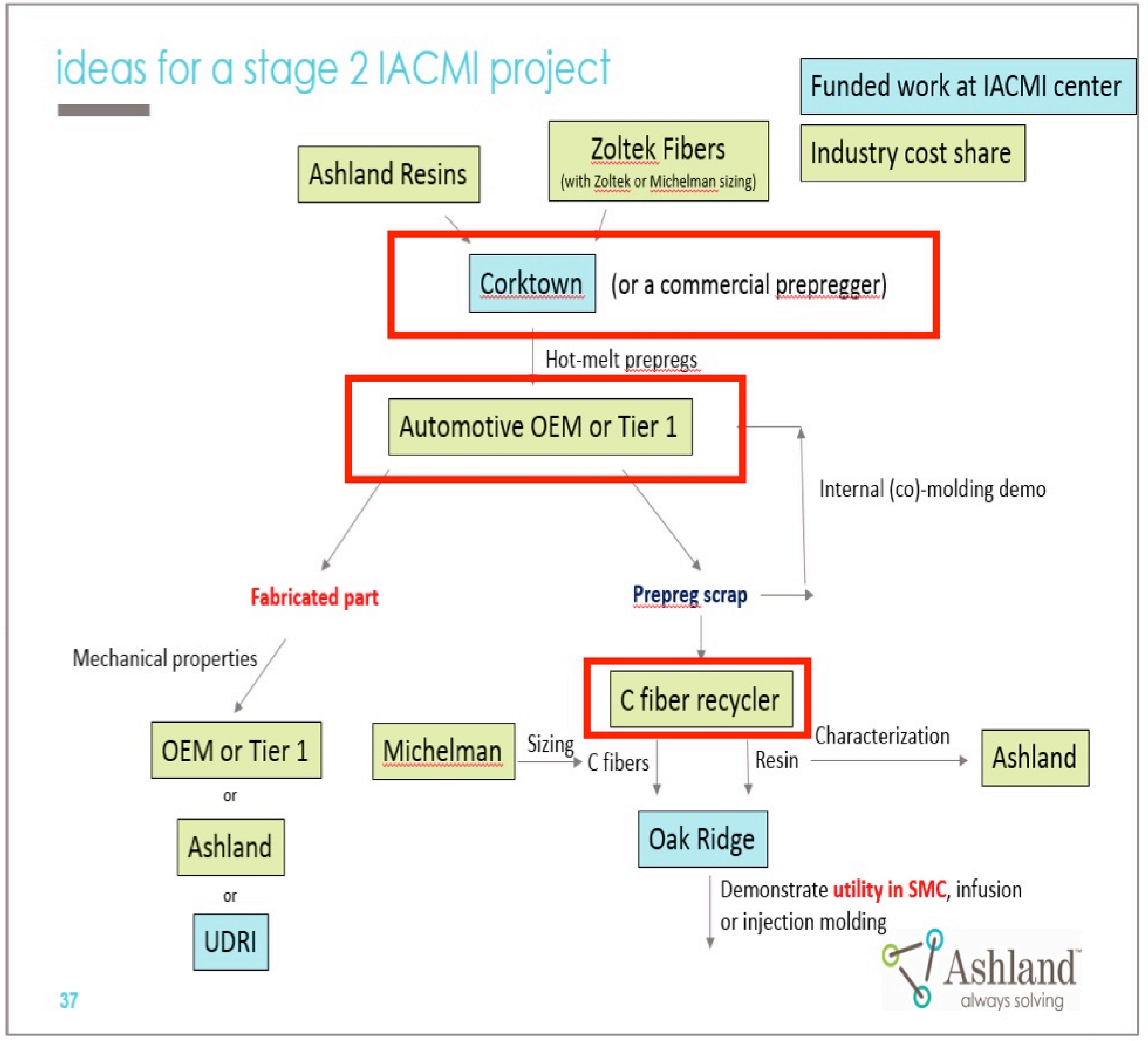
potential partners for a stage 2 project

- options for a Stage 2 project:
  1. fabrication of parts from optimized prepreg formulation + recycling component
  2. fabrication of parts with prepreg
  3. stand-alone project focused on recycling
- there is a potential role for all of the Stage 1 partners
  - Ashland, Michelman, Zoltek
  - Michigan State, UDRI
- we would need new, additional partners
  - **prepregger**
  - **OEM or Tier 1 with a specific part in mind**
  - **recycling partner**
  - Oak Ridge



what's next?

- complete final report for Stage 1 project
- define a Stage 2 project
- participate in the ACMA recycling conference in April
  - **Title:** *Recycling and Re-use of Vinyl Ester Prepreg Scrap*
  - **Authors:** *Joe Fox, Jonathan McKay, Jim Emrick*
- pursue non-automotive opportunities for vinyl ester / carbon fiber prepregs
  - Infrastructure repair
  - filament winding applications (tanks, rollers….)
  - unmanned aircraft & drones
  - others

benefits of involvement in IACMI & IACMI projects

- connections
  - IACMI connected us to Michelman and Zoltek
  - recycling and modeling connections

- new opportunities
  - we have been pulled into 3 other IACMI projects
  - two additional projects are going through the approval process

- leverage
  - access to existing equipment and expertise
  - access to $ from the DOE, the state of Ohio, and our industrial partners

acknowledgements

Partner	Responsibilities	Team members
Ashland always solving	Resin Development, Mechanical & Thermal Analysis Testing	Jon McKay, Jim Emrick, Allison Michaels, Tom Grentzer, Laura Littlejohn, Stephanie Fulmer, Nicole Clark
MICHELMAN	Sizing Development	Steve Bassetti, Norman Seung
ZOLTEK Toray Group	Sizing Application to PX35 Fiber	Phil Schell, David Corbin
MICHIGAN STATE UNIVERSITY	Characterization of Resin-Fiber Interface	Mike Rich, Larry Drzal, Ed Drown, Brian Rook, Per Askeland
UDRI UNIVERSITY of DAYTON RESEARCH INSTITUTE	Fabrication & Molding of Prepreg Surrogates, Project Management	Jared Stonecash, Mike Pratt, Andy Muno, Brian Rice
RENEGADE MATERIALS CORPORATION UNBRIDLED INNOVATION	Prepregging	Laura Gray
vartega	Recycling of carbon fiber from prepreg scrap	Andrew Maxey, Sean Kline, Jordan Harris

acknowledgements to DOE, Jobs Ohio and IACMI

- DOE
  - funding support — Kelly Visconti
- Jobs Ohio:
  - funding support — Glenn Richardson
- IACMI:
  - general guidance — Cliff Eberle, Dale Brosius
  - embodied energy — Komal Kooduvalli, Sujit Das, Kristina Armstrong
  - recycling — Soydan Ozcan
  - cost share — Lisa Fitzpatrick, Chelsea Ensey
  - press releases — Robin Pate
  - meeting logistics — Jill Hill
  - project administration — Erin Brophy, John Unser, Lisa Lee

Thank you for your attention.

Questions ??

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