New Applications for ADVALITE™ Vinyl Hybrid Snap Cure Resins in Filament Winding, RTM and Prepreg Processes

Jim Bono

JEC Paris, March 10th, 2015

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Background

- Advanced Material Market
- Styrenated Systems are Unacceptable
  - Governmental Regulations
  - Control Technologies Needed
  - Minimize Capital Investment
- Development Need for
  Reactive Diluent Free Thermoset Resin Systems
  - Cost Effective
  - Improved Dry/ Wet Tg
  - Improved Production Rates- approach 3 minute cycle

Nomenclature

Styrene Free Resins

ADVALITE™ Vinyl Hybrid Resins

Alternative Reactive Diluents

- VT
- Acrylates
- Others

Reactive Diluent Free

Solids: "Prepreg Monomer Free Hot Melt Vinyl Hybrids"

ADVALITE™ – Monomer Free Hot Melts

Applications:
Fiber Reinforced Prepregs
Unidirectional Fiber Reinforced Tapes
Unidirectional Fiber Reinforced Tow Preg's

Liquids: Reactive Oligomers "Vinyl Hybrid Liquid Resins"

ADVALITE™ – Vinyl Hybrid Liquid Resins

Applications:
Filament Winding, Resin Transfer Molding
Liquid Molding, Vacuum Infusion, Pultrusion

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RTM
Filament Winding
Vacuum Infusion
Gelcoats
Pultrusion
Closed Mold

ADVALITE™ Vinyl Hybrid Liquid Resins- Reactive Diluent Free

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Application Overview

Process Applications:

- Vacuum Infusion
- RTM
- Closed Mold
- Filament Winding
- Pultrusion

Uses standard catalysts and initiators – processes the same as UPR and Vinyl Ester resins.

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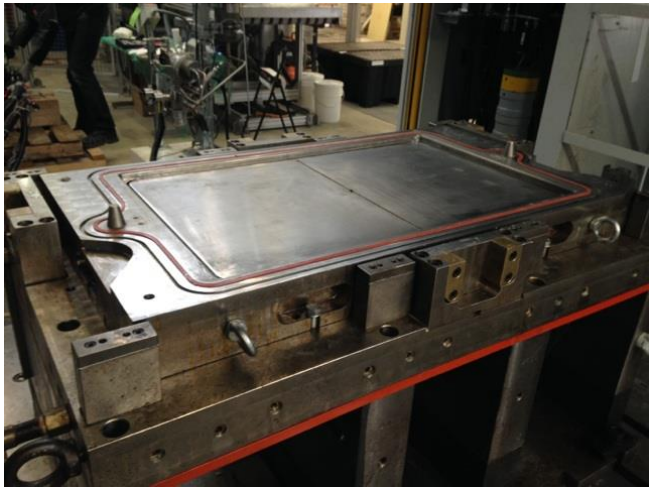
ADVALITE™ Liquid Vinyl Hybrid Resins Comparison of Cast Resin Properties

Property	Units	35065-00	35060-00	X4844-90	X4622-88
Tensile Strength	M Pa	80,3	45,0	35,5	70,0
Tensile Modulus	G Pa	4,37	3,72	3,25	3,02
Tensile Elongation	%	3,0	1,5	1,2	3,2
Heat Distortion Temperature	°C	72	155	154	134
Water Absorption 48 hours @ 100°C	% by wt	2,16	0,83	3,50	1,67
Dry Tg	°C	104	170	201	155
Wet Tg	°C	93	166	161	151
Viscosity- 25 °C	cps	600	1200	2809	860

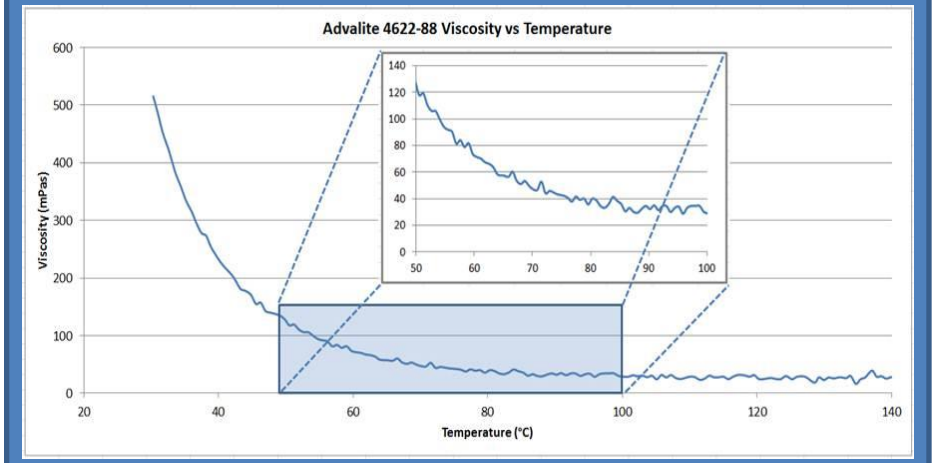
RTM- ADVALITE™ Requirements

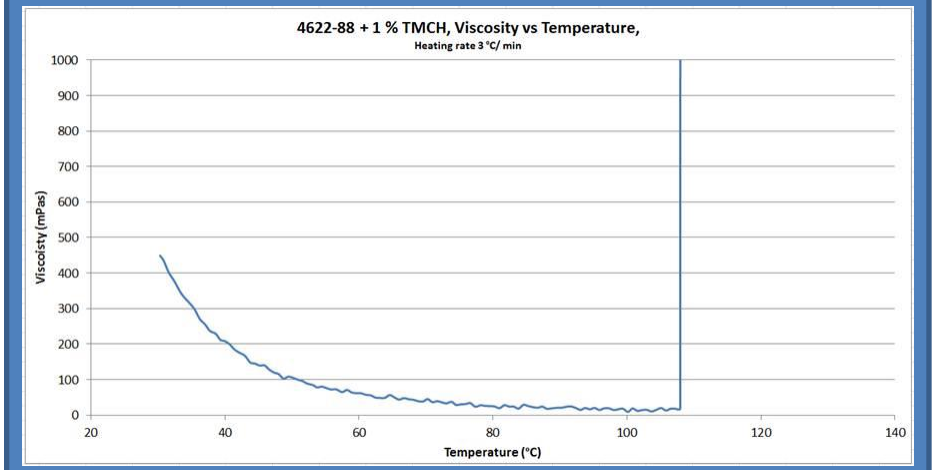
Process Requirements

- Low initial processing viscosity
  - Not constrained to injection temperature
  - Thermal Initiated Stability
- Glass Mat Wetting Capabilities
- Fast Cure Cycles
  - Exceed prep time for next preform and finish on previous part
  - Minimal cure required
- Low Shrinkage
- Good Mechanical Properties



RTM– Processing Conditions of ADVALITE™ X4622-88 LVH





Rheometer Study

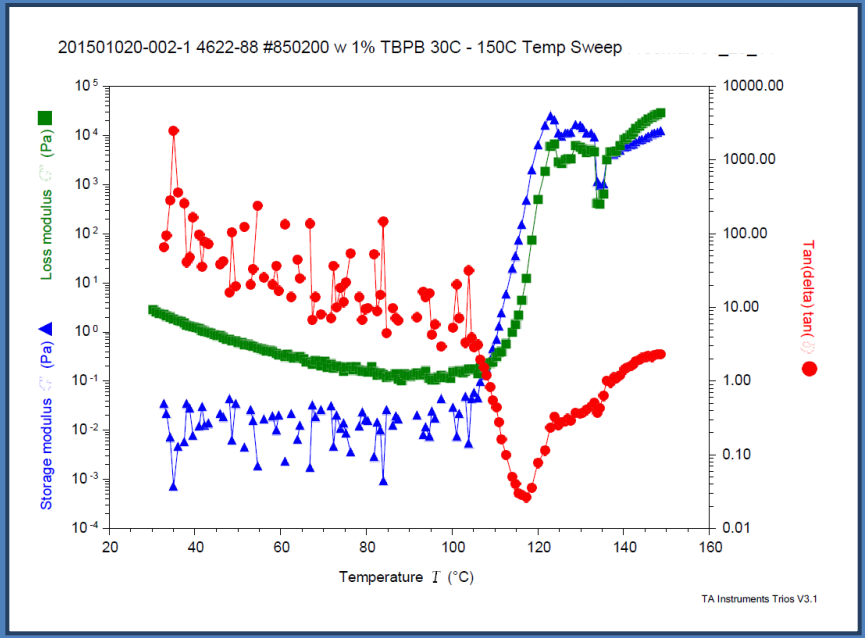
ADVALITE™ X4622-88 with and without 1% TMCH Initiator
Establish Processing viscosity against temperature sweep

Rheometer Study

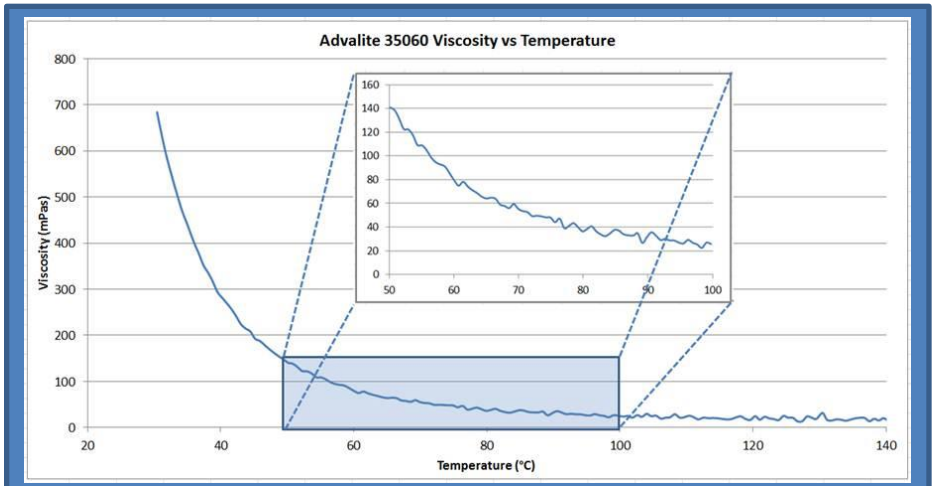
ADVALITE™ X4622-88 with 1% TBPB Initiator

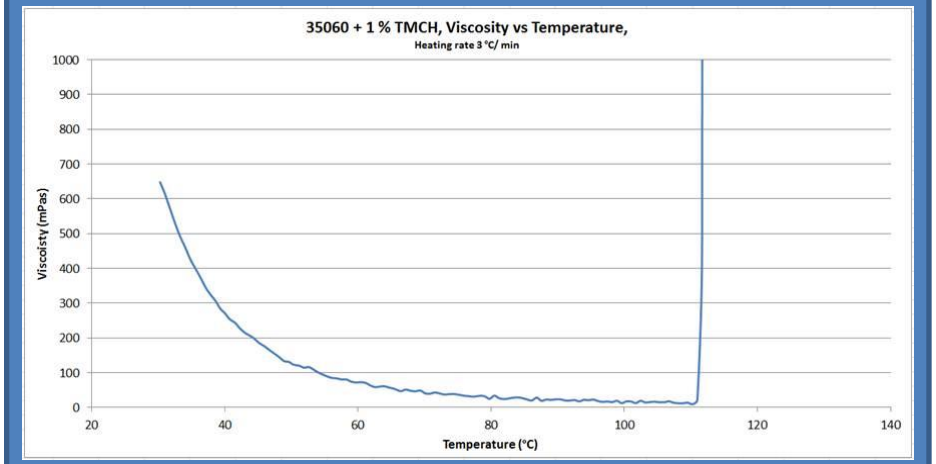
Establish cure profile against temperature sweep

Initiator to be added Inline or batch mixed



RTM– Processing Conditions of ADVALITE™ 35060-00 LVH





Rheometer Study

ADVALITE™ 35060-00 with and without 1% TMCH Initiator
Establish Processing viscosity against temperature sweep

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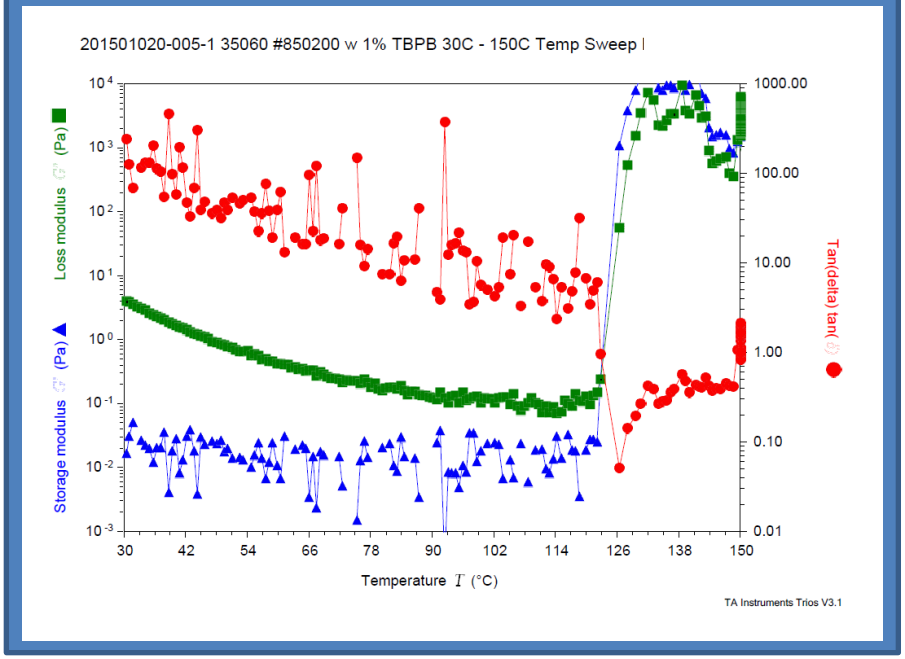

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RTM– Dielectric Cure Response

ADVALITE™ 35060-00 & X4622-88 LVH

TBPB Initiator Cure Studies

Resin	Initiator	Initiator Amount (pHR)	Mold Temperature (°C)	Thickness (mm)	Vf Glass (% by vol)	Gel Time (sec)	Cure Time (sec)
X4622-88	TBPB	1,0	119	3,1	11	180	253
X4622-88	TBPB	3,0	119	3,1	11	92	132
X4622-88	TBPB	1,0	130	3,1	11	84	129
X4622-88	TBPB	2,0	130	3,1	11	50	81
X4622-88	TBPB	3,0	130	3,1	11	44	75
X4622-88	TBPB	3,0	130	3,1	21	43	74
X4622-88	TBPB	1,0	139	3,1	11	41	75
X4622-88	TBPB	2,0	139	3,1	11	29	60
X4622-88	TBPB	3,0	139	3,1	11	26	55

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RTM– Dielectric Cure Response

ADVALITE™ 35060-00 & X4622-88 LVH

TMCH Initiator Cure Studies

Resin	Initiator	Initiator Amount (pHR)	Mold Temperature (°C)	Thickness (mm)	Vf Glass (% by vol)	Gel Time (sec)	Cure Time (sec)
35060-00	TMCH	0,8	103	3,1	22	148	234
35060-00	TMCH	0,8	112	3,1	22	49	91
35060-00	TMCH	0,8	140	3,1	22	27	51
X4622-88	TMCH	0,8	100	3,1	22	453	575
X4622-88	TMCH	0,8	110	3,1	22	145	187
X4622-88	TMCH	0,8	140	3,1	22	72	99

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RTM - Styrene Free Low Profile Additive Work
ADVALITE™ 35065-00

Data Table on Shrinkage Results- LP RTM Flat Panels

Base Formulation:
Utilizing Cell 10 from Low Shrinkage DOE
Filled with microspheres and calcium carbonate
Solid PE: Solid LPA Ratio = 5:1
35% CSM

	1	2	3	4	5	6	7	8	9	10
LPA Type	LPA Control - Customer Driven	LPA 1	LPA 2	LPA 3	LPA 3	LPA 4	LPA 5	LPA 6	LPA 7	LPA 8
Solvent/ Monomer -LPA	Styrene	Non- HAP Monomer 1	Non- HAP Monomer 1	Non- HAP Monomer 1	Non- HAP Monomer 2	Non- HAP Monomer 1	35065-00	None	None	None
LPA Dilution percent by wt	30% SBS	30%	35%	45%	45%	30%	10%	100%	100%	100%
Styrene Content- Paste	5,23%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Total Monomer Content Paste	5,23%	21,76%	18,00%	12,61%	12,61%	21,61%	0,00%	0,00%	0,00%	0,00%
Total Monomer Content Laminate	3,40%	14,14%	11,70%	8,20%	8,20%	14,05%	0,00%	0,00%	0,00%	0,00%
Shrinkage % Linear Shrinkage -negative value indicates expansion	0,027	-0,034	-0,025	-0,046	-0,050	-0,005	-0,020	-0,036	-0,025	0,003

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RTM - Styrene Free Low Profile Additive Work
ADVALITE™ 35065-00

Data Table on Mechanical Properties- LP RTM Flat Panels

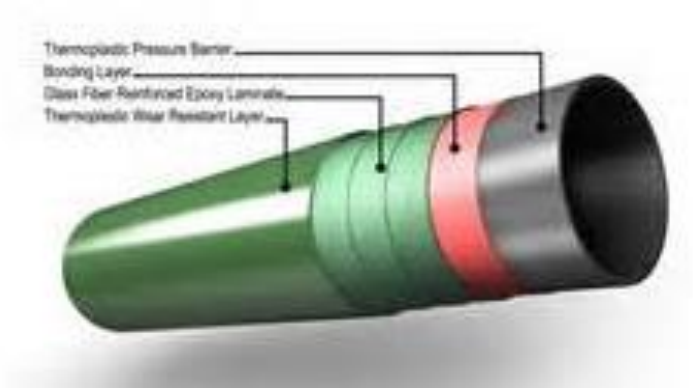
Base Formulation:
Utilizing Cell 10 from Low Shrinkage DOE
Filled with microspheres and calcium carbonate
Solid PE: Solid LPA Ratio = 5:1
35% CSM

	1	2	3	4	5	6	7	8	9	10
LPA Type	NO LPA	LPA 1	LPA 2	LPA 3	LPA 3	LPA 4	LPA 5	LPA 6	LPA 7	LPA 8
Flex Strength (M Pa)	130,3	144,8	174,9	139,3	168,3	158,9	182,0	133,7	128,8	151,1
Flex Modulus (G Pa)	7,01	7,48	9,34	11,07	11,92	9,33	8,06	6,84	7,21	6,83
Tensile Strength (M Pa)	80,6	91,2	104,1	71,6	88,7	100,4	101,4	87,7	84,7	85,7
Tensile Modulus (G Pa)	7,20	8,66	9,79	6,82	7,61	9,19	8,70	7,70	7,00	7,00
Elongation at Break (%)	1,69	1,54	1,54	1,53	1,55	1,69	1,62	1,55	1,69	1,73
Izod Impact Strength (kJ/ m^2)	74,23	95,90	98,48	108,13	92,72	85,38	88,43	73,57	77,77	73,66

Filament Winding
ADVALITE™ Vinyl Hybrid Composite Pipe

- **Objective**:
  Develop a liquid vinyl hybrid solution to initiate a snap cure through customer's process while maintaining their fitness for use for the composite.

- **Critical Success Factors:**
  - Improvement to Throughput : > 40%
  - Adhesion to PE Tie Layer
  - Water Absorption < 1.5%
  - Tg: > 115 C
  - Elongation: > 3.5%
  - Tack Free Surface

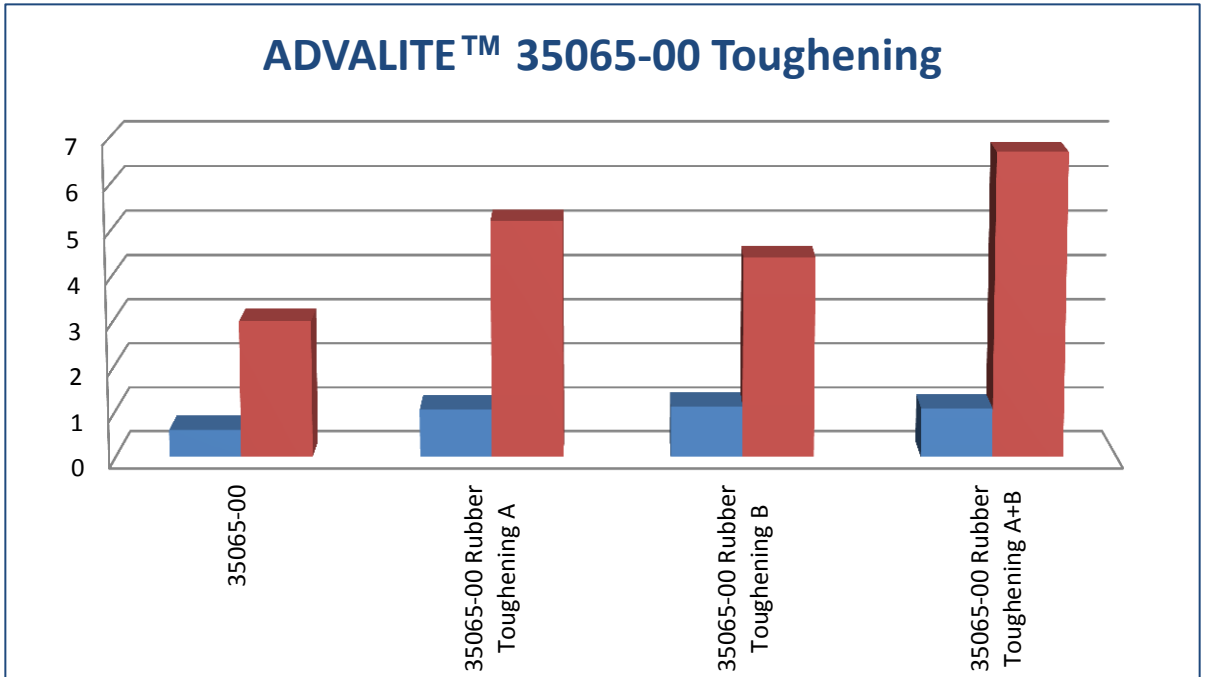


- **Status/Updates:**
  - Tg and Elongation factors controllable through acrylate and rubber modifications to resin formula. Incorporation of toughening additives significantly increased elongation.
  - Cure and Gel controllable through inhibitor/ initiator selection
  - Tack free surface obtained on composite pipes
  - Tie layer adhesion improved- critical to understand and control multiple factors: Initiation of gel vs. tie layer softening temperature, elongation and adhesion promoters.

Filament Winding
ADVALITE™ Vinyl Hybrid Toughening

Clear Cast Resin Testing

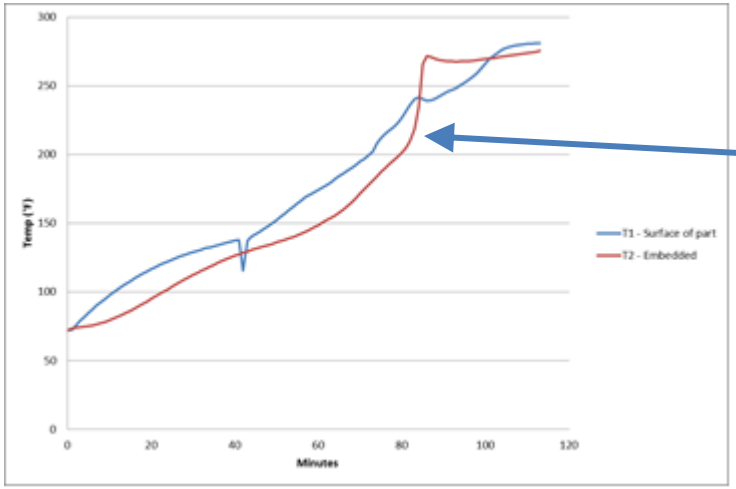
- Toughening Additive
  - Improvement in Fracture Toughness
    82 % Increase
  - Improvement in Elongation
    123 % Increase



	35065-00	35065-00 Rubber Toughening A	35065-00 Rubber Toughening B	35065-00 Rubber Toughening A+B
Fracture Toughness (M Pa/m0.5)	0,594	1,053	1,117	1,078
Elongation (% Tensile Strain)	3	5,2	4,4	6,7

Filament Winding- ADVALITE™ 35060-00 LVH

- Develop filament winding resin and Prepreg Wrapped Pipe Oven Cured Samples



Cure was completed in less than 80 minutes- mostly based on ability of oven to heat up the laminate profile. Once pipe reached appropriate temperature, cure was accomplished in less than 8 minutes.

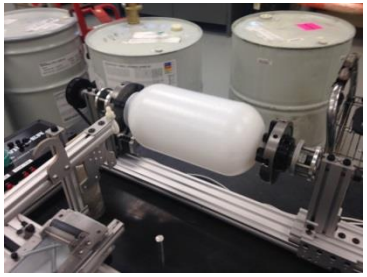
Same cross section of epoxy wound pipe took 36 hrs to cure to manage the exotherm with gradual changes in heat profiles of the oven.

Filament Winding- ADVALITE™ Development

Composite Tanks

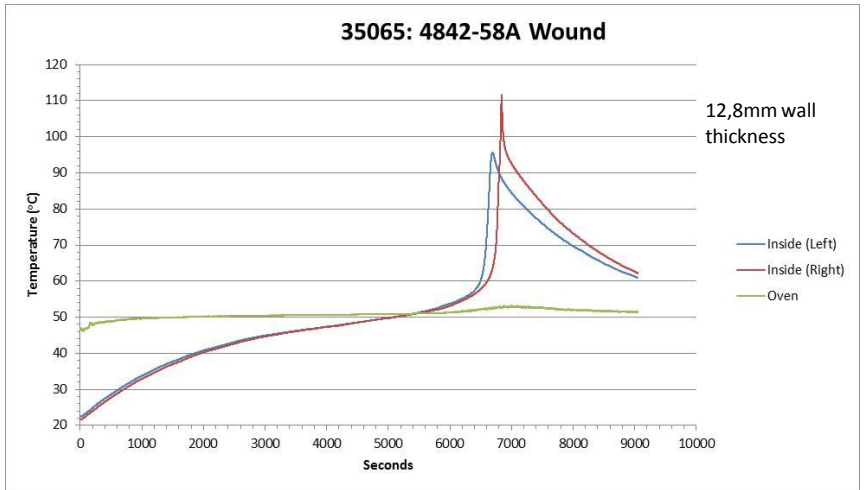
- **Promoted Resin**
- **Initiator**
  TBPB - 1,00% by Wt
- **Inhibitors**
  Different Inhibitors evaluated- selection based on cure response and catalyzed stability

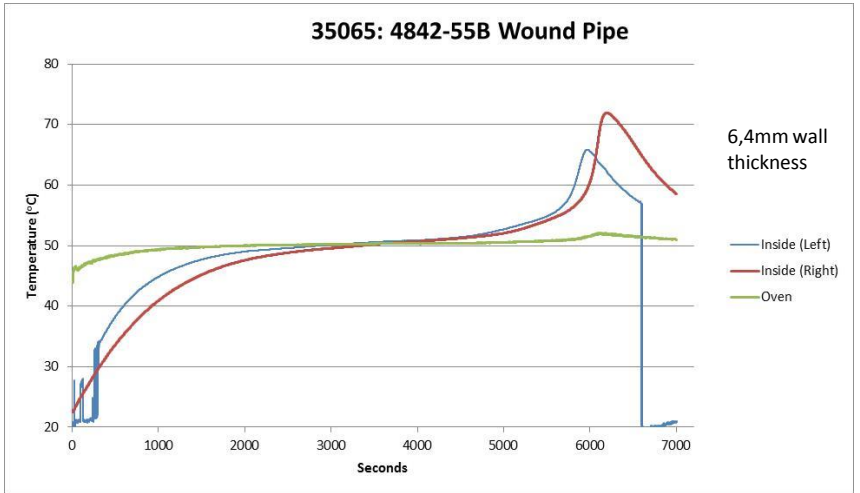
Tank on X- Winder in Lab



35065-00 Gel Times- SPI in 50 deg C Bath

	1	2	3
Insert to 50° C (min)	14,43	15,57	15,00
50° C to Peak (min)	68,63	67,35	67,99
Peak Exotherm (° C)	115,1	113,6	114,3
Catalyzed Stability (hrs)	> 12 hrs	> 12 hrs	> 12 hrs





Prepreg (Woven and Unidirectional) Mats, Tow Pregs and Tape

ADVALITE™ Vinyl Hybrid Solid Hot Melt Resins

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ADVALITE™ Vinyl Hybrid Hot Melt Resins

Clear Cast Properties

Property	Units	35000-00	35051-00	X4833-37	X4710-16
Tensile Strength	M Pa	57,6	82,5	65,3	46,3
Tensile Modulus	G Pa	3,92	3,42	3,04	3,86
Elongation	%	1,6	4,0	2,5	1,3
HDT	C	94	84	116	151
Dry Tg	C	146	109	154	173
Wet Tg	C	124	98	149	157
Water Absorption 48 hours @ 100°C	%	1,7	3,0	1,5	0,7
Viscosity @ 100C	poise	18	19	14	18

Transportation Market Requirements

- Automotive Market Needs:
  - Fast cure: 2 minutes
  - E-Coat Capable HDT: > 160 C.
  - Automation Capable: Pre-preg Format
  - Room Temperature Storage
- ADVALITE™ can meet the market needs.

Requirement	ADVALITE™	Epoxy
Fast Cure	2 minutes	10 minutes
HDT	> 160 C	> 160 C
Pre-preg	Yes	Yes
Storage Temp/Time	Ambient / 1 Year	Refrigeration: 6 weeks

Continuous Fiber Inner

Continental Structural Plastics

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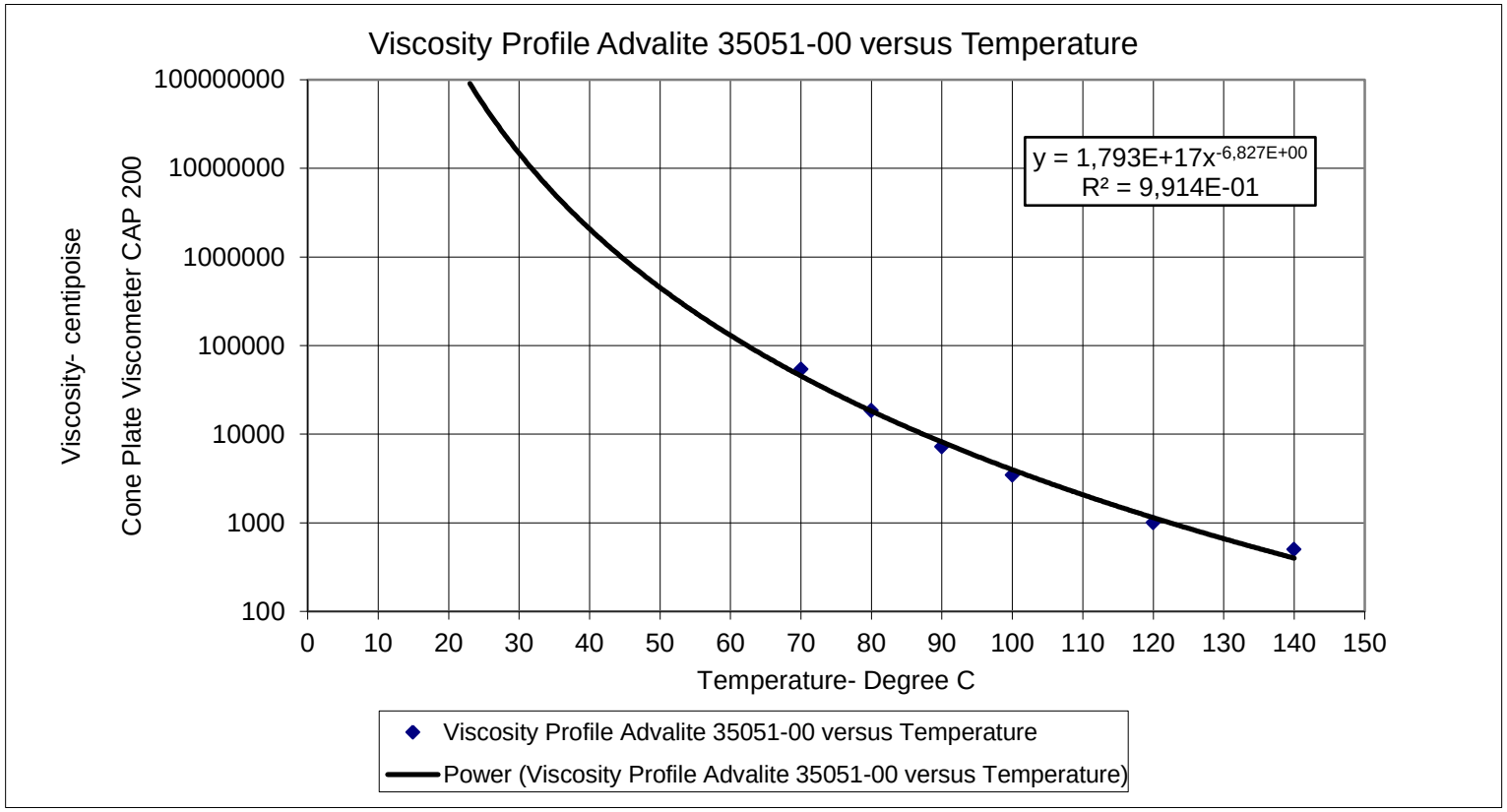
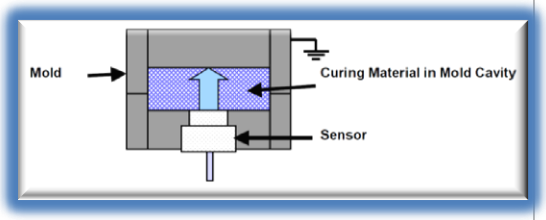
Viscosity versus Temperature Profile

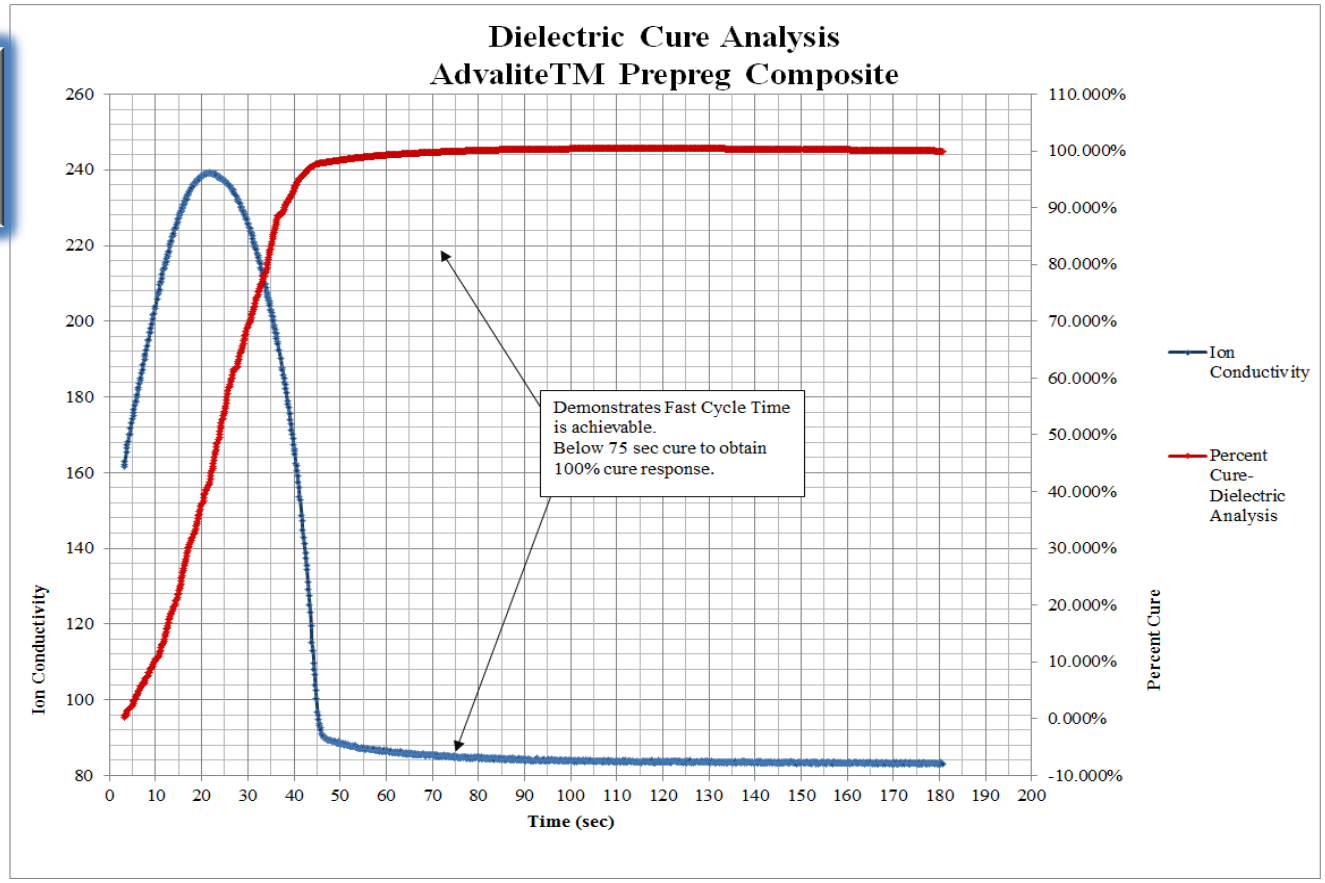
Monomer Free Hot Melt Vinyl Hybrid Resin- MF-HM-VHR



Dielectric Cure Analysis- Signature Controls

Monomer Free Hot Melt Vinyl Hybrid Prepreg- Fiberglass Reinforcement





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ADVALITE™ Vinyl Hybrid Prepreg
Mechanical Properties of Fiberglass Prepreg

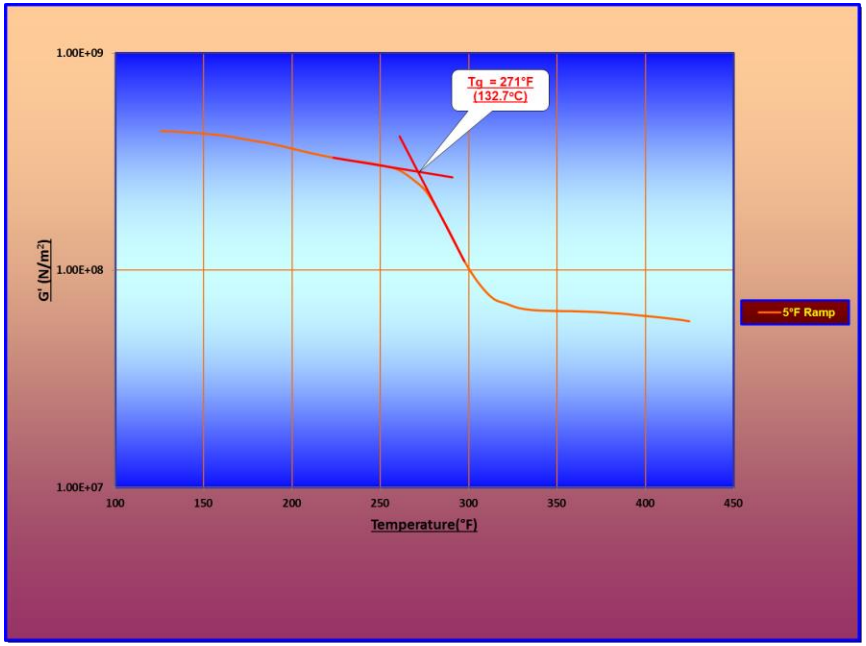
Property	Units	ADVALITE™ X4710-16 Composite	ADVALITE™ 35051-00 Composite
Tensile Strength	M Pa	414	415
Tensile Modulus	G Pa	26	23
Short Beam Shear	M Pa		48
Flexural Strength	M Pa	692	584
Flexural Modulus	G Pa	15	25
Tg Temperature	°C	173	109
Fiberglass Content	Percent by Wt	65	65

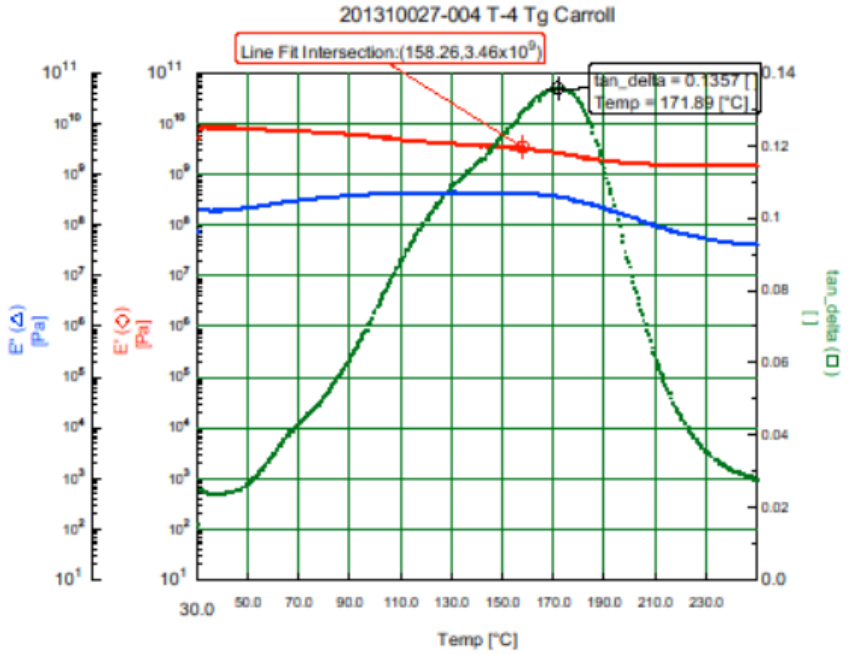
UD Lamination Schedule – 90/45/0/45/0/0/45/0/45/90

Woven Mat Construction

Tg Determination

DMA Curves of Typical Epoxy Resin vs Vinyl Hybrid Resin





Epoxy DMA Curve

Vinyl Hybrid DMA Curve

- Epoxy fabricators depend on Tg values based on the sharp change in the modulus of the material
- ADVALITE™ Vinyl Hybrids do not experience same profile – resulting in gradual loss of modulus through temperatures at or above their Tg

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Flex Properties at Temperature

E Coat Capability -Elevated Temperature Mechanical Property

	Unidirectional Fiberglass Fabric Prepreg ADVALITE™ X4710-16 : 0 º Laminate Schedule : 70 % Fiberglass by Weight				SMC Material Used on Hood Inners Customer Supplied SMC Formulation Discontinuous Fiberglass- 26% by wt			
Temperature	**Flex Strength**	**Retention of Flex Strength**	**Flex Modulus**	**Retention of Flex Modulus**	**Flex Strength**	**Retention of Flex Strength**	**Flex Modulus**	**Retention of Flex Modulus**
ºC	M Pa	%	G Pa	%	M Pa	%	G Pa	%
22	1528	100	45.19	100	138.8	100	8.45	100
100	774	50.6	39.48	87.4	108.4	78.0	7.36	87.1
125	621	40.6	34.66	76.7	100.1	72.1	5.93	70.2
150	457	29.9	30.54	67.6	85.2	61.3	5.77	68.2
175	347	22.7	29.09	64.4	70.4	50.7	4.82	57.0

Standard Composite Material Used for Hood Inner Application

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Tensile Properties at Temperature

E Coat Capability -Elevated Temperature Mechanical Property

	Unidirectional Fiberglass Fabric Prepreg ADVALITE™ X4710-16 : 0 º Laminate Schedule : 70 % Fiberglass by Weight				SMC Material Used on Hood Inners Customer Supplied SMC Formulation Discontinuous Fiberglass- 26% by wt			
Temperature	**Tensile Strength**	**Retention of Tensile Strength**	**Tensile Modulus**	**Retention of Tensile Modulus**	**Tensile Strength**	**Retention of Tensile Strength**	**Tensile Modulus**	**Retention of Tensile Modulus**
ºC	M Pa	%	G Pa	%	M Pa	%	G Pa	%
22	1098	100	47.59	100	89.1	100	11.83	100
100	924	84.2	46.63	98.0	48.5	54.5	7.71	65.1
125	898	81.9	47.11	99.0	57.4	64.4	8.36	70.6
150					47.0	52.7	6.42	54.2
175					37.2	41.7	6.97	58.9

Standard Composite Material Used for Hood Inner Application

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Prepreg/ Pultrusion ADVALITE™ Hot Melt Vinyl Hybrid Carbon Fiber Trials

- Pultruded 50K Carbon Fiber

			4-Point	4-Point
	Void	ILSS	Strength	Modulus
Resin System	Content	M Pa	M Pa	G Pa
DION® 9100/31038-00 Styrenated Vinylester Resins	2,3	68,3	1561	142
ADVALITE™ X4622-88 – Vinyl Hybrid	0,8	60,0	1636	149

- Uni-directional Prepreg

ADVALITE™ X4622-47/ 50K PAN 35 Carbon Fiber Unidirectional Tape			
	Size A	Size B	Size C
Short Beam Shear (M Pa)	91,88	73,30	95,98
Transverse Tensile Strength (M Pa)	41,07	18,96	47,44
Transverse Tensile Modulus (M Pa)	9,15	8,19	9,31

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Prepreg Unidirectional ADVALITE™ Hot Melt Vinyl Hybrid Carbon Fiber Trials

- Unsized and Sized Carbon Fiber with ADVALITE™ X4622-47

	12K CF without Sizing ADVALITE X4622-47		12K CF with Formulated Sizing ADVALITE X4622-47		12K CF with Epoxy Sizing ADVALITE X4622-47	
Properties	Result as Tested	Normalized to 60% FV	Result as Tested	Normalized to 60% FV	Epoxy 12K CF - 60%FV	Epoxy 24K CF - 60%FV
O° Flexural Strength -M Pa	228	231	230	233	265	262
O° Flexural Modulus -M Pa	17,48	17,7	17,7	17,9	14,4	19,5
O° Short Beam Shear, M Pa	13,0		13,7		12,8	12,8
O/90° Short Beam Shear M Pa	5,7		11,4			

100% Increase in Transverse Short Beam Shear with Sizing

Results meet or exceed epoxy sized CF

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Prepreg Unidirectional ADVALITE™ Hot Melt Vinyl Hybrid

Carbon Fiber Trials- 2nd Set of Test Results

Characteristic	ADVALITE™ 35051-00 24 K Tow Sizing A	ADVALITE™ 35051-00 50K Tow Sizing B	Epoxy Control 50K Tow Sizing C
Flex Strength- 0° (MPa)	1531	1518	1695
Flex Modulus- 0° (GPa)	114,4	112,9	131,4
Flex Strength- 90° (MPa)	69	86	85
Flex Modulus- 90° (GPa)	9,1	8,8	8,8
Tensile Strength- 0° (MPa)	1979	1655	1962
Tensile Modulus- 0° (GPa)	133,9	160,7	156,0
Tensile Strength- 90° (MPa)	40,8	56,5	51,9
Tensile Modulus- 90° (GPa)	11,0	9,7	9,8
Interlaminar Short Beam Strength (MPa)	90,5	90,2	94,9

Comparative Analysis of Weight Savings

Comparison of Different Material Selections versus Forecasted Part Weights

Automotive OEM Projected Weight Savings per Application **Comparison of Different Material Selections on Part Weight using Steel as control**	
High Strength Steel	7 - 10 %
Aluminum	30 - 50%
Cast Magnesium	50 – 60%
SMC	10 – 25%
Carbon Fiber (Epoxy RTM)	40 – 70%
ADVALITE™ MF-HM-VHR Vinyl Hybrid/ Fiberglass Prepreg	45 – 55%
ADVALITE™ MF-HM-VHR Vinyl Hybrid/ CF Prepreg	45 – 70%

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Questions?

Acknowledgements

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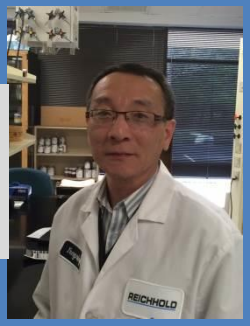
Reichhold
R&D- ADVALITE Product Line



Tamra Williams
Chemist Associate Reichhold
Applications - Closed Mold

Dr. Samuel Freeman
Senior Chemist Reichhold- Applications
Closed Mold- ADVALITE Product Line

Visit Reichhold at booth F19, Hall 7.2

THANK YOU FOR YOUR ATTENTION!