PUSHING the BOUNDARIES with NOVEL THERMOSET POLYOLEFIN COMPOSITES

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2019 SPE ACCE

AGENDA

- Background on Materia and its technology
- Composites for automotive: Materials and Processes
- Proxima Composite Resin performance

MATERIA AT A GLANCE

- Manufacturer of high-performance thermoset resins with unique performance properties
- Founded in 1998
- Applying Nobel-prize winning chemistry to materials
- World-class technical services and support
- Only resin system that utilizes Grubbs Catalyst® technology

PROXIMA®

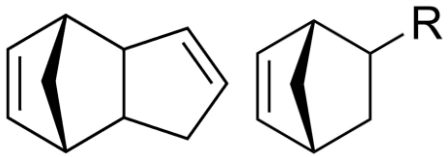
THERMOSET RESINS

We enable our global customer base to be more competitive in the market with…

- High Temperature Subsea Insulation and Buoyancy Products
- Tough, Downhole Tools for High Pressure and High Temperature
- High Speed and High Frequency Electronics
- Advanced Composites

PROXIMA® THERMOSET POLYOLEFINS

CYCLIC OLEFIN MONOMERS



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GRUBBS CATALYST

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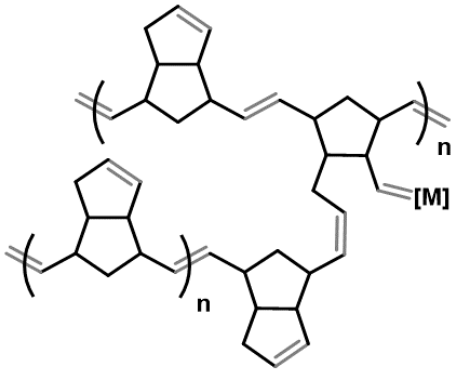
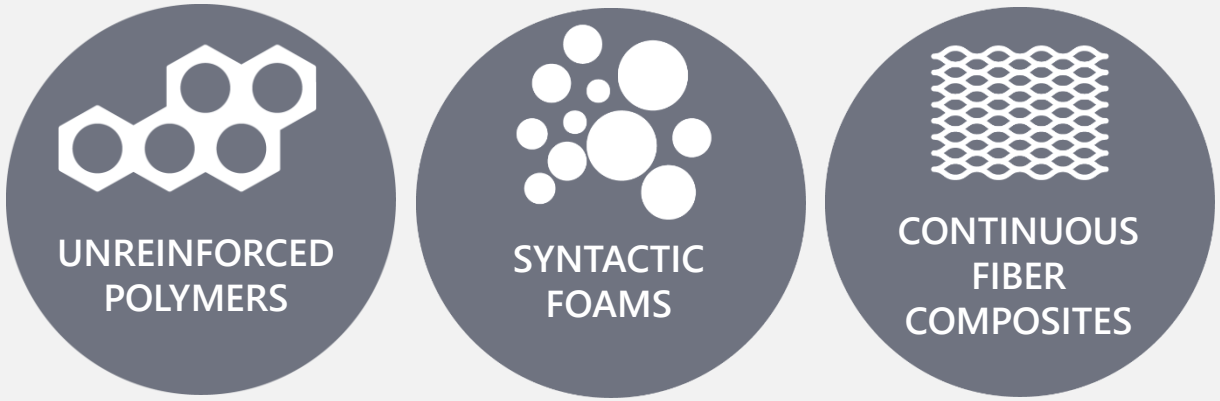
PROXIMA® THERMOSET POLYOLEFINS

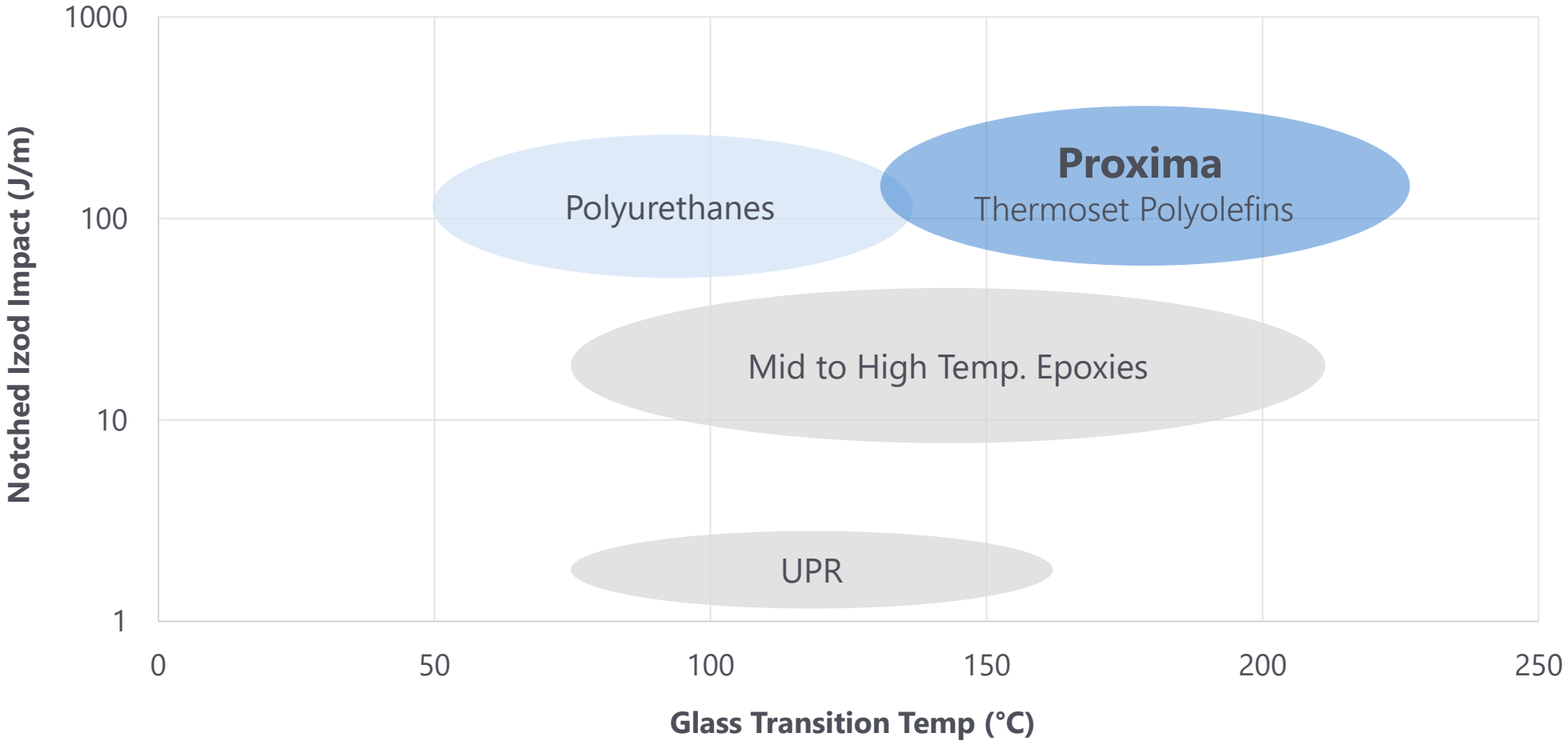


- Two-part liquid thermoset resin systems
- Based on dicyclopentadiene (DCPD) and a family of co-monomers
- Ring Opening Metathesis Polymerization enabled by Ru-based Grubbs Catalyst® technology
- Wide range of performance and processing capability



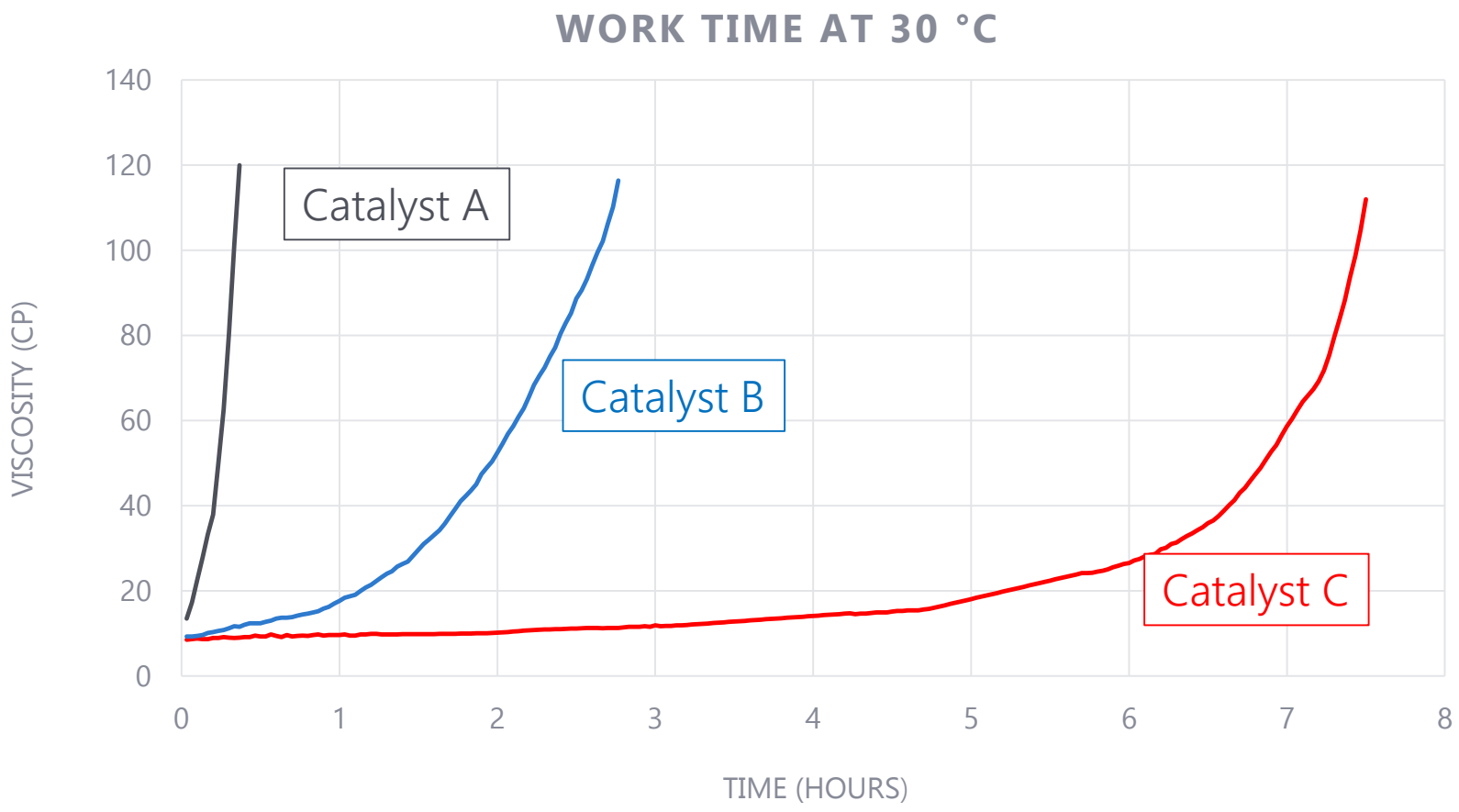
THE PROXIMA® RESIN DIFFERENCE

Proxima® Thermoset Polyolefin Resins combine high temperature stability with high impact toughness.

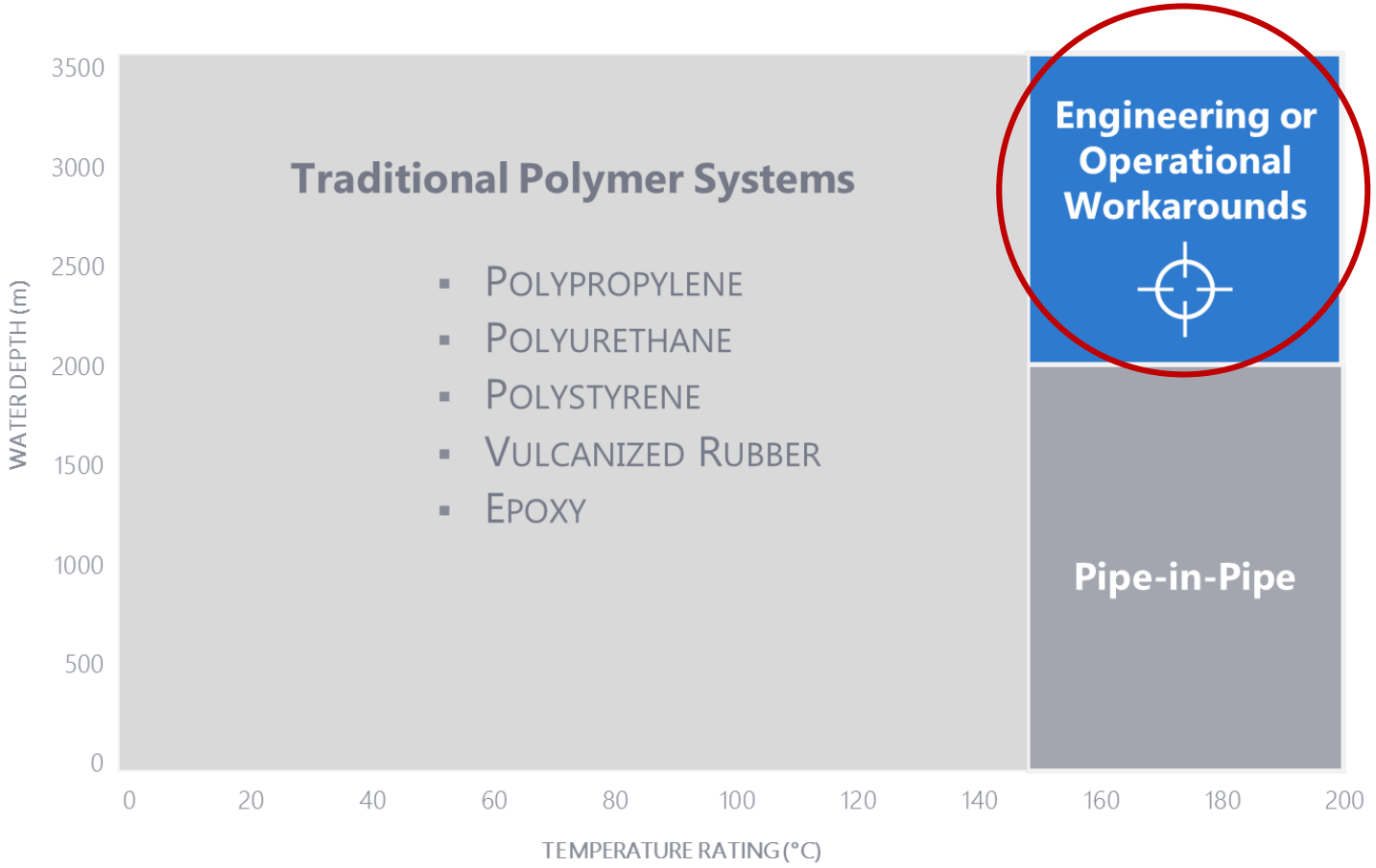


CURE RATE CONTROL FOR CYCLE TIME OPTIMIZATION

Proxima® composite resins enable significant formulation flexibility with controlled curing, from seconds to hours; enabling customers to optimize processing / molding.

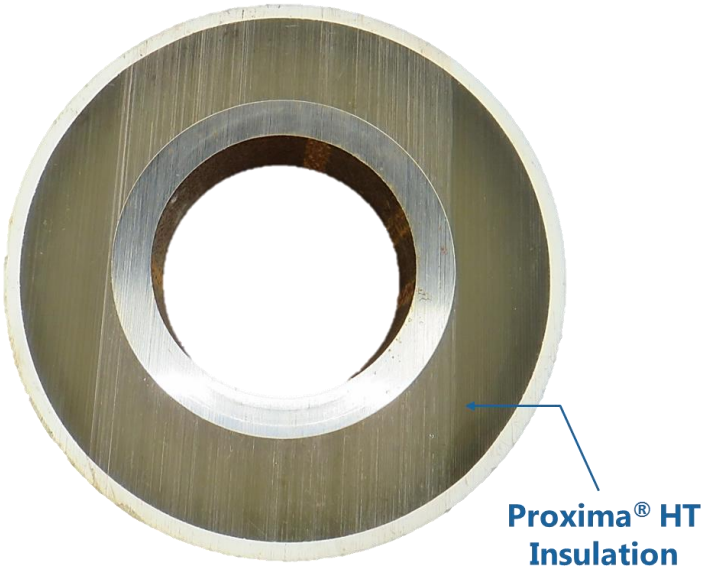


SUCCESS IN HIGH TEMPERATURE SUBSEA INSULATION



WHY PROXIMA?

- Low Water Uptake, No Hydrolysis
- Flexibility allows low internal stress
- Low viscosity for easy / tunable processing



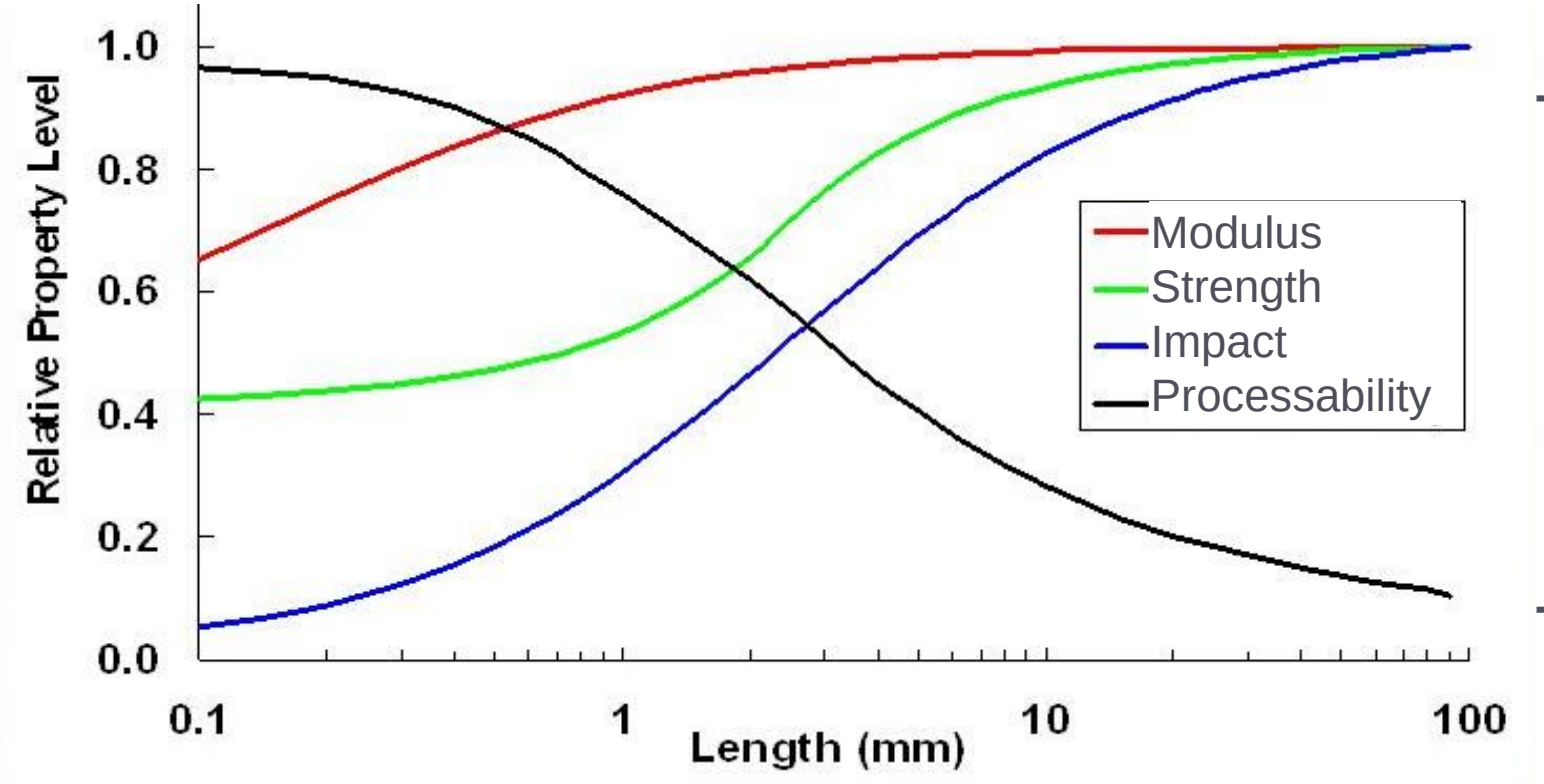
The in-field success of Thermoset Polyolefin Resins in Oil & Gas has been extended to Automotive

COMPOSITES FOR AUTOMOTIVE: MATERIALS AND PROCESSES

TYPES OF FIBER-BASED COMPOSITES

Different industries define composites in various ways, and performance varies….

Fillers **Short Fiber** **Long Fiber** **Continuous Fiber**



How to address the trade-off in Processability / through-put ?

Thomason, J.; Vlug, M.A.. (1997). Composites Part A. 27. 277-288..

STRUCTURAL COMPOSITES: AUTOMOTIVE TRENDS

CompositesWorld has recently summarized the industry trends as follows:

Pre-2013 — Direct use of "aerospace materials" for small volume auto

Aluminum saves 400 kg in 2012 Range Rover

2013 (i-Series) — Demonstration of HP-RTM for Structural parts / BIW

Aluminum saves 300 kg in 2015 F-150

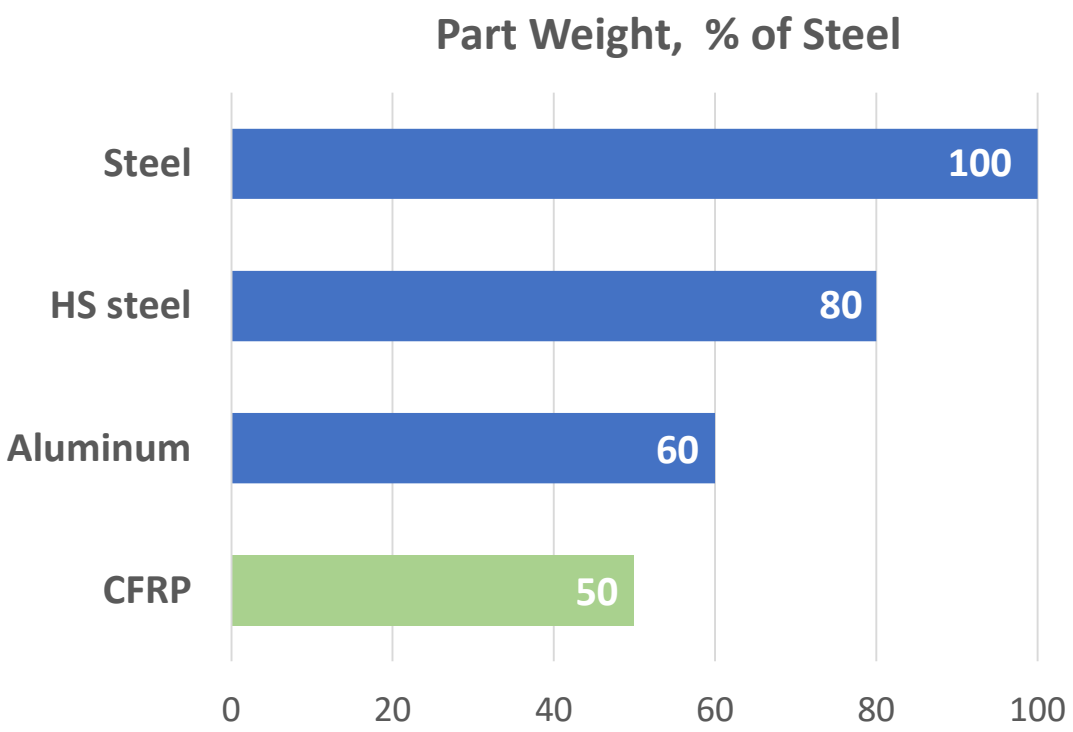
2016 — Multi-materialism: steel, aluminum, CFRP, GFRP
BMW 7-series saves 130 kg

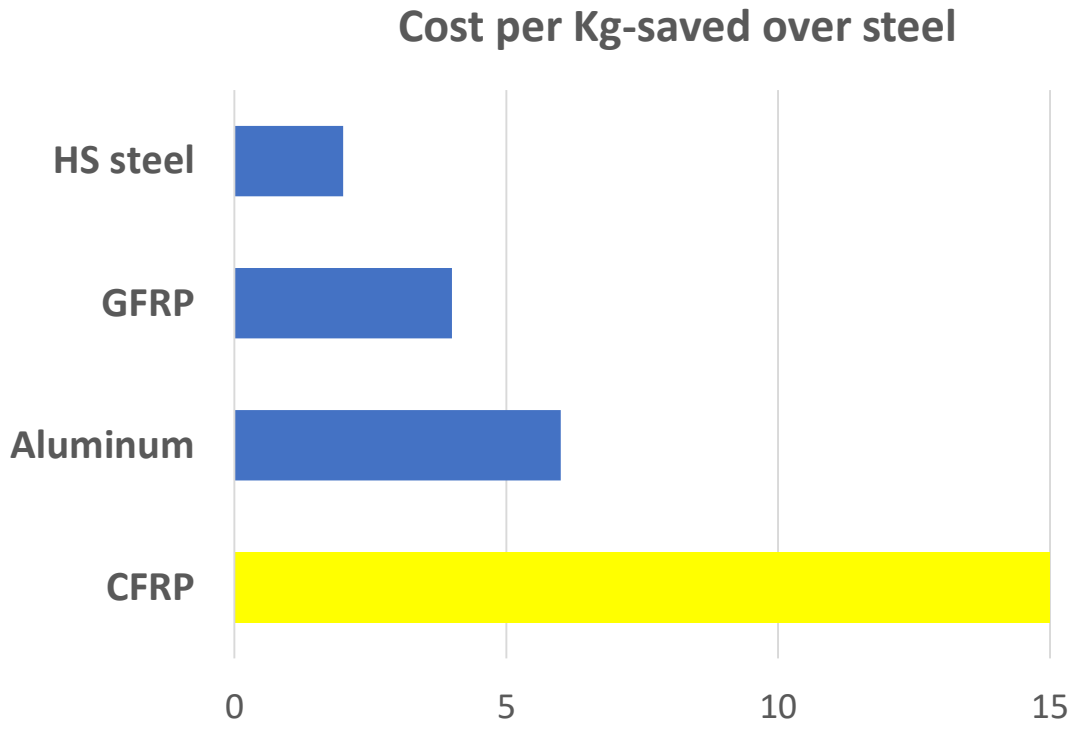
CFRTP saves 28 kg in 2019 GMC Sierra

Current — Optimizing Matrix/Fiber/Process to meet performance/cost (thermoplastic vs. thermoset, continuous vs. chopped fiber)

PROCESSES FOR FIBER-BASED COMPOSITES

Industry analysis (McKinsey, 2016) highlights weight savings and costs for various materials



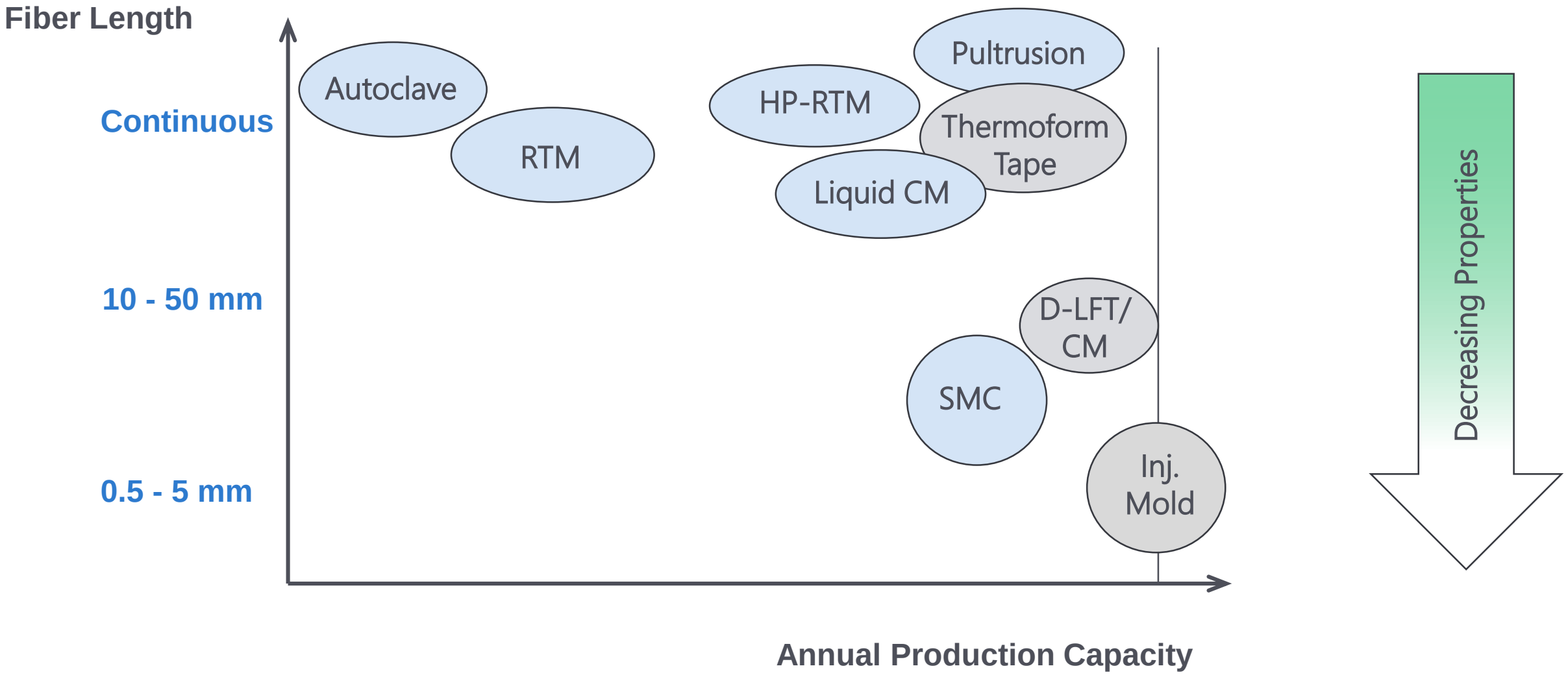


<u>Processing limitations account for 50% of CFRP Cost</u>

Potential Remedies: fast-cure matrix, process optimization, automation

Data from 2016 https://www.automotiveworld.com/articles/time-reassess-materials-automotive-lightweighting/

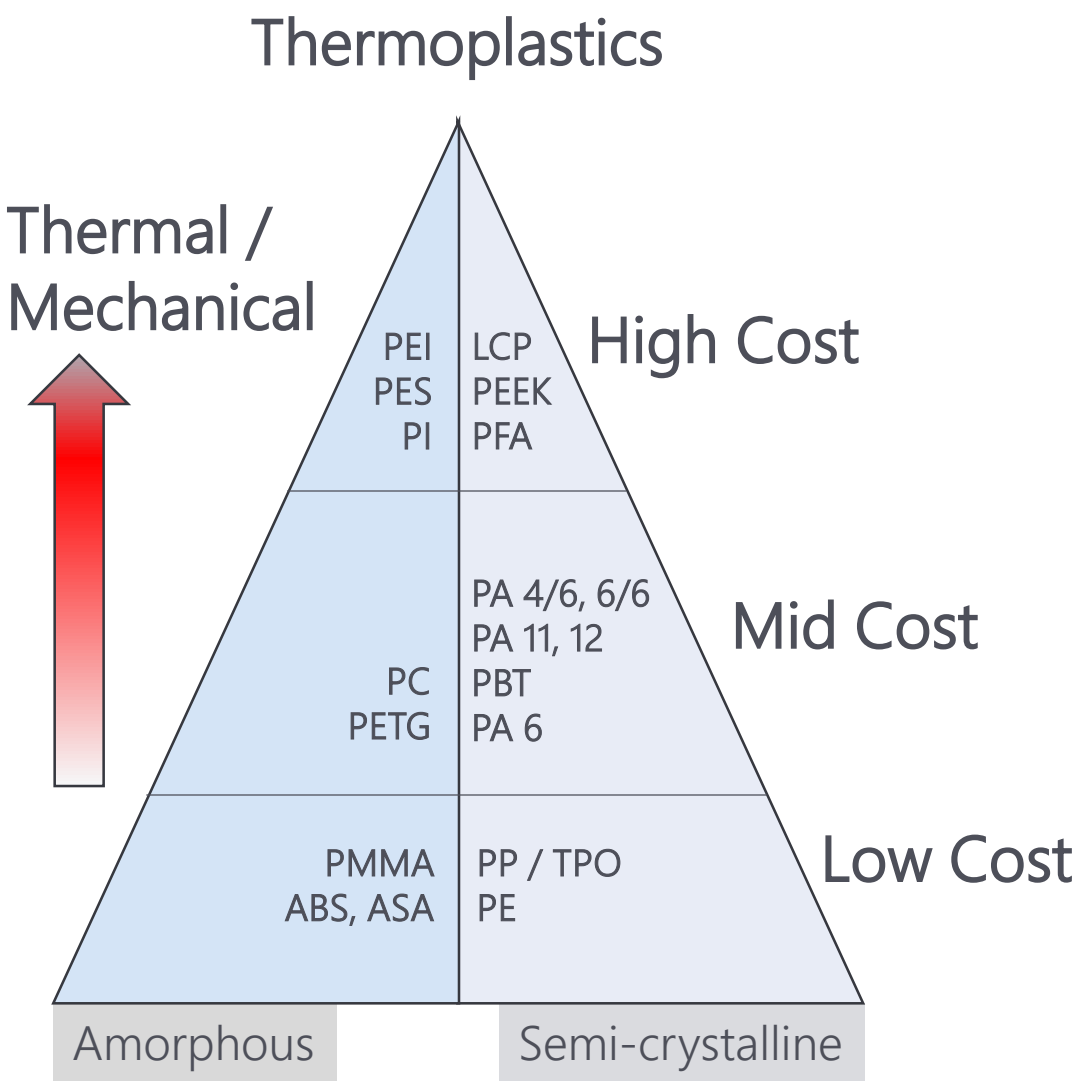
PROCESSES FOR FIBER-BASED COMPOSITES

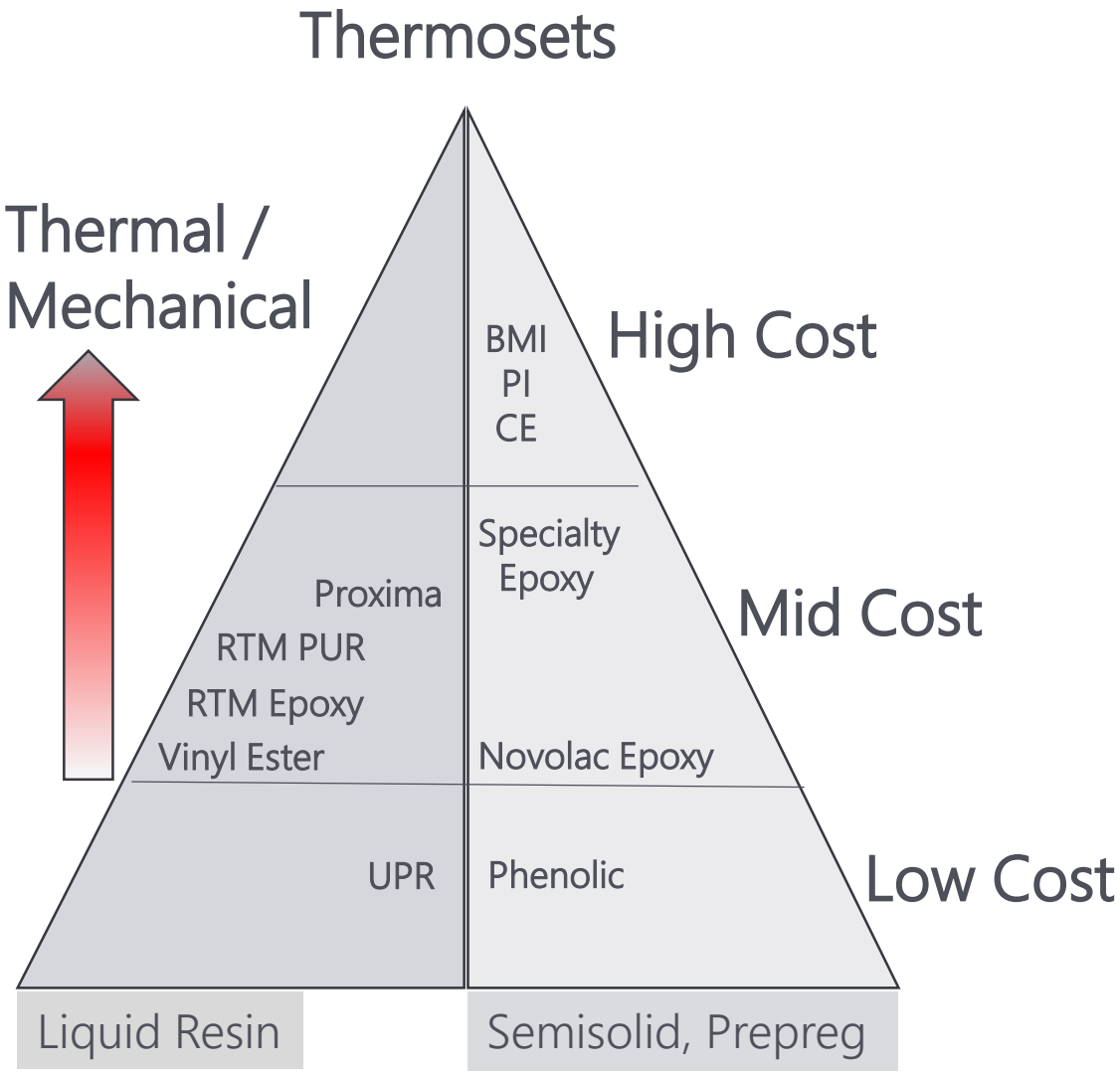


PROCESSES FOR PARTS WITH SHAPE COMPLEXITY

HP-RTM	• Requires low viscosity resin to achieve high FVF composites with fast cycle time (<90 sec)
Wet Comp. Molding (LCM, DFCM)	• Allows injection pressure < 140 psi which eliminates fiber movement
Prepreg / UD Tape	• Automation demonstrated with increasing fiber placement speed

MATRIX SELECTION





*Plasticprop.com

PROXIMA® vs. EPOXY

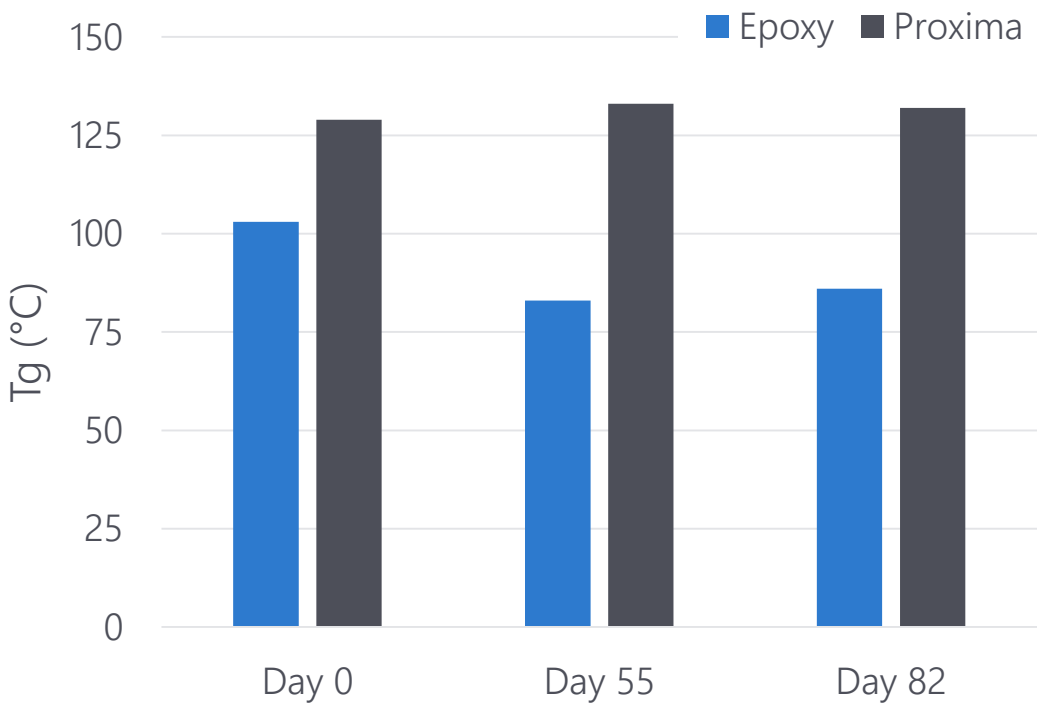
(Scale represents Proxima/Competition performance ratio)

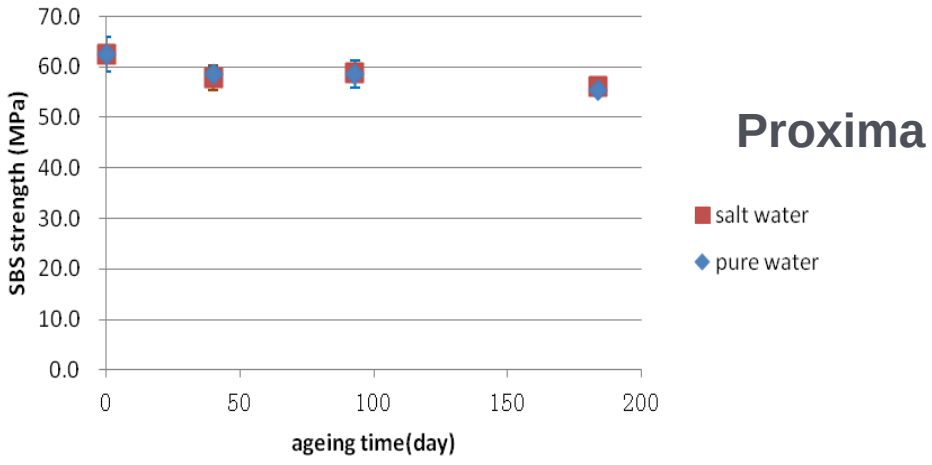
Ultra-Low Viscosity	***20x less viscous*** (7 cP at 25 °C)
Lightweight	***10% lower density*** (1.04 g/mL)
Ultra-Tough	***5x tougher*** (K_{IC} = 2.8 MPa·$m^{1/2}$)
Fast Heat Cure	***50-75% faster*** *cure profile*
Cost Competitive	***Comparable*** *to epoxies*

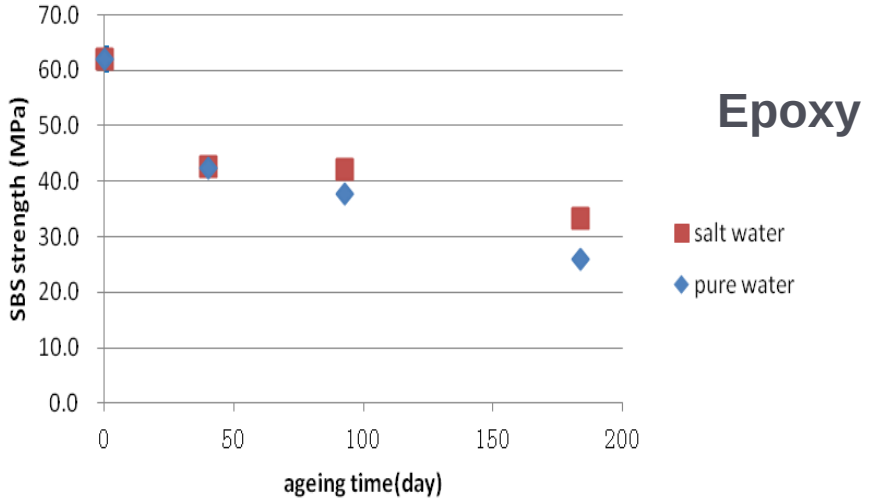
MOISTURE RESISTANCE TO PRESERVE PROPERTIES

Proxima® laminates **absorb less water and retain properties** better than market leading epoxy laminates

Effects of water aging of GFRP at 60 °C on SBS and T_g were compared





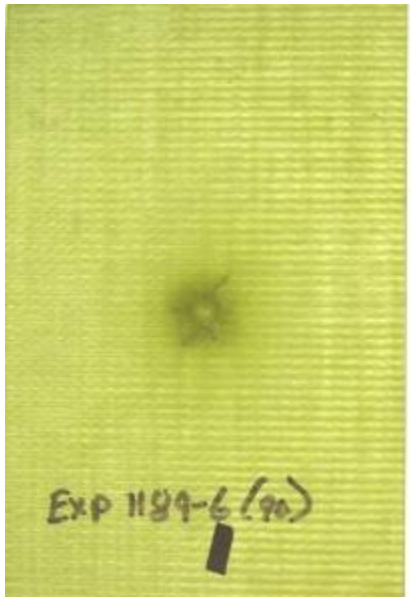


Nutt et al, Polymer Degradation and Stability, 124, (2016), 35-42.

TOUGH COMPOSITES USING A TOUGH POLYMER

Laminates produced with Proxima® resins resulted in 48% less damage than epoxy laminates.

Epoxy



Damage zone of Proxima® laminate is 48% smaller than that of the epoxy laminate

PROPERTY	METHOD (ASTM)	UNIT	ACR 4100	INFUSION EPOXY
Fracture Toughness, K_{IC}[1]	D5045	$MPa \cdot m^{1/2}$	2.6	0.5
Interlaminar Fracture Toughness, G_{IC}[2]	D5528[1,2]	J/m^2	1,700	330
Damage after impact[3]	D7136-07	mm^2	403	779

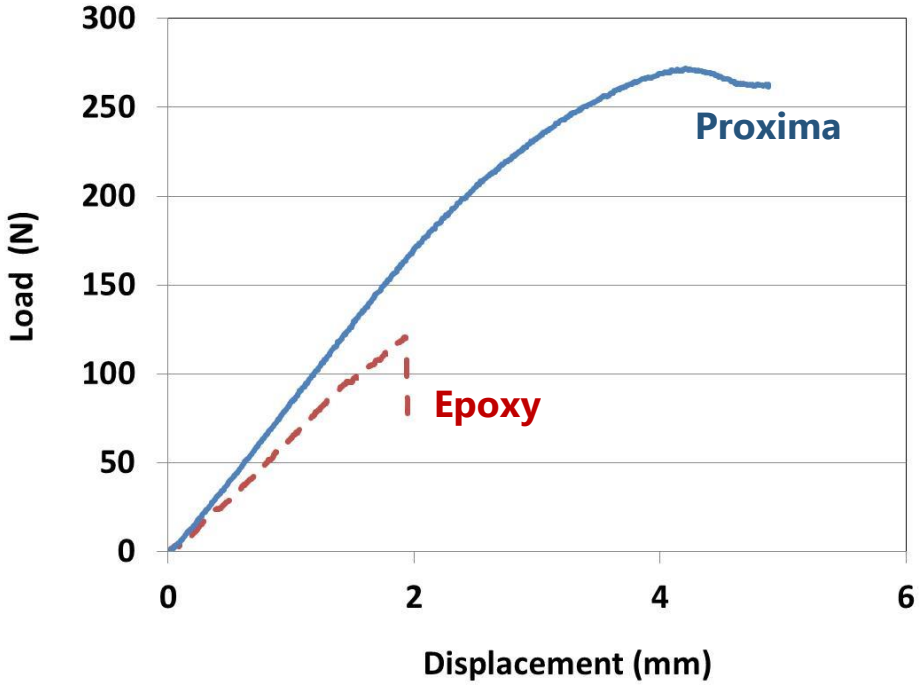
[1] Data treatment per Reeder and Crews (NASA) for fracture toughness at crack initiation

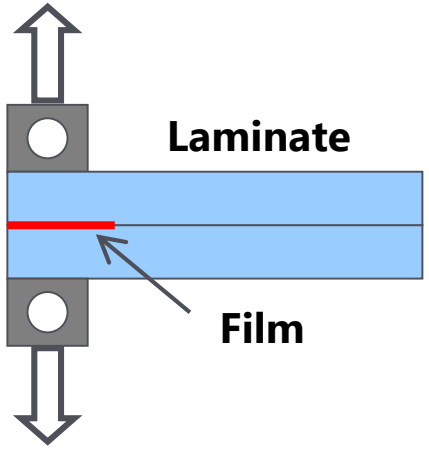
[2] Laminates prepared by VARTM of 1200 gsm unidirectional glass fabric and cured at 120 °C for 2h

[3] Tested by Delsen Testing Laboratories

PROXIMA® INTERLAMINAR FRACTURE TOUGHNESS (G_{IC})

- Compared to epoxy infusion resins, Proxima shows **very high crack resistance** Interlaminar Fracture toughness at crack initiation:
  - Proxima: G_{1c} = 1700 J/m^2
  - Epoxy: G_{1c} = 330 J/m^2
- Proxima laminates exhibit a ductile failure mode similar to thermoplastic resins

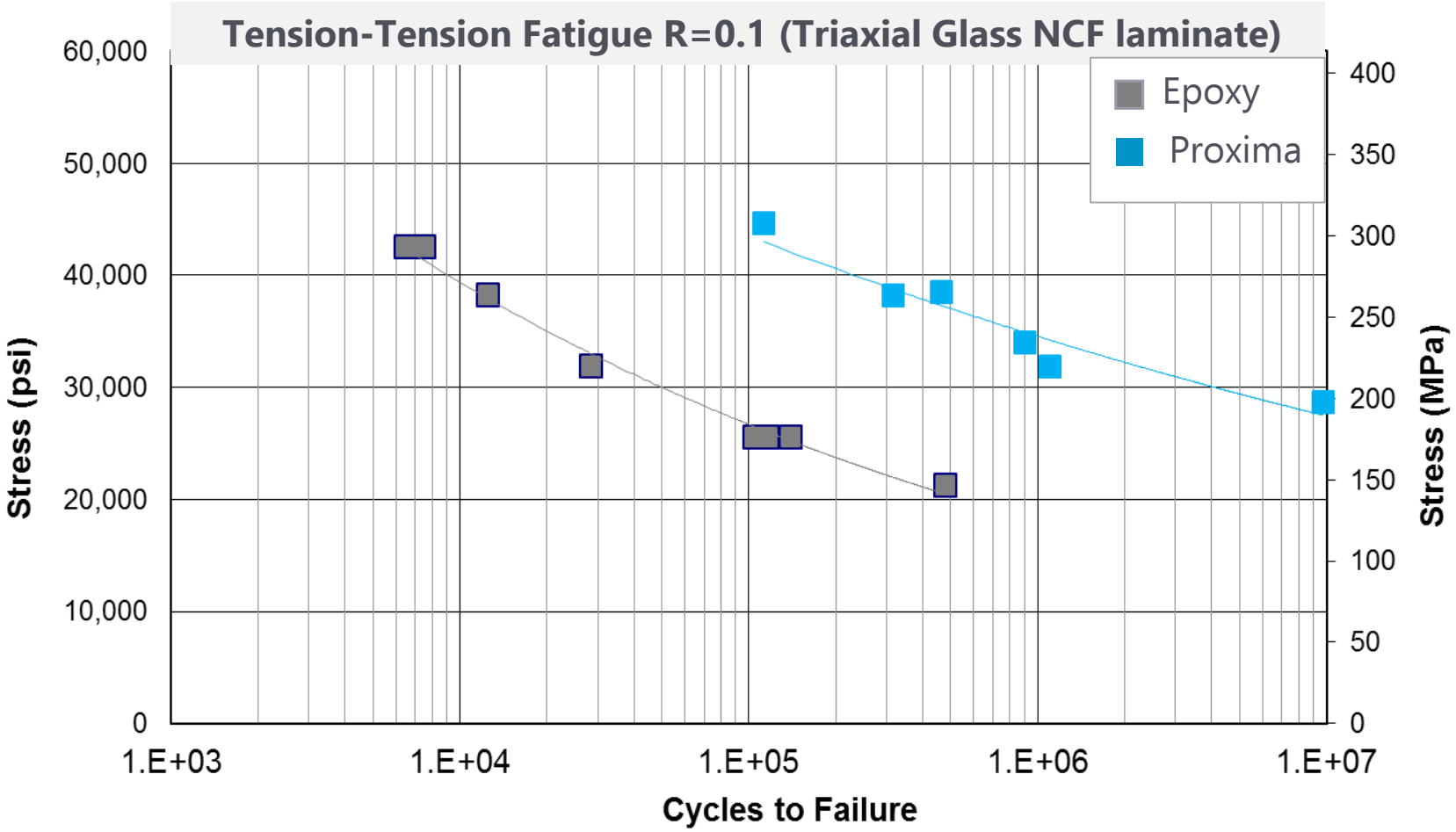




ASTM D5528, data treatment per Reeder and Crews (NASA)

FATIGUE TESTS: PROXIMA® VS. EPOXY

Proxima glass fiber laminates provide high fracture-toughness which translates to improved fatigue performance and off-axis properties



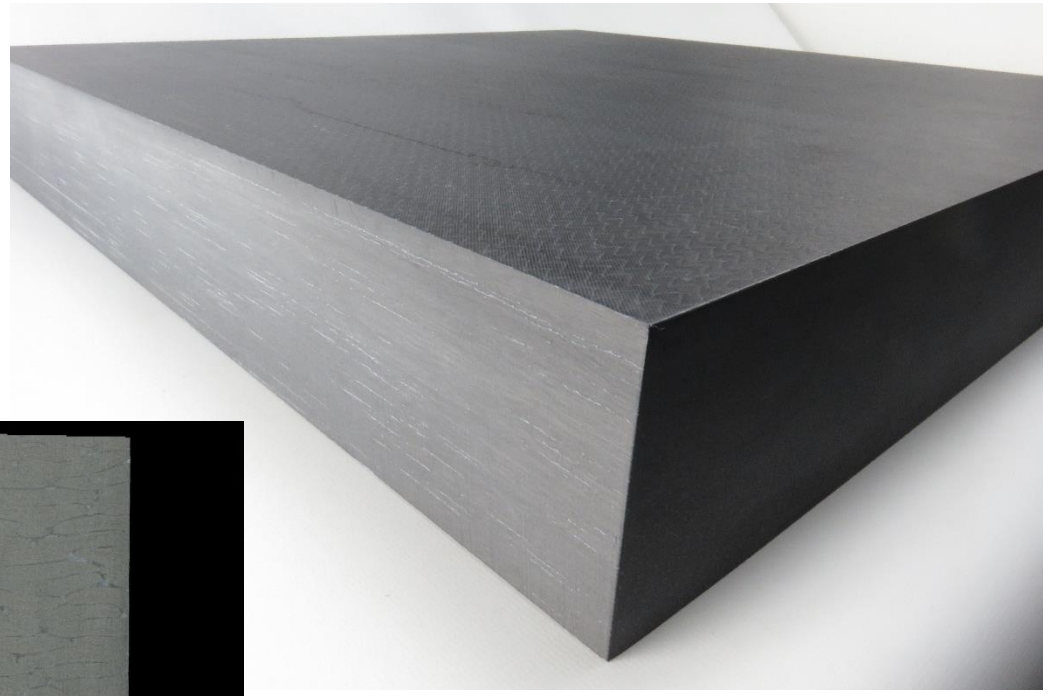
THICK CF SECTIONS VIA INFUSION

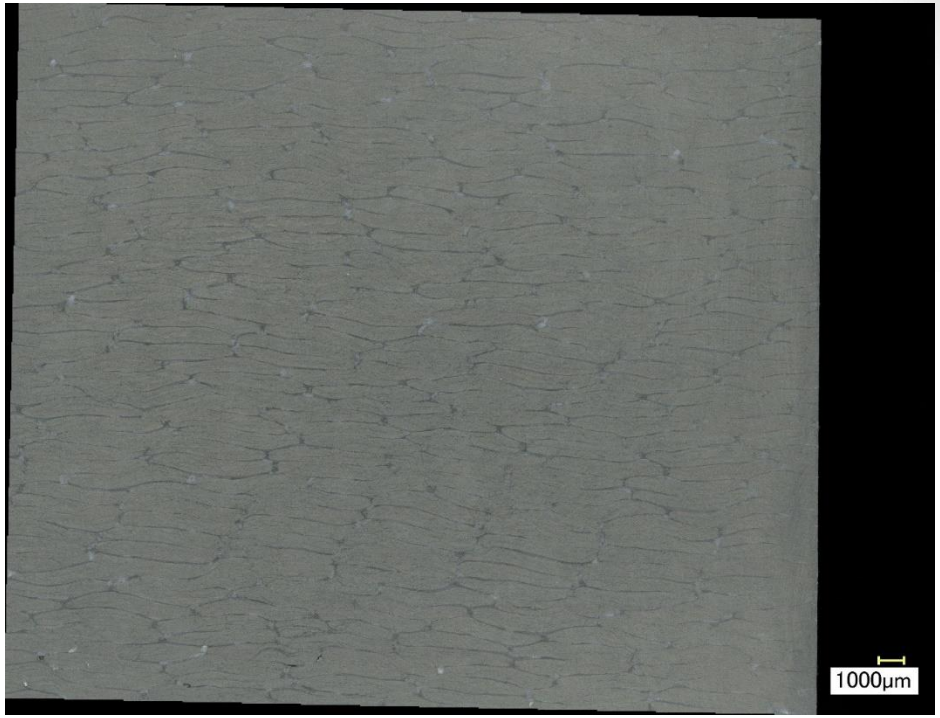
- 130 plies
  Fabric: Saertex U-C-603gsm,
  Zoltek Panex 35, 50K Carbon Tow

- 500mm x 500mm x 76mm

- FVF = 0.62

- Void-free





UPDATE ON CF LAMINATE TEST RESULTS

Test Performed	Test Method	Mean Value	95/5 C.V.	Units
0° Tensile Strength	ISO 527	1651	1371	MPa
0° Tensile Modulus	ISO 527	112	96	GPa
90° Tensile Strength	ISO 527	38	31	MPa
90° Tensile Modulus	ISO 527	6.5	6.2	GPa
0° Compression Strength	ISO 14126 *	923	712	MPa
0° Compression Modulus	ISO 14126*	110	103	GPa
90° Compression Strength	ASTM D 6641	133	121	MPa
90° Compression Modulus	ASTM D 6641	8.0	6.2	MPa
Shear Strength at Failure	ISO 14129	56	54	MPa
Shear Modulus	ISO 14129	3.5	3.1	GPa
Short Beam ILSS	ISO 1430	62	58	MPa

Saertex U-C-603 (603 gsm based on Panex 35 tow)
FVF (4-ply) = 0.55
* Zwick-IMA HCCF fixture used (6 breaks), showing COV for Comp. Strength = 0.10

BUILDING A PATH TO FAST CYCLE COMPOSITES

VARTM

Benchmark setting (ILSS, Tg, …)

Confirm laminate construction

LP-RTM – Screening

Carbon Fiber NCF
45 psi, Inj. Pressure
110 – 140 °C tool

FVF > 0.50
>90% vs. ILSS control
for 90 to 120 sec

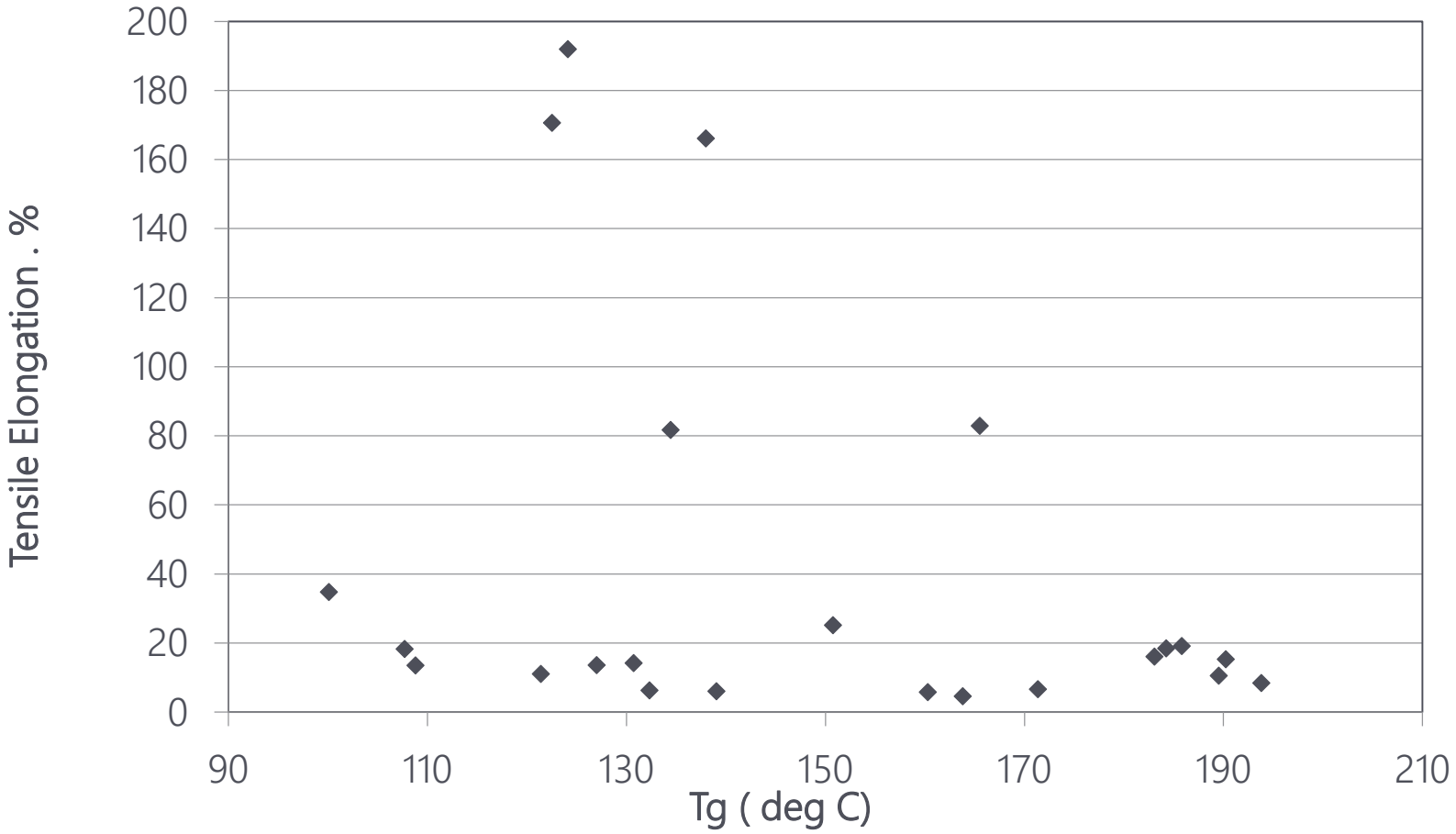
HP-RTM

Validate predictions of screening

On-going efforts

FUTURE DEVELOPMENTS: LEVERAGING TOUGHNESS

- Range of Tg and ductility by moving beyond DCPD
- Stepping beyond DCPD while maintaining hot / wet performance



CONCLUSIONS

- **Materia sees composites materials as being tailored to designer's needs and the Proxima® portfolio will be extended in collaboration with customers**
- **Proxima resins provide a new path to high toughness / low defect parts**
- **Materia continues to partner with OEMs in Automotive, Wind, and Oil & Gas to qualify resins for continuous GF and CF composite parts**
- **Engaging fabricators / molders across multiple processes is critical to meet demand for complex molded parts, pultruded profiles and FW pressure vessels**

Next Steps:

- Developing a better understanding of Auto Industry needs for next 1-3 years
- Defining a framework for collaboration and material qualification

THANK YOU

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