



Low HAP Materials



TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

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Report Documentation Page

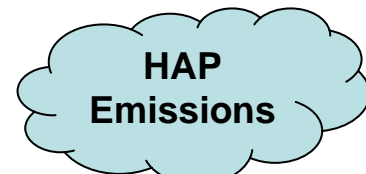
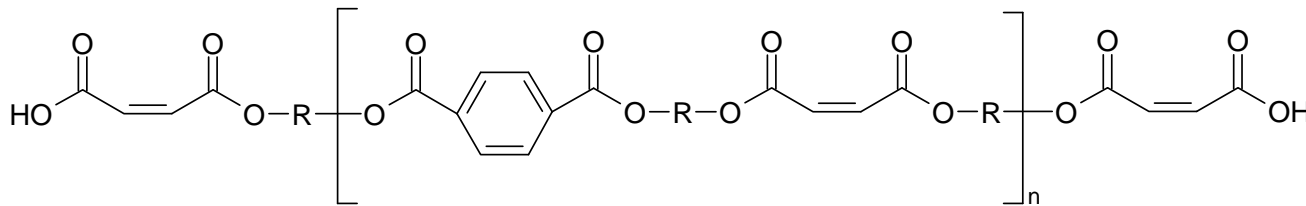
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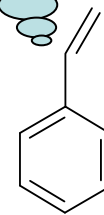
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- **Fatty Acid Vinyl Ester Resins/Composites with low hazardous air pollutant contents**
- **Other low HAP composite resin developments**
- **Low HAP Adhesives and Sealants**

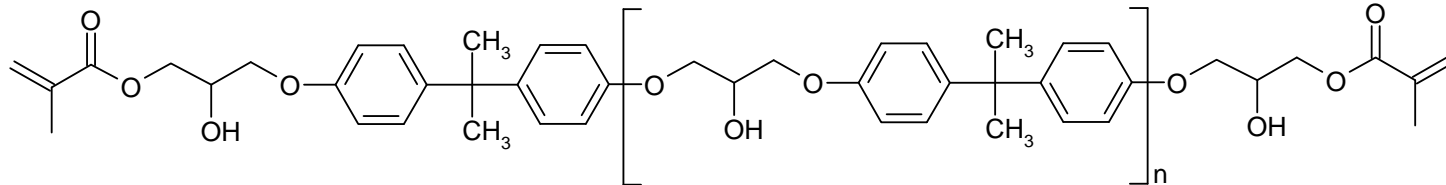
Unsaturated Polyester



+

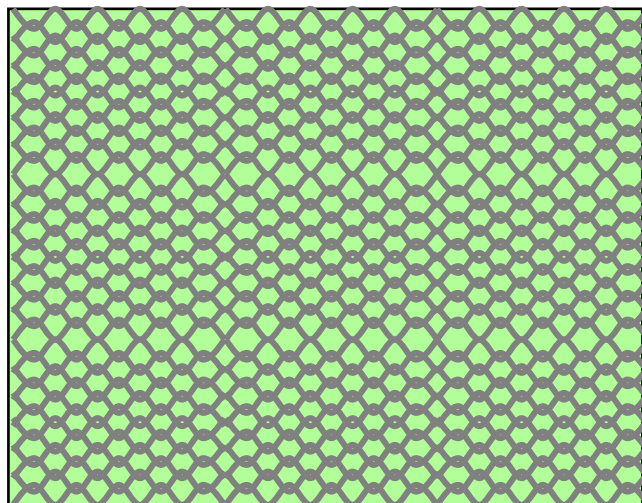


Styrene



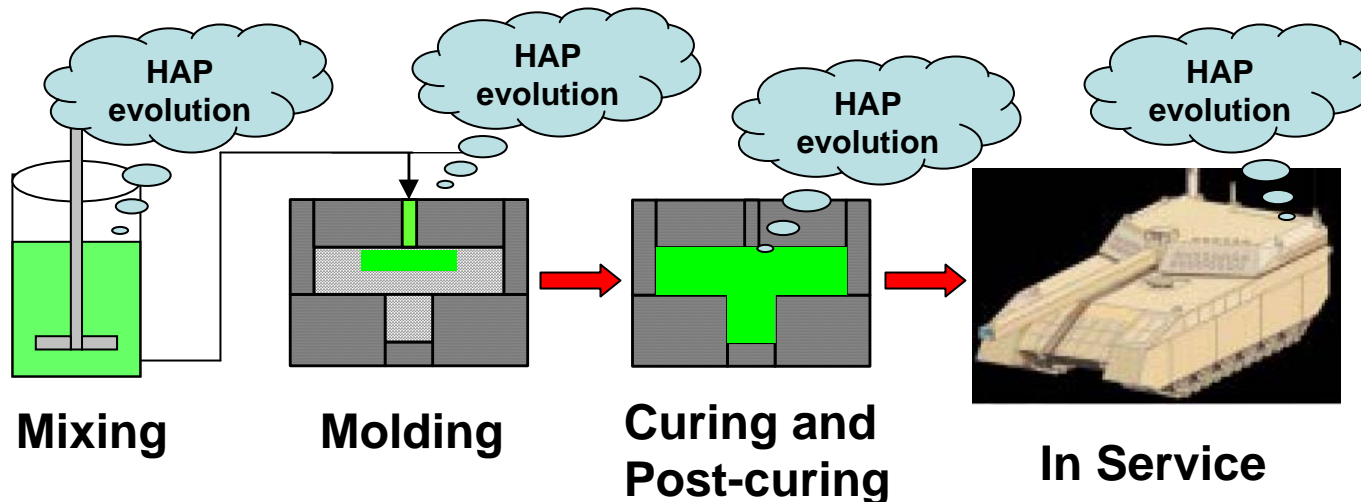
Vinyl Ester

Initiator + Heat



Thermosetting
Polymer

- Liquid resins used in molding large-scale composites are a significant source of Hazardous Air Pollutants (HAP)



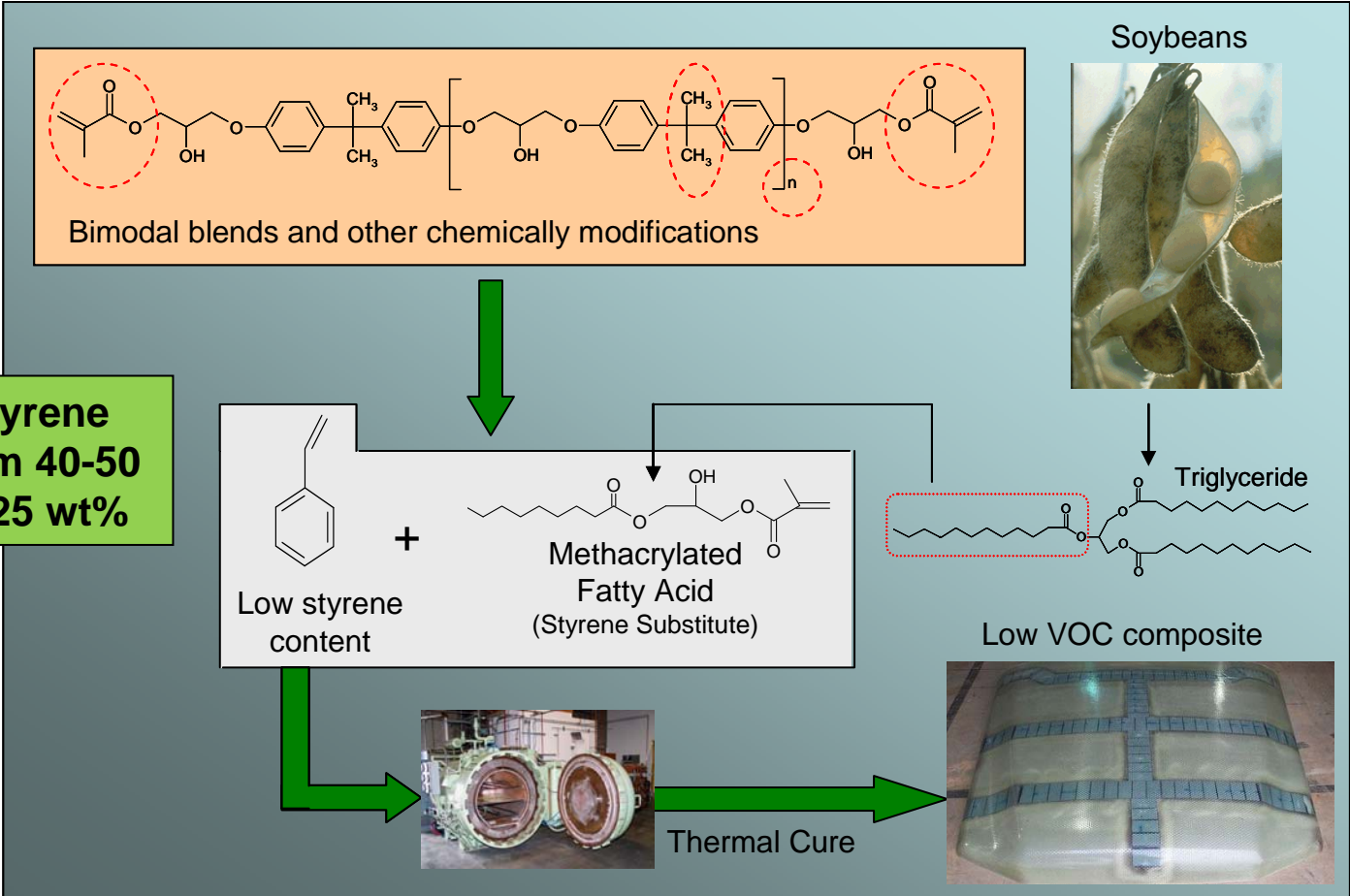
Composites industry consumes 9% of the styrene, but accounts for 79% of styrene emissions

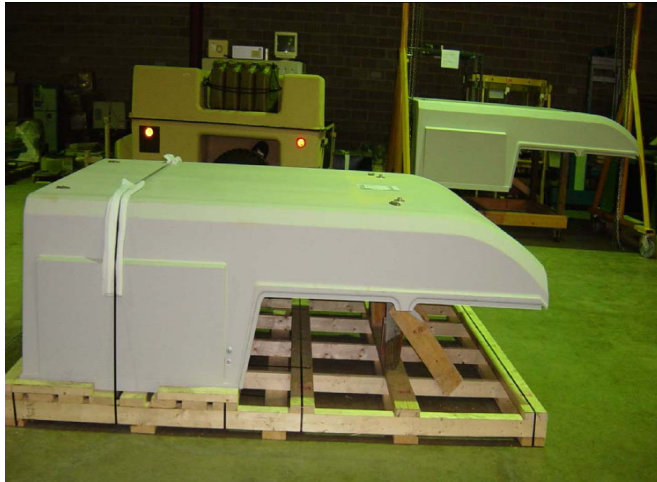
- EPA - Reinforced Plastic Composites National Emissions Standards for Hazardous Air Pollutants (NESHAP)
 - Executed and legally enforceable as of April 28, 2003
 - Regulation imposes a **substantial barrier to fielding and development of new composite technologies** for military platforms.

- Use fatty acid monomers to reduce styrene content.

- Non-volatile
- Maintain low viscosity

FAVE: Fatty Acid-Based Vinyl Ester Resin





HMMWV ballistic hardtop



HMMWV transmission container



M35A3 hood



T-38 dorsal cover

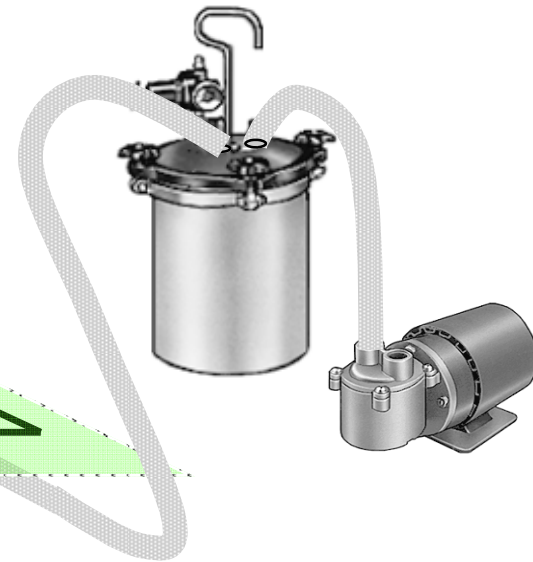
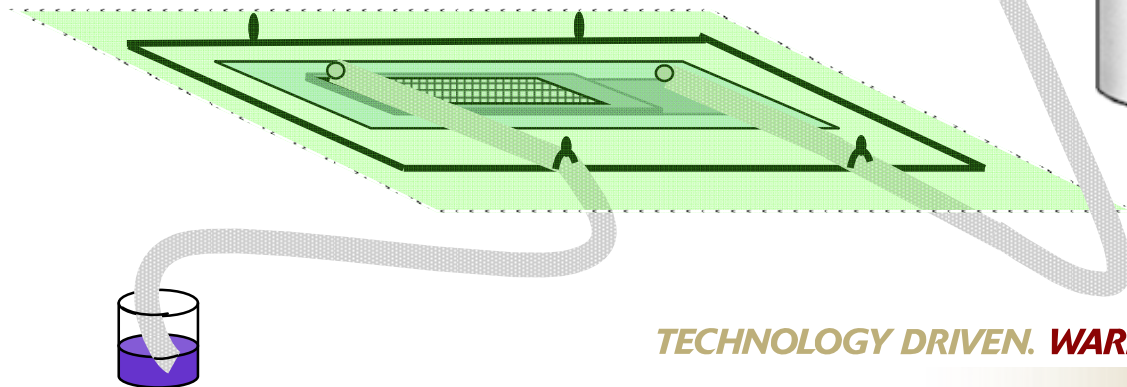
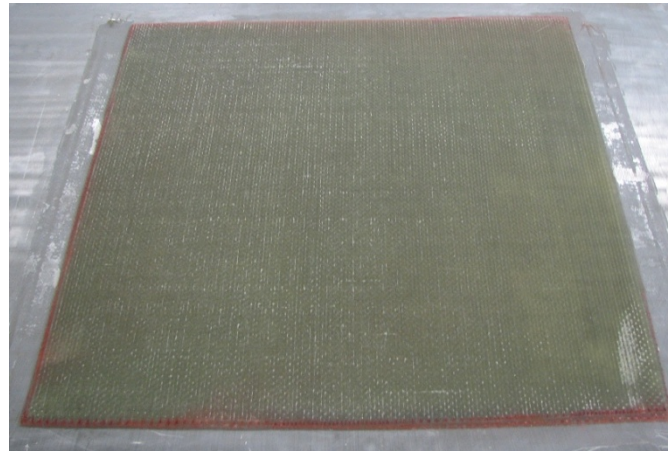
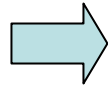
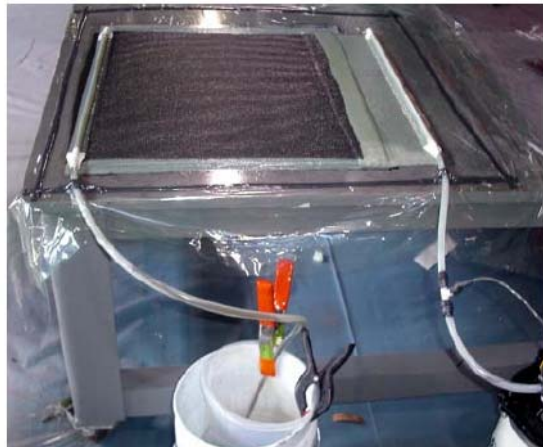


MCM composite rudder

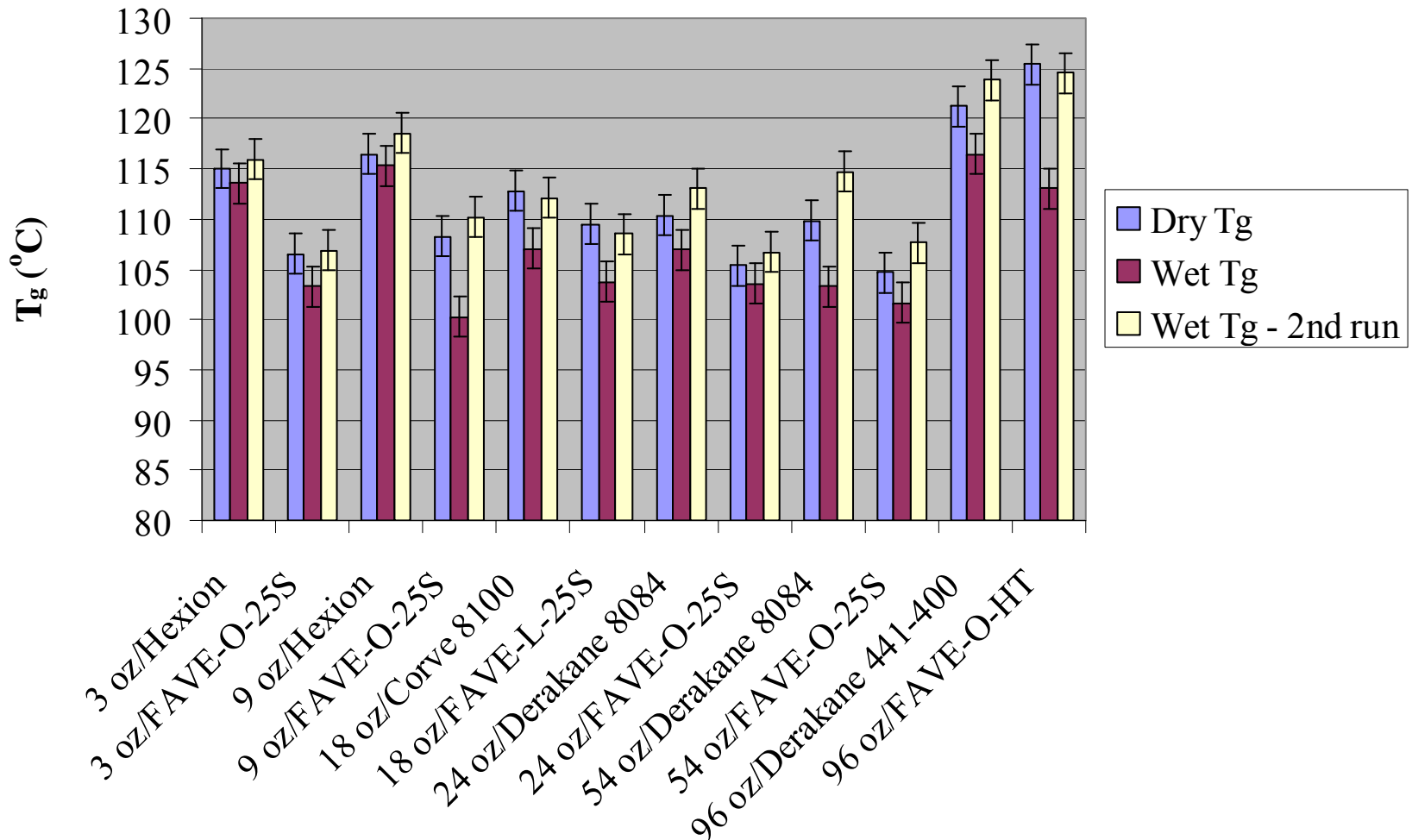


M939 hood

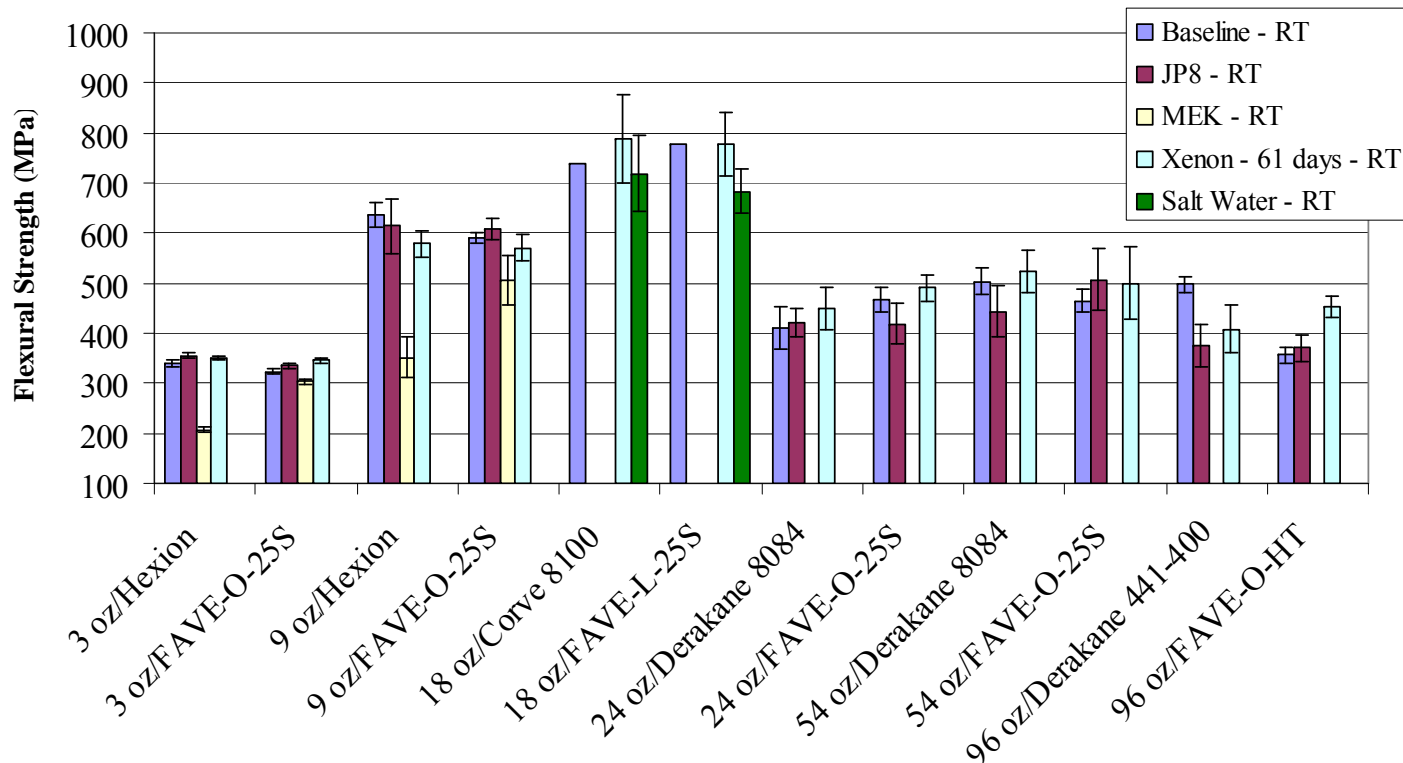
- **Vacuum Assisted Resin Transfer Molding (VARTM)**
 - Cured at room temperature using CoNap and DMA catalysts, 2,4-P inhibitor, and Trigonox initiator
 - Post-cured for 2 hours at 130°C



- Very similar T_g for FAVE composites relative to commercial composites.
- T_g decreases as a result of water ingress



- **Water (DI and salt) and Xenon weathering:**
 - T_g, strength, and modulus reduced for wet samples.
 - FAVE and commercial resins performed similarly.
- **Solvents/fuel immersion:**
 - T_g, strength, and modulus reduced for wet samples.
 - FAVE performed similarly or out-performed commercial resins.



- **Straight rudder (MCM)**
- **Composite twisted rudder (CTR) – DDG51 and DDG1000**
- **Easier to fabricate and less cavitation than steel twisted rudders**
- **Composite rudder on MCM-9 has good success after 6 year fielding trial**

Demonstrate/Validate low VOC/HAP formulations for one of these applications





Completed rudder



Trailing Edge



Leading Edge

- 1 hr resin infusion
- Rudder fabrication done by **Structural Composites, Inc.**, overseen by **NSWCCD**



- **Some excess resin pockets (wrinkling)**
- **One rudder will be demo piece.**
- **The other rudder was sectioned and is being analyzed by NSWCCD to validate the structure.**

- Corrosion issues with M35A3
- Sheet molding compound (SMC) HMMWV hood has poor performance
- Transmissions damaged in shipment without good packaging
- Test demo parts
 - Flexural, impact, cyclic load, High T, etc.



- **Container designed to protect HMMWV transmissions from damage during shipping**
- **Container must have:**
 - desiccant port
 - lifting handles
 - latches – no accidental opening
 - humidity indicator
 - pressure relief valve
 - drainage plug
 - forklift and pallet jack tine pockets
- **Container designed by CCM/Sioux Manufacturing Corp. (SMC)**
- **Container manufactured by SMC**



- According to SMC, resin infused as well or better than incumbent resins
- Resin required only 30 minutes for infusion

Infusion

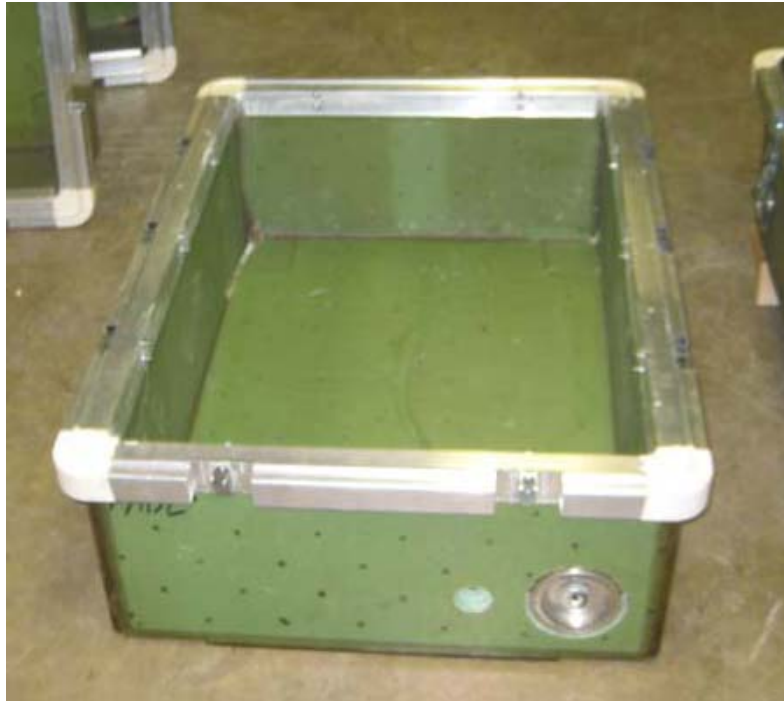


Infused Top



Infused Bottom

HMMWV Trans. Container: Commercial Prod.



Top with hardware



HMMWV Trans. Container: Commercial Prod.



Assembled Container

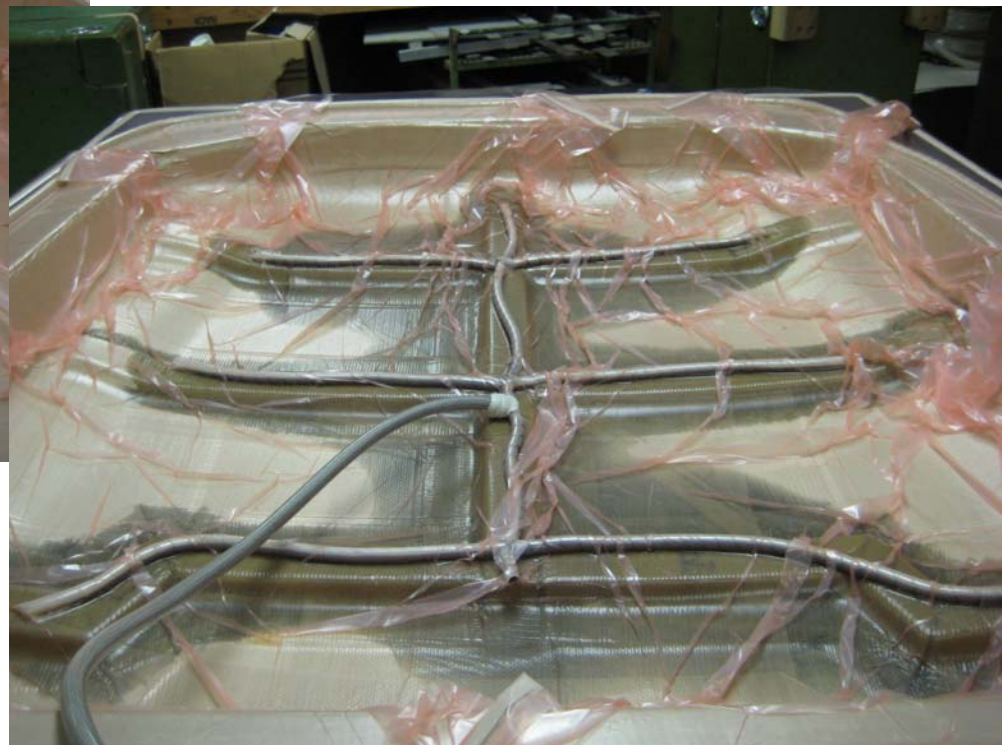
- **Drop tests**
 - Rotational Edge Drop Test per ASTM D6179 Method A
 - Rotational Corner Drop Test per ASTM D6179, Test Method B
 - Unsupported free fall drop test per ASTM D6179 Method D
 - Tipover Test per ASTM D6179, Method G
 - Vibration Test per ASTM D999 Test Method B
 - Later Impact Test per ASTM D880, Procedure B, 179, Test Method B
- **Leakage test**
 - Pressurize to 10 kPa, $\Delta P < 0.2$ Pa in 30 minutes
 - Pull a vacuum of 7 Pa, $\Delta P < 0.2$ Pa in 30 minutes
- **Validation tests are nearly completed at CCM**
- **Fielding trials are in progress at RRAD**



- M35A3 Truck hood manufactured by SMC



Bagged Hood



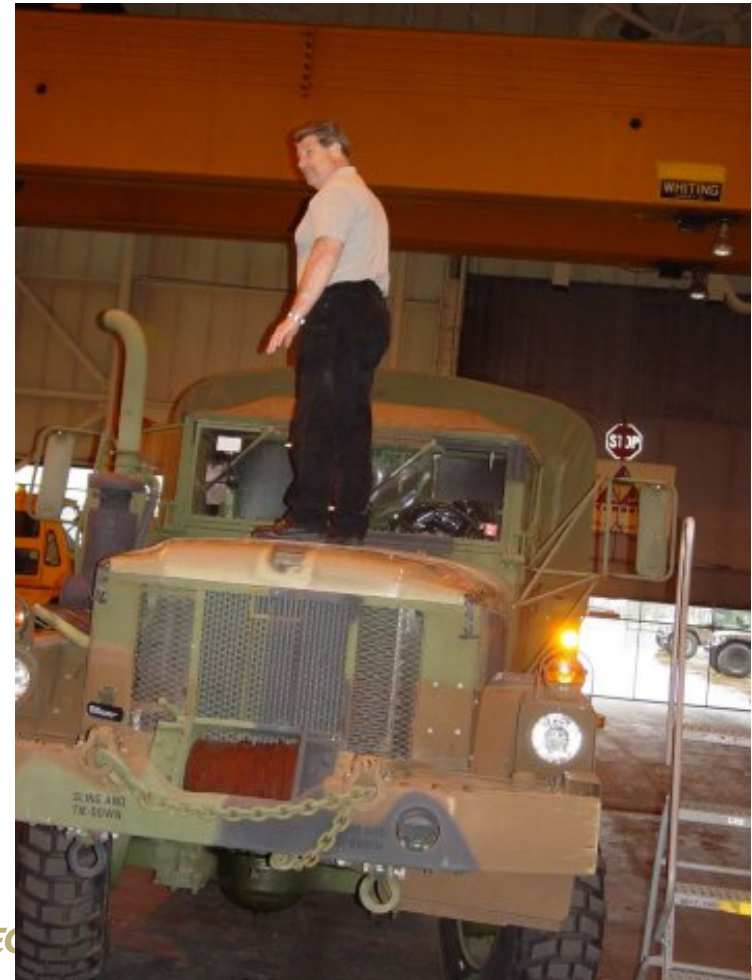
After 10 min of infusion
TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.



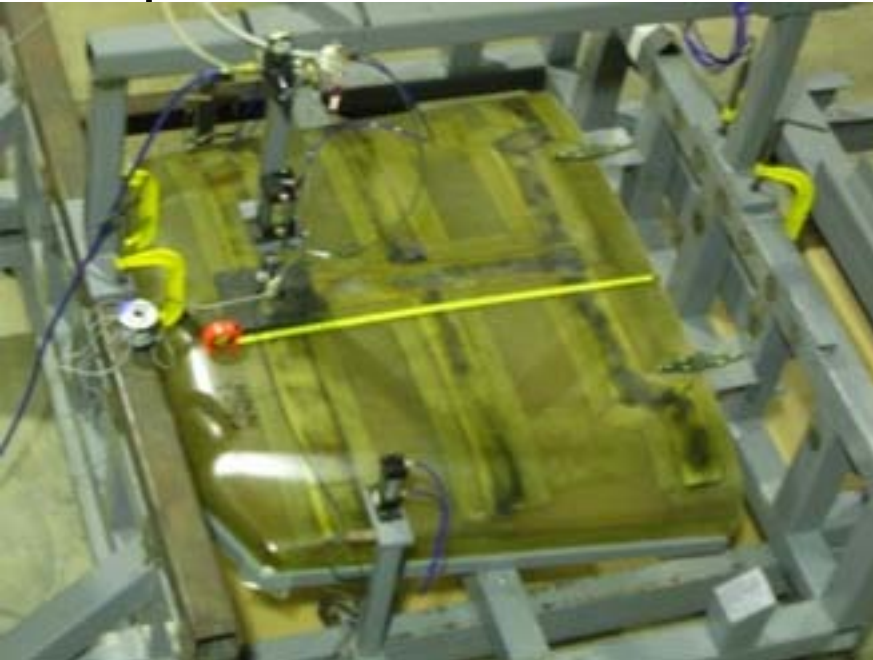
Final Hood

- According to SMC, resin infused as well or better than incumbent resins
- Resin required only 51 minutes for infusion

- **Low HAP hood painted with low VOC/HAP water-dispersible CARC (MIL-DTL-64159)**

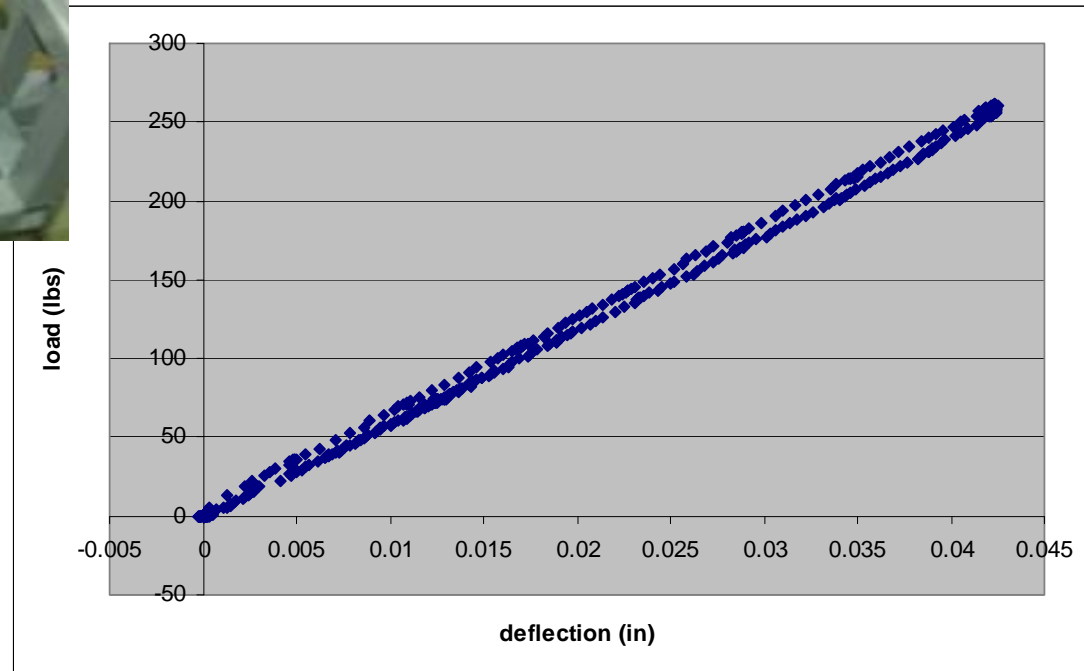


Top Front Load



- No permanent deformation.
- No separation of reinforcements from the hood.
- No cracks.
- **Test passed.**

- Elastic deflection **0.04"** at 250 lbs.
- Much less than **0.50"** allowed
- **Test passed.**

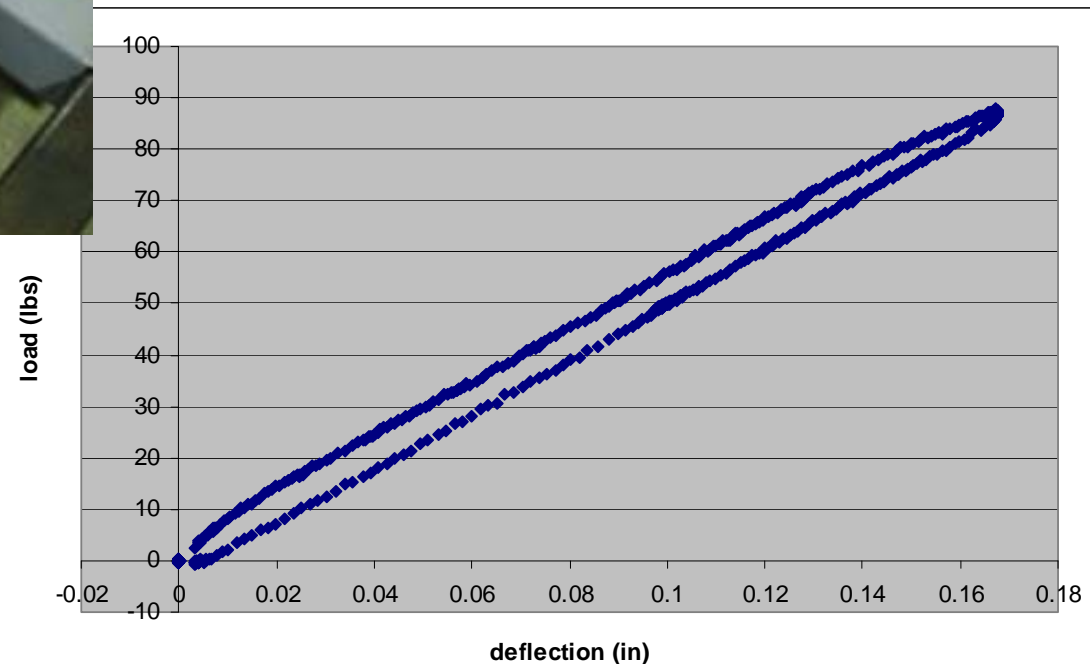


Driver Corner Lift

- No permanent deformation.
- No separation of reinforcements from the hood.
- No cracks.
- **Test passed.**



- Elastic deflection 0.16" at 85 lbs.
- More than 50 lbs required to lift corner 0.375"
- **Test passed.**

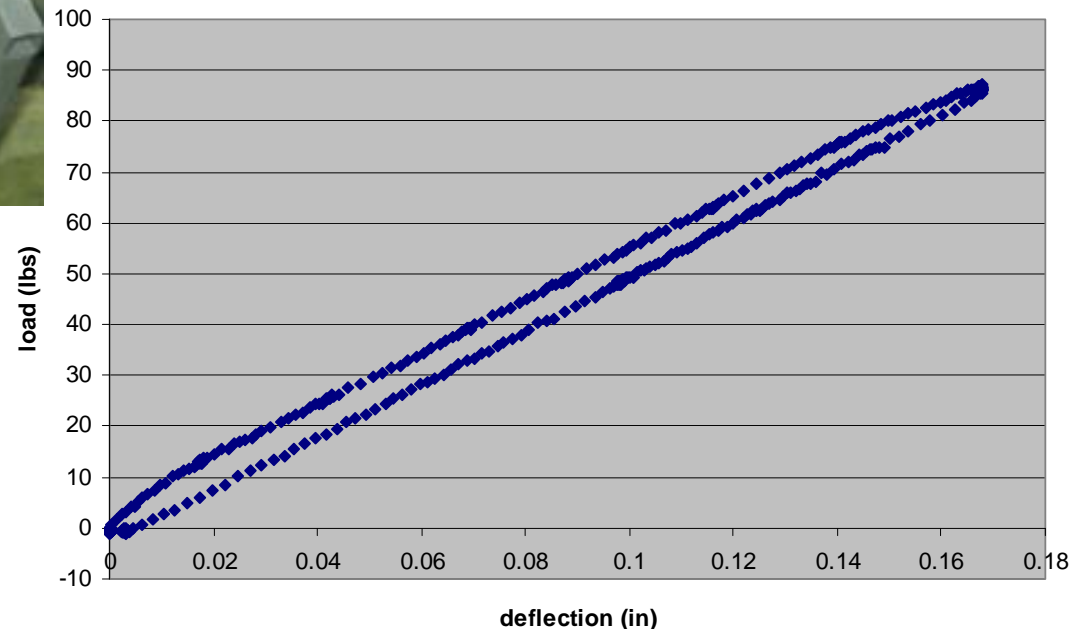


Cyclic Handle Load

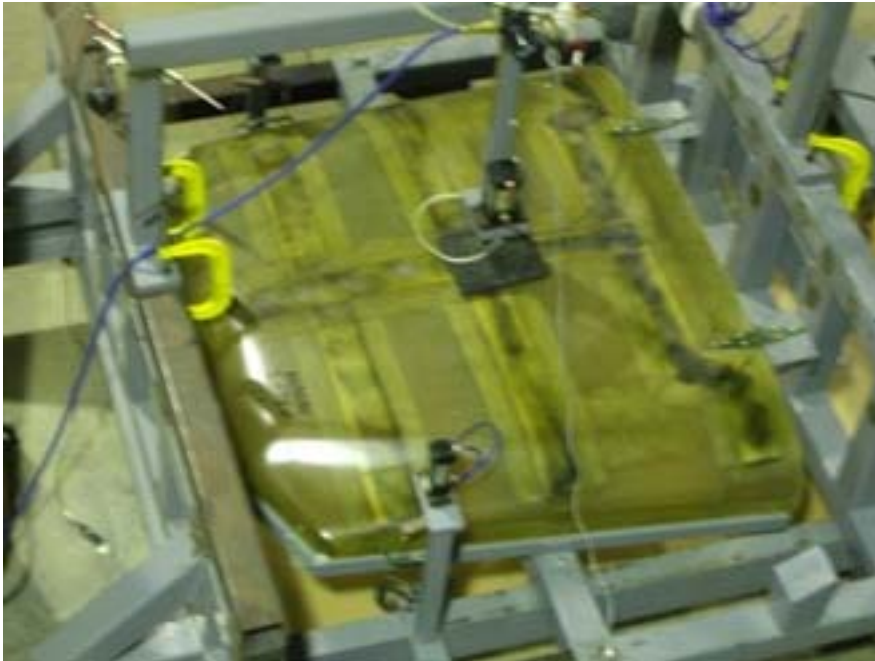


- No permanent deformation.
- No separation of reinforcements from the hood.
- No cracks.
- No broken fibers visible on areas where the hood contacts the fixture
- **Test passed.**

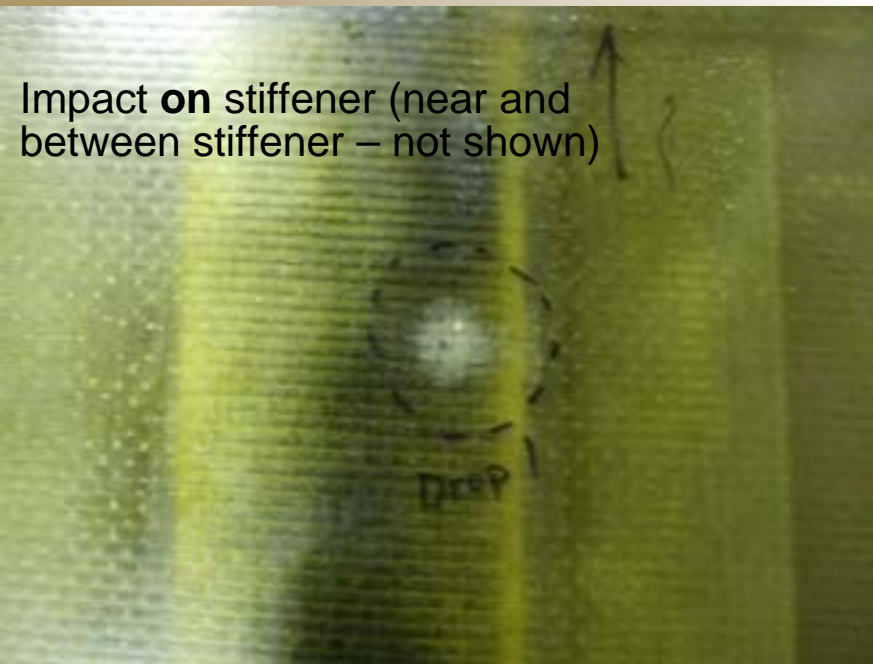
- Elastic deflection 0.16" at 85 lbs.
- More than 50 lbs required to lift corner 0.375".
- No significant change in stiffness after cyclic loading.
- **Test passed.**



Durability (cyclic loading followed by load deflection)



- **No permanent deformation.**
- **No separation of reinforcements from the hood.**
- **No cracks.**
- **No broken fibers visible on areas where the hood contacts the fixture**
- **Test passed.**

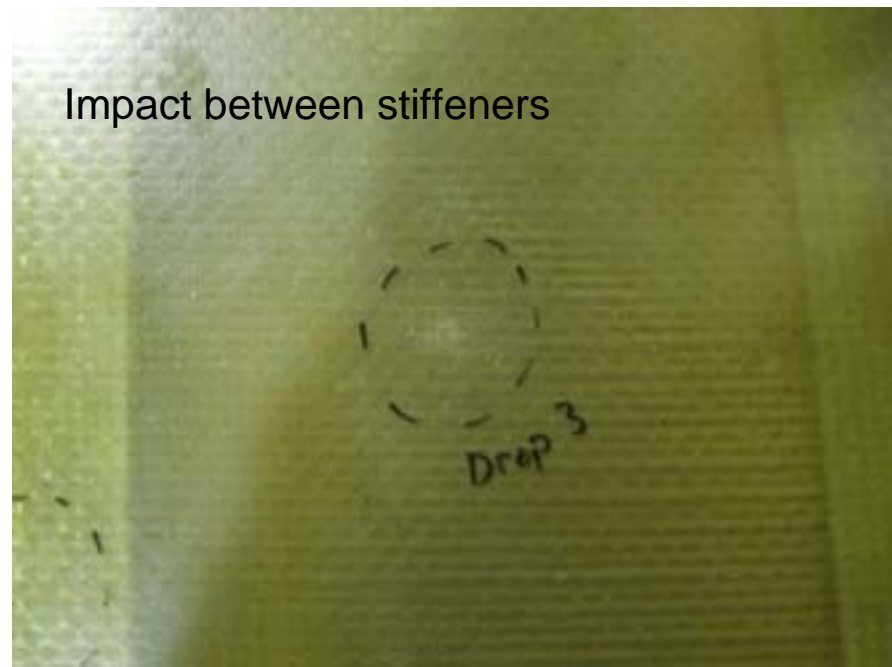


Impact on stiffener (near and between stiffener – not shown)



Impact on large radius corner

- No permanent deformation.
- No separation of reinforcements from the hood.
- No cracks.
- **Test passed.**



Impact between stiffeners

- **FAVE M35A3 passed all validation testing**
- **FAVE M35A3 performed nearly identically to baseline epoxy M35A3**

- **Hoods installed on M35A3 trucks at RRAD for field testing**

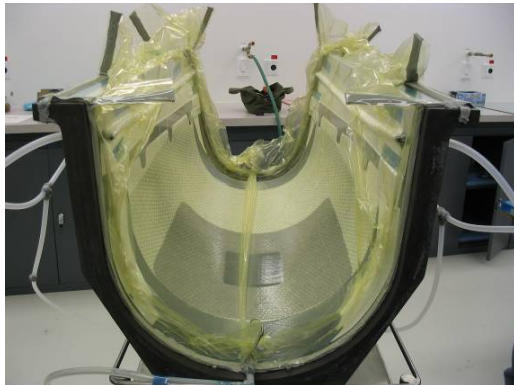
FAVE-O-25S Ballistic Performance

- **Performance assessed in all-composite panel form**
 - 100oz 3TEX 3WEAVE S2 Glass Construction
 - 4 ply panel for NIJ IIIa (44 magnum) equivalent
 - 12 ply panel for NIJ III (7.62 M80 Ball) equivalent
 - Compared directly to Derakane 8084 VE Resin – slightly different fabric architectures (24oz faces on 8084 panel) and FCS2 Epoxy
- **FAVE resin had similar or better performance with 44 mag. and M80 threats relative to both commercial resins**

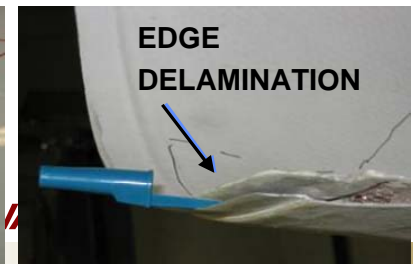
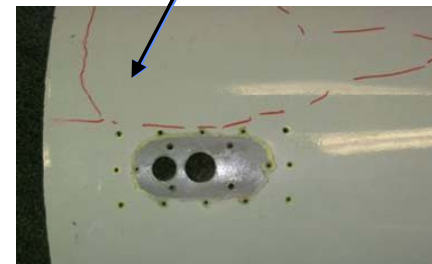
- 400 planes upgraded to 'C' model
- Upgrade caused pre-mature failure
- AFRL developed new VARTM dorsal cover
- Requirements
 - Drop-in replacement
 - Thermal, mechanical, electrical, solar



Demonstrate/Validate low VOC/HAP formulations for one of these applications

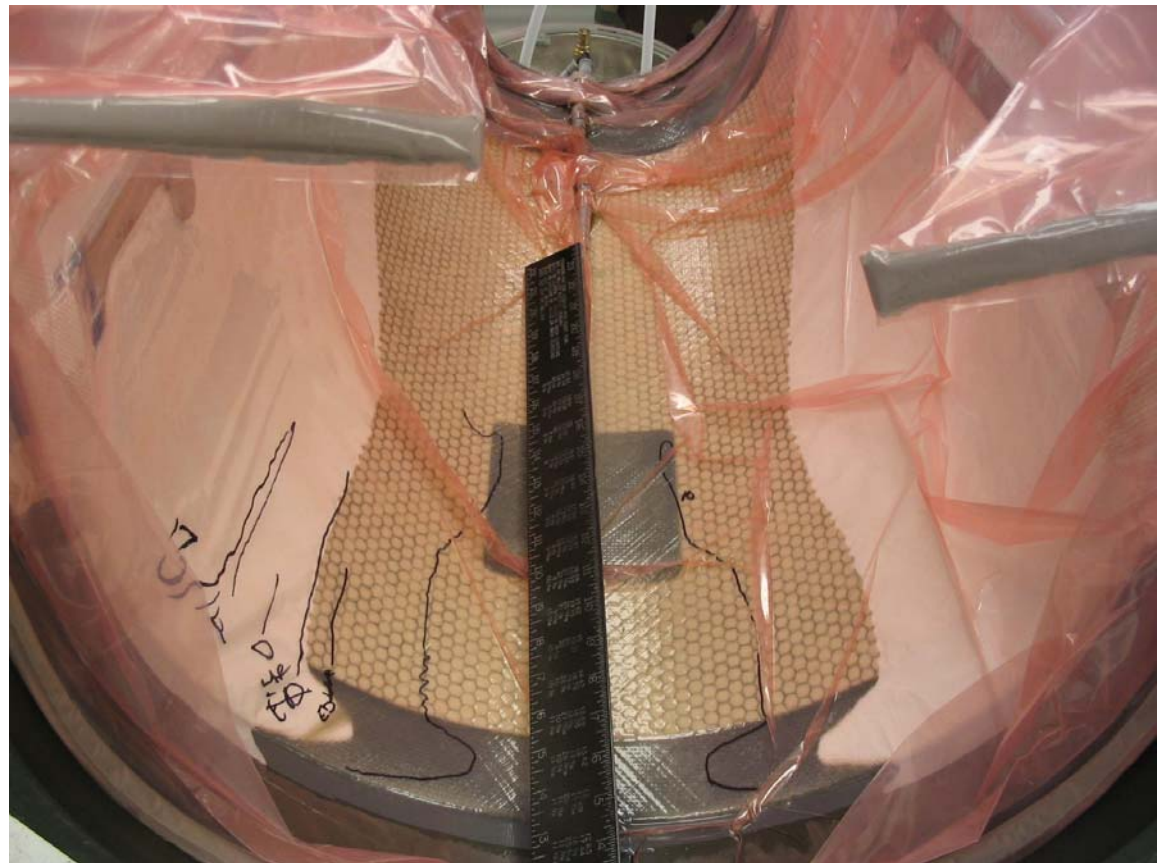


DISBOND



EDGE DELAMINATION

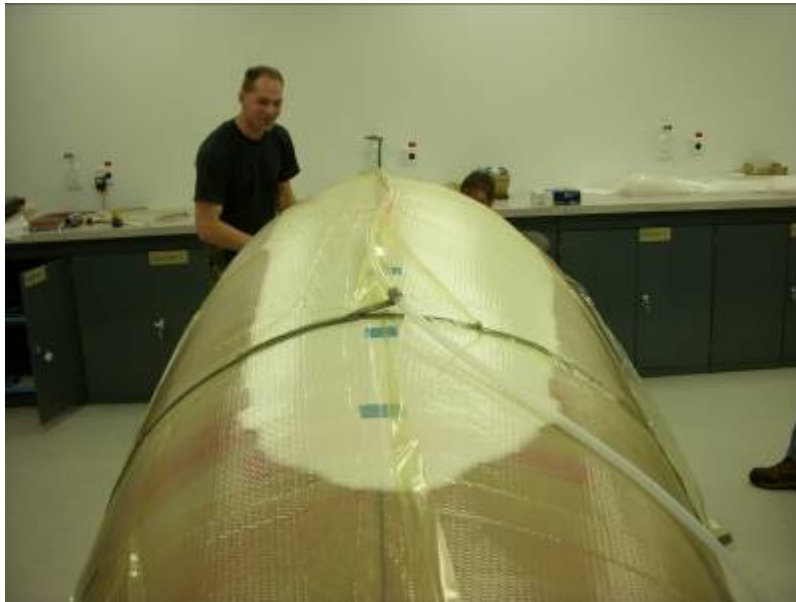
- **Short-shot infusion of T-38 dorsal cover**
- **FAVE-L resin viscosity was too high**
- ***Used FAVE-L-25S instead and solved processing issue***
- **Current resin uses 47% styrene – substantial reduction**



- ✓ **Manufactured and validated composite panels**
- ✓ **Manufactured T-38 dorsal cover**
- **Validation of structure will take place in the coming months**

- **AFRL expanded demonstration to F-22 canopy cover**
 - **Protects canopy against overspray during painting operations**
 - **Far easier and quicker than taping a cover in place**
 - **Used FAVE-L-25 resin to manufacture demo part**

Infusion of F-22 Canopy Cover



F-22 Canopy Cover Prototype

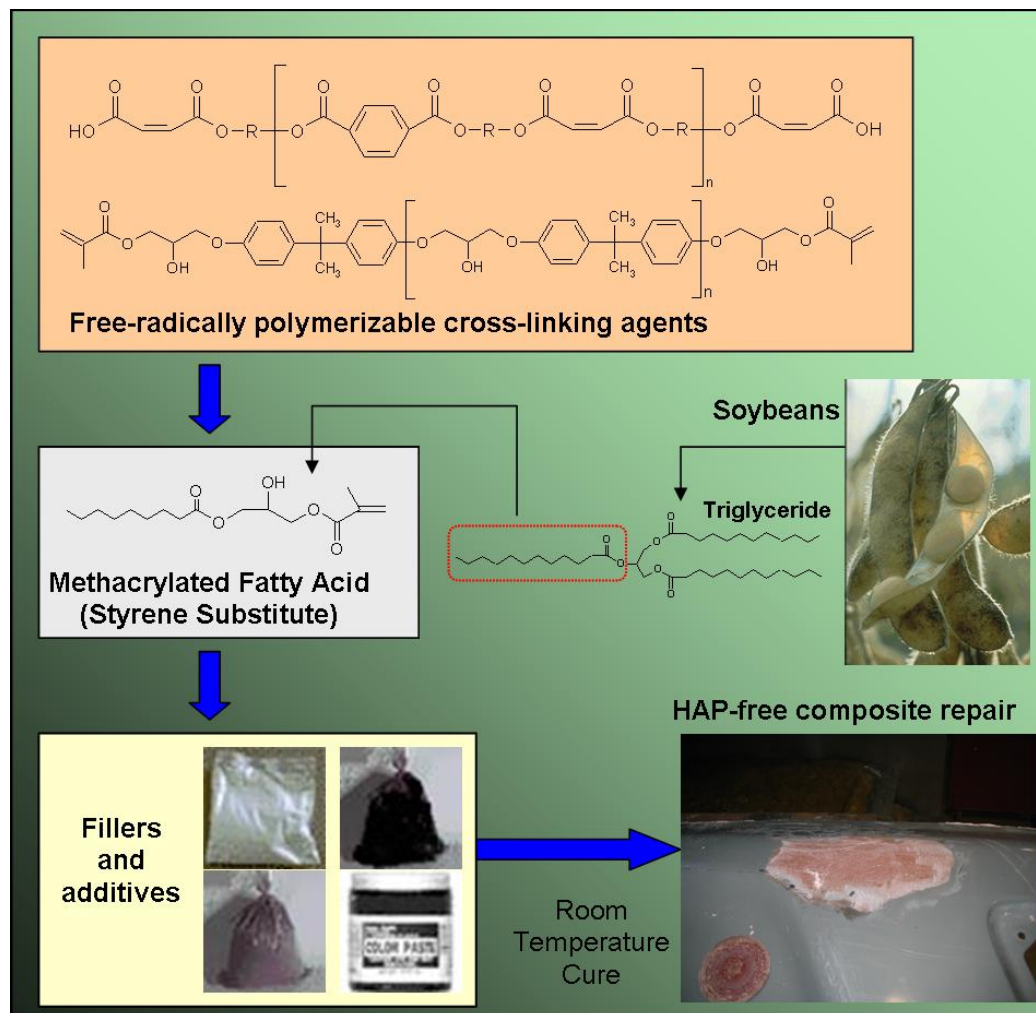


- **Current estimated MFA price range: \$1.23-\$2.85/lb**
- **Cost of fatty acid VE resin is \$0-\$1.16 higher per pound**
 - Depends on resin formulation and scale
- **Cost for emissions capture and treatment avoidance is \$1.13 per pound of resin**
- **Cost of carbon footprint is \$0.30 per pound of resin.**

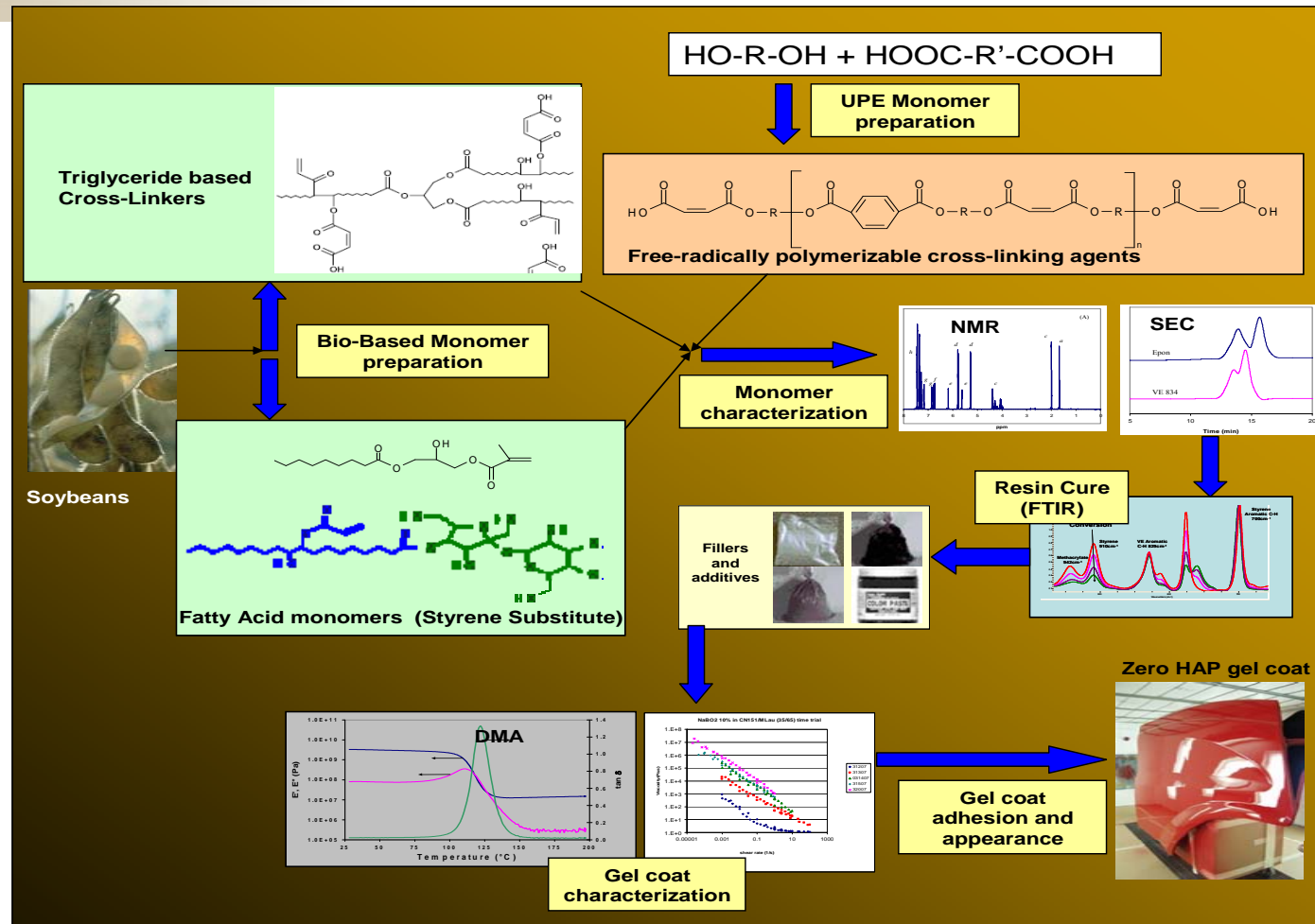
- **FAVE resins are more cost effective**
- **FAVE resins have a lower environmental impact**
- **FAVE resins have recently been licensed by Dixie Chemicals**

HAP-Free Repair Resin Similar to Bondo

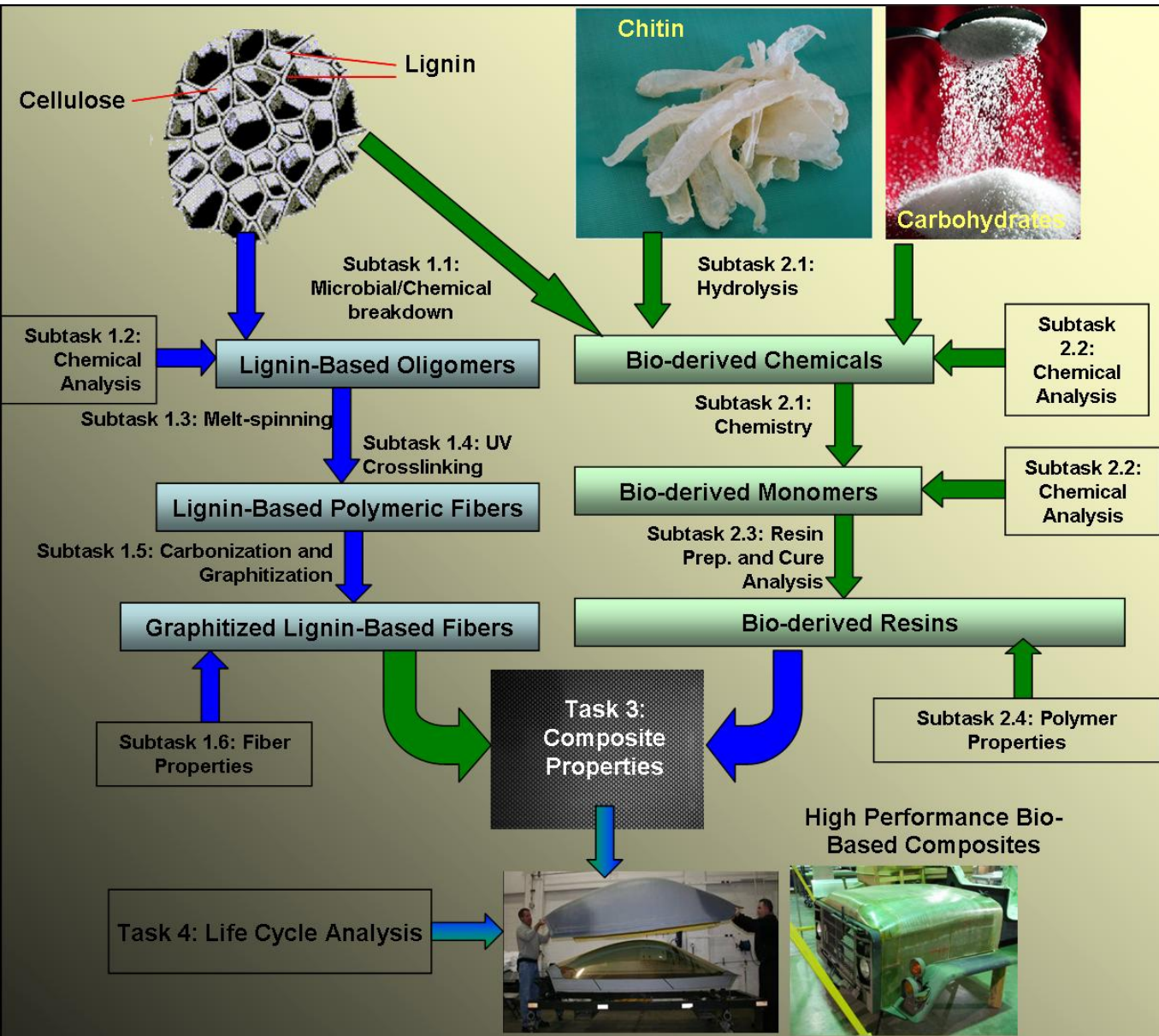
- **Binder**
 - Use MFA to replace styrene
 - Use VE and/or UPE cross-linkers
- **Fillers**
 - Use similar fillers/contents as in BONDO
- **Promoters**
 - Dimethylaniline
- **Curing agents**
 - Use BONDO hardeners
 - Formulate hardeners



- Gel coats used to provide smooth surface for composites
- Gel coats emit large HAP percentages.



- Use maleinized triglycerides to replace UPE
- Use novel bio-based reactive diluent to replace styrene



- SERDP proposed new start, FY10
- Microbially breakdown lignin into oligomers that can be melt spun and carbonized
- Modify renewable resources and bio-based chemicals to make bio-based monomers
- Assess, fiber, resin, and composite properties

Background:

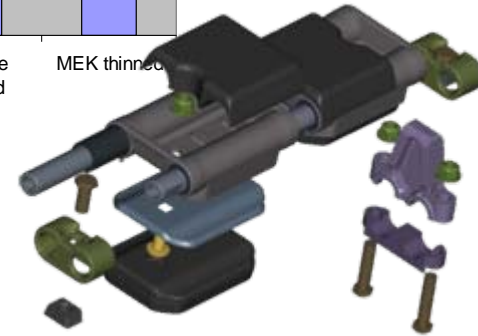
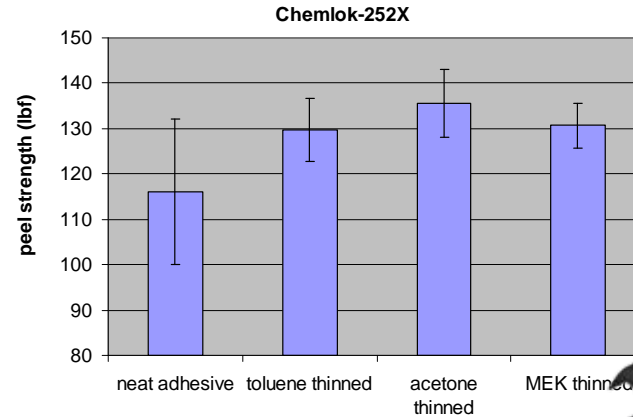
RRAD currently uses adhesives for tank treads and road wheels that contain very high HAP contents. The Defense Land Systems and Miscellaneous Equipment (DLSME) NESHAP is requiring reduced HAP in all DoD coating operations.

Objectives:

- Successfully replace current rubber to metal bonding adhesives with non-HAP alternatives or reduce HAPs through identification of compatible non-HAP thinners.
- Dem/Val best performing candidates at RRAD.

Participants:

U.S. Army Research Laboratory
 TARDEC
 RRAD
 Hayfire, inc.
 CTC/NDCEE



Progress to Date:

- Identified non-HAP thinners compatible with existing adhesive systems with similar bench-level performance.
- Identified low HAP alternative adhesives. Bench level testing of these adhesive systems is still in progress.

Benefits:

- Reduced HAP will comply with future EPA regulations, improve worker health, and improve mission readiness. **DRIVEN. WARFIGHTER FOCUSED.**

Background:

The Defense Land Systems and Miscellaneous Equipment (DLSME) NESHAP will require reduced HAP in all DoD coating operations. Rubber to metal contact adhesives under MMM-A-121 are used on various weapons platforms and produce ~1200 lbs/yr HAP emissions.

Objectives:

- Successfully replace current contact adhesives with non-HAP alternatives.



Participants:

SPOTA
 U.S. Army Research Laboratory,
 AMCOM G-4
 Fort Rucker
 Hayfire, inc., CTC/NDCEE

Progress to Date:

- Identified 3M Scotchweld 847 as a zero HAP, zero VOC alternative
- Laboratory testing showed similar performance relative to baseline
- Dem/val ongoing at Fort Rucker on blackhawk nose door seal and aviation helmet

Benefits:

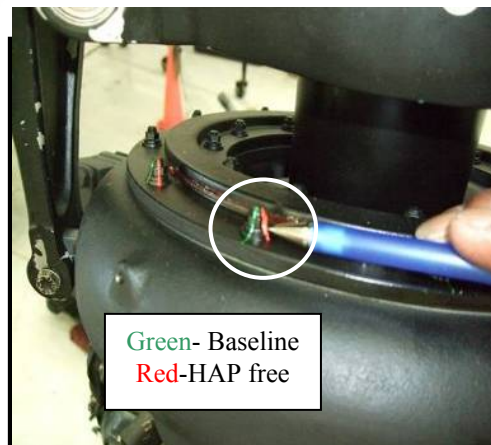
- Reduced HAP will comply with future EPA regulations, improve worker health, and improve mission readiness.
- Improved performance.

Background:

The Defense Land Systems and Miscellaneous Equipment (DLSME) NESHAP will require reduced HAP in all DoD coating operations. Inspection lacquers, such as F-900 Torque Seal, contain 20 wt% methanol HAP.

Objectives:

- Successfully replace current inspection lacquer with a non-HAP alternative.



Participants:

SPOTA
 U.S. Army Research Laboratory,
 AMCOM G-4, Fort Rucker
 Hayfire, inc., CTC/NDCEE

Progress to Date:

- Manufactured zero HAP Torque Seal
- Laboratory tested
- Successful dem/val of zero HAP Torque Seal on UH-1 rotor.
- HAP-free product is now listed on the GSA.

Benefits:

- Reduced HAP will comply with future EPA regulations, improve worker health, and improve mission readiness.
- Improved performance.

- **Environmentally friendly VE and UPE resins using fatty acid monomers and tailored VE molecular structure**
 - Effectively reduce HAP emissions
 - Comparable resin and composite performance
- **Variety of other uses for plant oils in composites**
 - Bio-rubber toughening agent increases toughness dramatically while maintaining T_g and viscosity.
 - HAP-free repair resin performs similar to Bondo™ similar
 - New generation of environmentally friendly bio-based composites in development.
- **Low HAP adhesives and sealants.**
- **“Army Green” does not *only* refer to Army colors!**

- **Army Research Laboratory**
 - J.M. Sands, S. Boyd, K. Andrews, T. Glodek, C. Lochner, P. Myers, F. Levine, D. De Bonis, R.E. Jensen, R. Hayes
- **Drexel University – Palmese research group**
- **CCM, University of Delaware**
 - S. Anderson, David Fudge, N. Shevchenko, K. Brand
 - Jack Gillespie, Prof. Wool Research Group
- **NSWC, Carderock Division – R. Crane, M. Foley**
- **Advanced Composite Office, Hill AFB and Air Force Research Lab**
 - Larry Coulter, Ken Patterson, Lt. Dane Morgan, Frank
- **Resin Suppliers: Applied Poleramics, Inc., Ashland, Hexion, Corezyn**
- **ESTCP WP-0617, SERDP PP-1271, EQBRD, SPOTA for funding**

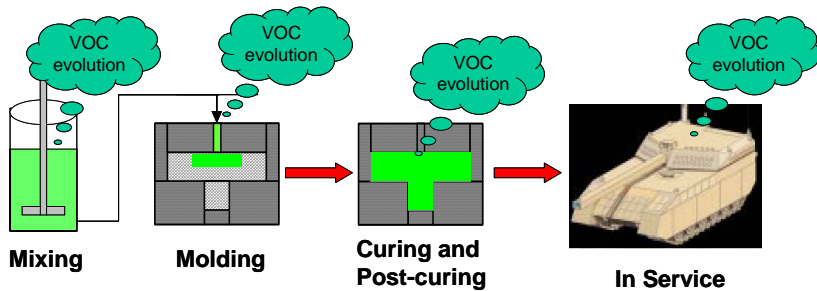


Low VOC Resin Technology

Low Cost and High-Impact Environmental Solutions for Composite Structures

Need for Low VOC Resins

Liquid resins used in molding large-scale composites are a significant source of Volatile Organic Compound (VOC) emissions. In fact, the composites industry only consumes 9% of the styrene, but produces 79% of the emissions. For this reason, the EPA has enacted the Reinforced Plastic Composites NESHAP, which mandates the maximum HAP content in liquid molding resins.



Applications

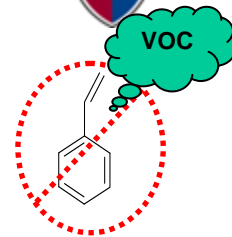
Applicable to all uses of unsaturated polyesters and vinyl esters, including all methods of manufacture.

- Military vehicles and structure
- Automobile parts
- Boats
- Gel coats

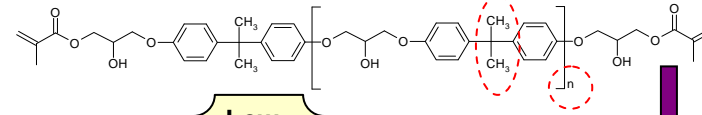


Solutions

- Fatty acid monomers as styrene replacements
- Tailor molecular structure of vinyl ester monomers



Soybeans



Low VOC Resin

Resin Processing

- Low viscosity
- VARTM, SCRIMP, SMC capabilities



Composite hood

Polymer Properties

- High T_g , strength, toughness
- Comparable to commercial resins

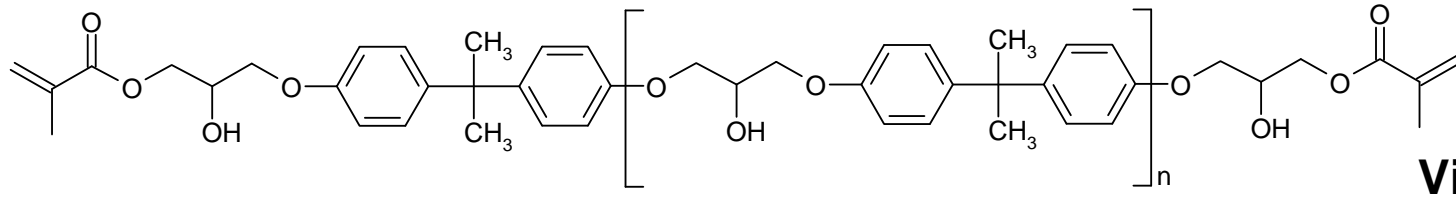
Facilities

Army Research Laboratory
Rodman Materials Building
APG, MD

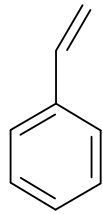


Drexel University
Philadelphia, PA



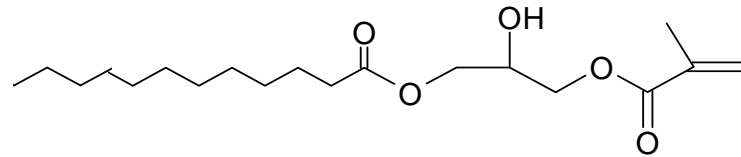


Commercial Resins
 Low VOC ~ 33 wt% Sty
 Standard ~ 40-50 wt% Sty



Styrene
 10-25 wt%

+



MFA – methacrylated fatty acid

FAVE: Fatty Acid-Based Vinyl Ester Resin

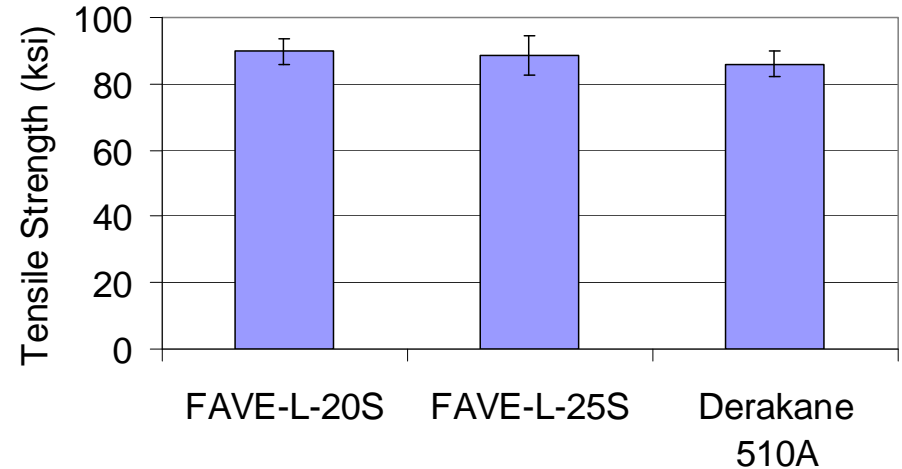
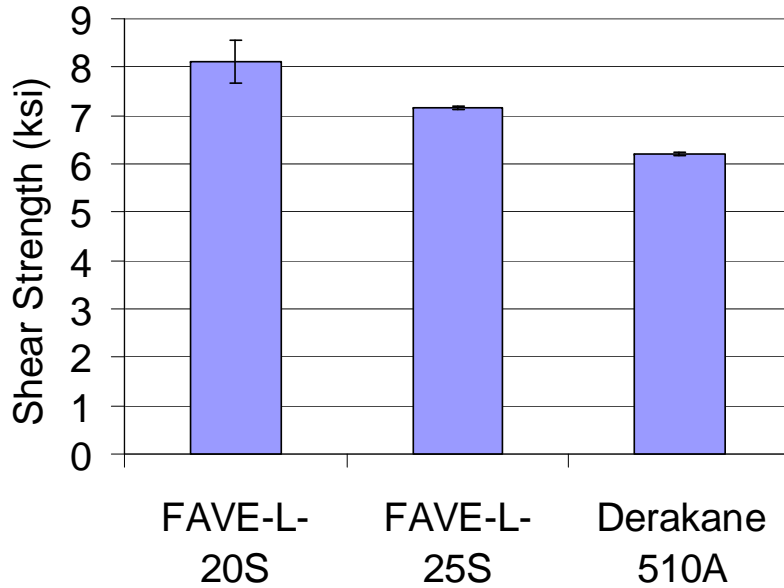
- **Use fatty acid monomers to reduce styrene content**
 - Non-volatile and inexpensive
 - Copolymerizes with styrene and vinyl ester
 - Soluble in VE and UPE
 - Increases renewable content in polymers
 - Reduces VOC/HAP emissions by 55-78%



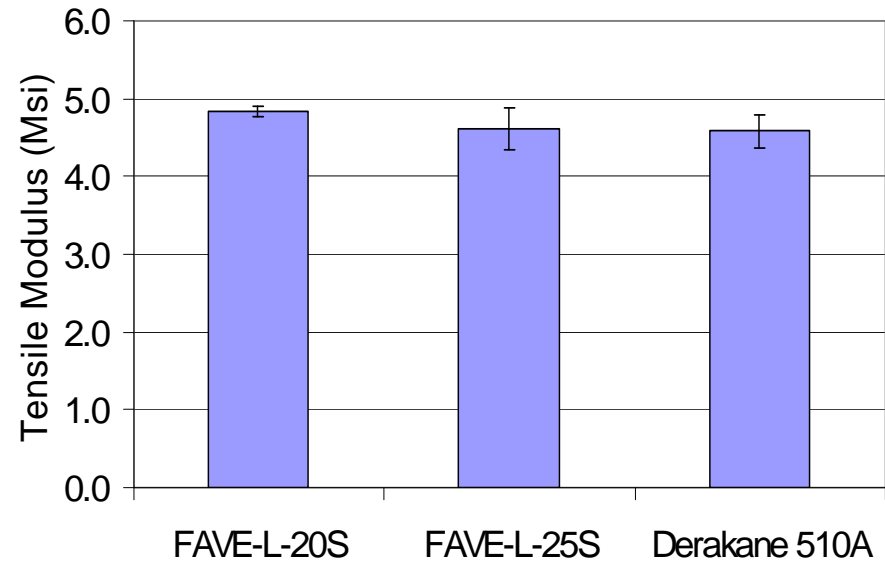
Application	Fabric	Resin	Resin Replacement
Amtech Helmet Hardtop	3-Tex 100 oz S2-glass and 24 oz S2-glass	Derakane 8084	FAVE-O-25S
HMMWV Hood	3D E-glass	Hetron 980-35	FAVE-L-HT/O-HT
M35A3 and M939 Hood	3-Tex 96 oz E-glass	Hetron 980-35 (VE) or Huntsman 8605 (Epoxy)	FAVE-L-HT/O-HT
Transmission Container	3-Tex 54 oz E-glass	Derakane 8084	FAVE-L-25S/O-25S
T-38 Dorsal Cover and F22 Canopy Cover	Fibre Glast Developments Corp. 120 3 oz E-glass and Style 7781 E-glass 9 oz	Hexion 781-2140	FAVE-L-25S/O-25S
Rudders	Fiber Glass Ind. 18 oz E-glass	Corezyn Corve 8100 and Derakane 510A-40	FAVE-L-25S

- **Derakane 8084:** ~40 wt% styrene
- **Hexion 781-2140:** 47 wt% styrene
- **Corve 8100:** 50 wt% styrene
- **Hetron 980/35** <35% styrene
- **Derakane 441-400:** 33 wt% styrene (low HAP resin)
- **FAVE-L/FAVE-O-25S:** 25 wt% styrene, L – methacrylated Lauric acid
O – methacrylated Octanoic acid
- **FAVE-O-HT:** 25 wt% styrene, Novolac VE

FAVE Meets Navy Composite Panel Validation



- **Both FAVE-L and FAVE-L-25S are similar or exceed performance of commercial resins**
- **Toughness alone decreased, but this was likely due to incomplete cure**





FAVE-O-25S and FAVE-L-25S Performance



Property	Strength (ksi)	Requirement (ksi)	Modulus (msi)	Requirement (msi)
FAVE-O-25S 4 pt bend Room Temp	62.0	55.0	3.70	3.70
FAVE-O-25S Short beam shear Room Temp	4.80	4.50	-	-
FAVE-L-25S 4 pt bend Room Temp	70.0	55.0	3.85	3.70
FAVE-L-25S Short beam shear Room Temp	5.10	4.50	-	-

- FAVE-O-25S and FAVE-L-25S meet specs for Army transmission containers and HMMWV hardtop

	Batch 2 Strength (ksi)	Batch 1 Strength (ksi)	Require- ment (ksi)	Batch 2 Modulus (msi)	Batch 1 Modulus (msi)	Require- ment (msi)
4 pt bend Room Temp	62.0	56.6	55.0	3.76	3.67	3.70
4 pt bend 250 F	36.2	29.3	30	2.9	2.69	3.0
Short beam shear Room Temp	4.08	3.70	4.50	-	-	-
Short beam shear 250 F	3.20	2.90	3.0	-	-	-

- Reformulated (Batch 2) FAVE-O-HT meets specs for Army hoods.



Impact 4 – large radius corner

Impact 5, 6 – Small radius corner

- No permanent deformation.
- No separation of reinforcements from the hood.
- No cracks.
- **Test passed.**





Composite Hub



Foam with Composite Hub and Cut outs for installation of Vertical Shear Ties



Installation of Vertical Shear Ties



After Infusion of Vertical Shear Ties

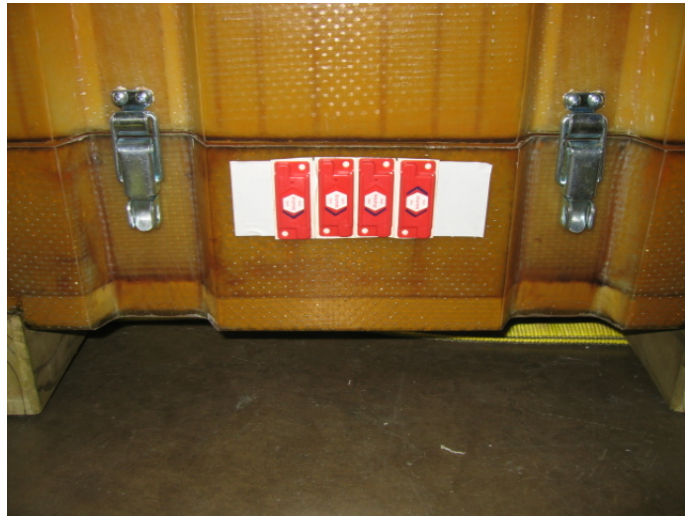


During infusion of first packet (5 layers)

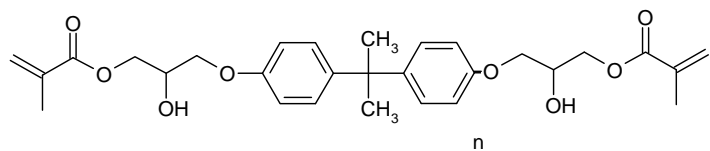


After infusion of first packet

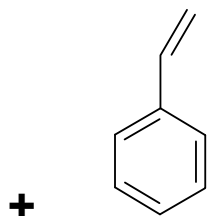
Container Testing



- **The major steps in hood production are:**
 - **cut 3Tex 96 oz main ply**
 - **stiffeners consisting of a foam core and wrapping ply are purchased pre-cut**
 - **lay-up plies and stiffeners. Place additional reinforcement plies over the stiffeners and along the perimeter of the hood**
 - **bag part**
 - **mix resin, CoNap, and MEKP and infuse with FAVE-L vinyl ester resin or vantico 8605 epoxy resin**
 - **post-cure part**
 - **trim hood in router**
 - **drill holes for hardware**
 - **bond safety latch and handles**



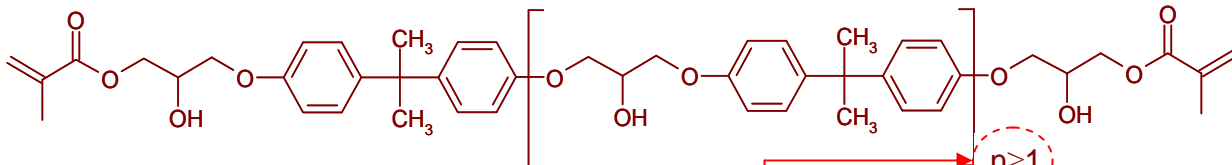
Low Molecular Weight VE



+

Styrene

Reduces Styrene content to 28-38 wt.%



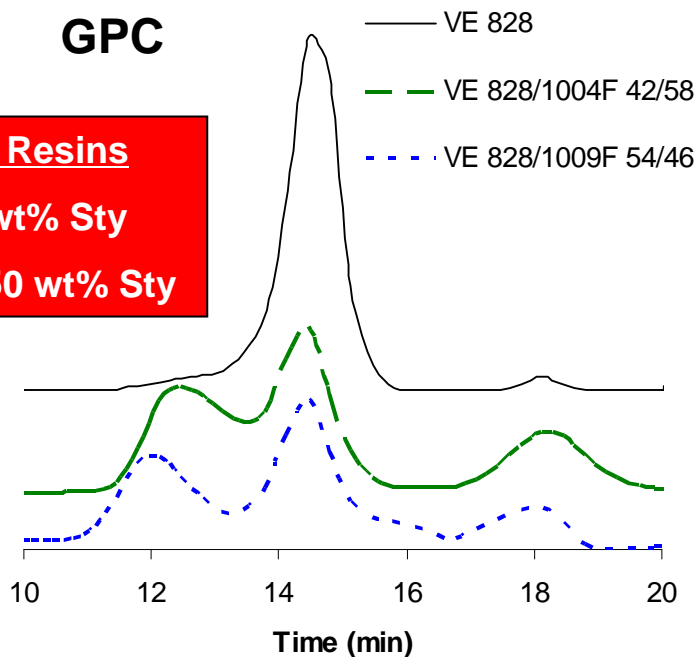
High Molecular Weight VE

VE molecular weight affects resin and polymer properties

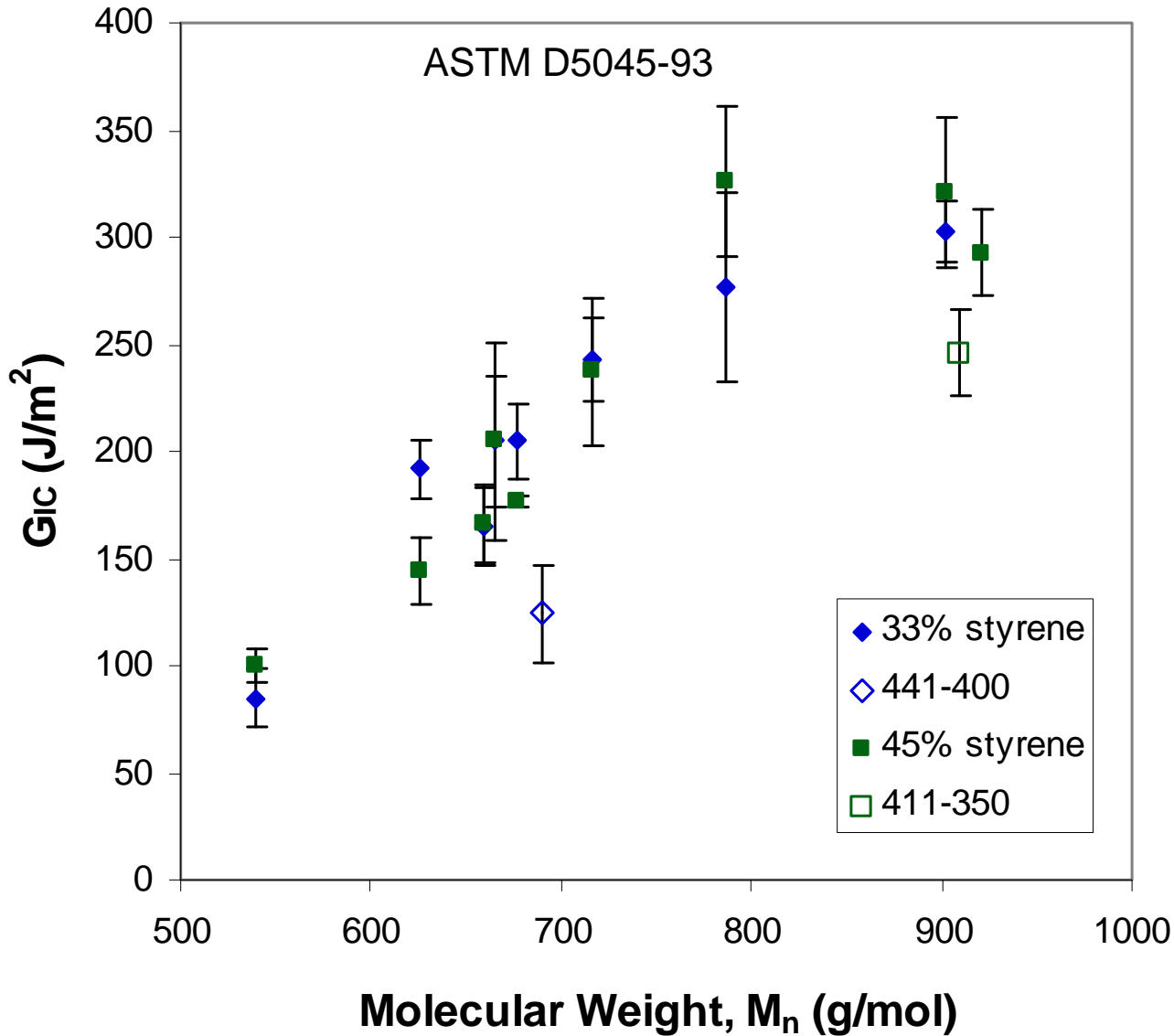
- Low VE molecular weight
 - Low viscosity
 - Low fracture properties
- High VE molecular weight
 - High viscosity
 - High fracture properties

Commercial Resins
 Low VOC ~ 33 wt% Sty
 Standard ~ 40-50 wt% Sty

GPC

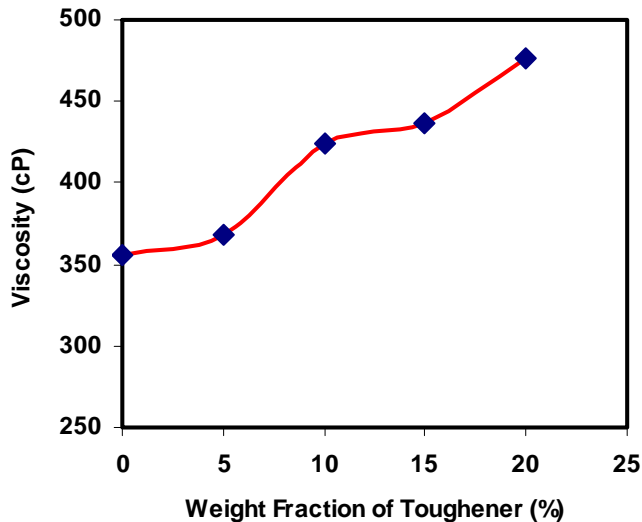
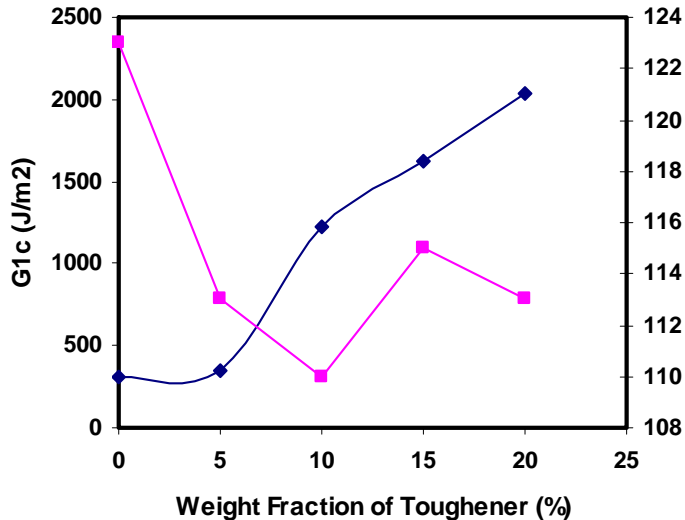
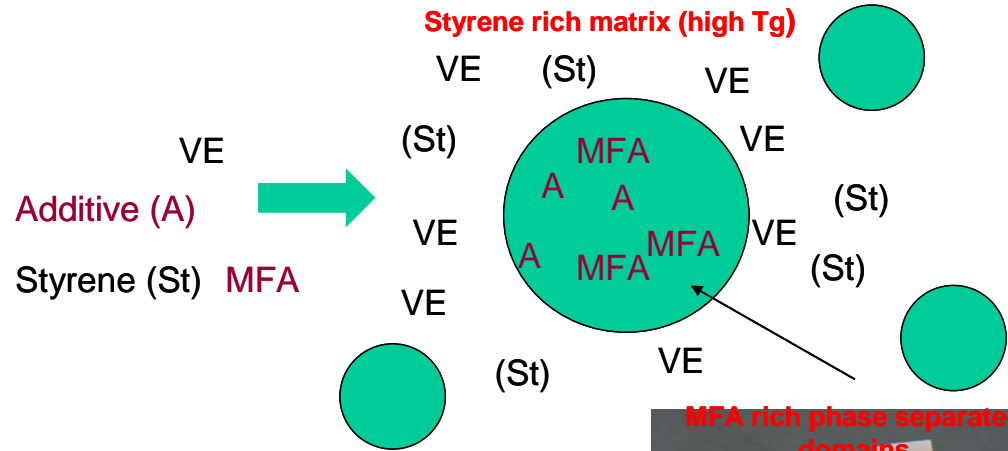


* Source: ARL/Drexel patent application, April 2005.



- **Bimodal resins have superior fracture properties**

- Designed plant oil-based toughening agents
- Uses phase separation to capture MFA reactive diluent
- Increases toughness while decreasing styrene content and maintaining viscosity



Increasing BR content

