

DEMONSTRATION OF MILITARY COMPOSITES WITH LOW HAZARDOUS AIR POLLUTANT CONTENT

John J. La Scala, Felicia Levine, Philip Myers, and James M. Sands
Army Research Laboratory
Aberdeen Proving Ground, MD 21005

Stephen Andersen and John Gillespie, Jr.
University of Delaware, Center for Composite Materials
Newark, DE 19716

Ken Patterson and Lawrence Coulter
AFRL/MLS-OL
Hill AFB, UT 84056

Roger Crane
Naval Surface Warfare Center Carderock,
West Bethesda, MD 20817

Michael Starks and Jorge Gomez
Red River Army Depot, US Army TACOM
Texarkana, TX 75507-5000

Xing Geng and Giuseppe R. Palmese
Drexel University, Dept. of Chemical and Biological Engineering
Philadelphia, PA 19104

ABSTRACT

Liquid resins used for molding composite structures are a significant source of volatile organic compounds (VOC) and hazardous air pollutant (HAP) emissions. One method of reducing styrene emissions from vinyl ester (VE) resins is to replace some or all of the styrene with fatty acid-based monomers. Fatty acid monomers are ideal candidates because they are inexpensive, have low volatilities, and promote global sustainability because they are derived from renewable resources. This patent pending technology allows for the formulation of high performance composite resins with no more than 25 wt% styrene. These resins have low viscosities suitable for vacuum infusion methods, and have excellent polymer and composite properties. As a result, these resins are currently being demonstrated/validated for DoD use on Army tactical vehicles, including HMMWV hoods, HMMWV helmet hardtops, T-38 dorsal covers, and composite rudders for the Navy.

1. INTRODUCTION

Polymer matrix composites are materials made by combining a polymer with another class of materials, such as a ceramic. In general, the intention of making polymer-composites is to have low-weight, high-performance materials that are superior in a number of ways to the individual components. Fiberglass

automobile bodies and tennis racquets are examples of the combination of polymers with glass fibers. Composite materials are used in the DoD because of their low weight and excellent properties, enabling the production of lighter weight and stronger vehicles, ships, and structures. Programs have been initiated to replace metallic components of HMMWV and other Army vehicles and naval ships with composite parts. Future classes of vehicles and ships will use significantly higher amounts of composite materials, making these vehicles lighter faster and more maneuverable. However, aspects of these technologies have an adverse effect on the environment. Fabrication of composite materials produces volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions. Sources of pollution from these materials include disposal of hazardous polymer ingredients, solvents used for viscosity reduction, gases evolved during and after processing, and disposal of contaminated scrap materials (Sands, et al., 2001).

The Environmental Protection Agency (EPA) has established regulations limiting the amount of VOCs, HAPs, and heavy metals that can be used in composite materials under the National Emissions Standards for Hazardous Air Pollutants (NESHAP). This regulation established facility wide emissions limits, which make compliance through low emissions materials desirable before 2008. Reactive diluents in vinyl ester (VE) and unsaturated polyester (UPE) resins, such as styrene and

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methyl methacrylate, are used to reduce the resin viscosity to enable liquid molding. However, these diluents are VOCs and HAPs. Typical commercial resins contain 40-60 wt% styrene. There are some low HAP varieties that contain as little as 33 wt% styrene, such as Derakane 441-400. However, the viscosity and fracture properties of such resins are poor. Therefore, DoD facilities would need to implement add-on control devices to capture volatile emissions from composite processing in order to use the high performance commercial resins. Considering the number of current and future DoD sites using composite resins, the cost of implementing these add-on facilities is prohibitive (Vallone, 2004). The alternatives would be to use more expensive epoxy resins (approximately three times more expensive) or to reduce the usage of composites in the DoD, making it difficult to realize the initiative to make a lighter, faster, and more maneuverable military.

An obvious solution to reducing VOC/HAP emissions from composite resins is to simply reduce the reactive diluent content. There are a number of problems with this approach. First, the resin viscosity increases exponentially as the diluent content is decreased, making it difficult to use liquid molding techniques to produce the composite part. High viscosity is why thermoplastic materials, such as polycarbonate, cannot be used to a large extent in composite manufacture. In addition, properties such as the strength and toughness decrease significantly as the diluent content is reduced. Lastly, reducing the styrene content increases the cost of the resins because vinyl ester/unsaturated polyester monomers typically cost approximately double the amount of inexpensive diluents like styrene.

Various petroleum-based monomers with lower volatilities have been used as styrene replacements, such as vinyl toluene (Smeal and Brownell, 1994). However, these styrene replacements still produce significant emissions, and are therefore still regulated by the EPA (EPA, 2003). In addition, few monomers yield resins with performance comparable to styrene-based resins, and even fewer can match styrene's low cost.

Vapor suppressants have been used to reduce emissions from vinyl ester resins. These suppressants are typically a surfactant or paraffin wax that segregates to the air interface and reduces the styrene evaporation rate (Lacovara, 1999). Unfortunately, these suppressants also tend to segregate to the resin-fiber interface, which decreases fiber-matrix adhesion and the mechanical properties of the composite.

Another possible solution is to trap the VOC/HAP emissions during resin processing, composite production, and painting applications. These trapping devices need to absorb most of the VOC/HAP emissions and then

efficiently remove the emissions from the air before exhausting to the atmosphere. Trapping devices fail in two major aspects. First, their use is not feasible in the production of large-scale structures or in field repair. Large-scale structures are typically fabricated outside or in covered shelters, and building a device to trap a significant portion of the emissions is cost prohibitive. Secondly, although these devices remove the VOCs/HAPs from the atmosphere, the workers are still subject to the emissions and the health risks they pose.

Vinyl ester resins and unsaturated polyesters resins are being used in various military platforms and are being evaluated for use in additional platforms. Vinyl ester composites are excellent candidates for making parts for tactical vehicles, planes, and other structures. Their low weight and high performance translates into better fuel economy and greater durability relative to metal parts. Furthermore, VE and UPE repair resins are regularly used by the military. The current resins used for the applications will no longer meet EPA regulations within a few years. Because the use of these resins is integral to the development of a lighter, faster, and more maneuverable military, it is imperative to develop low VOC/HAP resins for the military applications.

Together ARL and Drexel University have developed low HAP vinyl ester and unsaturated polyester resin systems that would allow DoD facilities to continue manufacturing VE resins using current practices and facilities, while reducing pollution and health risks. These resins reduce HAP content in composite resins by using fatty acid monomers as styrene replacements and using bimodal molecular weight distributions of vinyl ester monomers to maintain high performance while using low styrene/HAP contents.

2. RESIN TECHNOLOGY

Typical commercial vinyl ester and unsaturated polyester resins contain 40-60 wt% styrene or other reactive diluents. These resins will not be emissions compliant under the EPA regulations. Commercial industry has developed low HAP resins with ~33 wt% styrene, such as Derakane 441-400 and Reichhold Hydrex 100, which are NESHAP compliant for most composite fabrication applications. However, the fracture toughness and viscosities of these resins are poor and unacceptable for most military uses. ARL/Drexel has developed a solution for making NESHAP compliant resins with excellent resin and polymer performance. These resin use fatty acid monomers (Palmese, et al., 2005) as a reactive diluent to replace all but ~20 wt% of the styrene HAP in the VE or UPE resin (La Scala, et al., 2004). The solution, which is in the process of being patented (Palmese, et al., 2005), involves replacing

conventional reactive diluents with plant oil derived monomers to reduce the styrene content in these resins.

Triglycerides are the main component of oils derived from plant and animal sources. Triglycerides are three fatty acids connected by a glycerol center. Triglycerides are simply broken down into fatty acids using industrial processes, such as saponification. A number of synthetic routes have been established by ARL/Drexel for making fatty acid-based monomers (Palmese, et al., 2005). The methacrylated fatty acid (MFA) monomer has proven to be the best fatty acid monomer for composite production. MFA monomers are produced through a simple addition reaction of the carboxylic acid of fatty acids with the epoxide group of glycidyl methacrylate to form a single product within a few hours at reaction temperatures ranging from room temperature to 80°C (Fig. 1). Each MFA contains one terminal polymerizable unsaturation site per molecule. In this way, the fatty acid monomers act as chain extenders, analogous to styrene, in VE resins. The resulting monomers have fairly high molecular weight and are non-volatile, making them excellent alternatives to styrene in liquid molding resins. Furthermore, these monomers promote global sustainability because they are made using a renewable resource. Due to the low cost of fatty acids and the simple modifications to produce fatty acid monomers, these monomers are inexpensive, with an estimated cost only slightly above that of styrene. Numerous fatty acids have been used to make MFA monomers. The molecular structures of the fatty acids used do have an effect on the polymer and resin properties. The resin viscosity decreases and polymer properties increase as fatty acid chain length decrease, but cost is also a factor. Methacrylated lauric acid (MLau) monomers represent a balance of these factors, as they have good resin and polymer properties, and low cost. Methacrylated octanoic acid (MOct) monomers are more expensive than MLau monomers, but have lower viscosity and polymer properties. Although plant oils have been used to make polymers for years, the use of fatty acid monomers as reactive diluents is a novel concept (Palmese, et al., 2005).

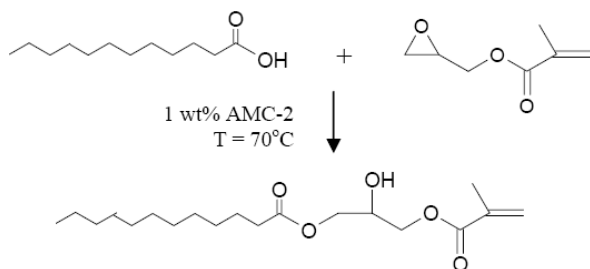


Fig. 1: Reaction scheme to produce MFA monomers.

Ideally, all of the styrene in vinyl ester and unsaturated polyester resins could be replaced with fatty

acid-based monomers; however, the resulting resin and polymer properties are poor relative to commercial resins. Therefore, rather than completely replacing styrene with fatty acid monomers, styrene was partially replaced with the fatty acid monomers. Styrene contents ranging from 10 wt% to 25 wt% (50-80% reduction in VOC/HAP content relative to commercial resins) were used resulting in good resin and polymer properties. In fact, thermogravimetric analysis results showed that the fatty acid monomers are not volatile and resins formulated with these monomers produce far less emissions (Fig. 2).

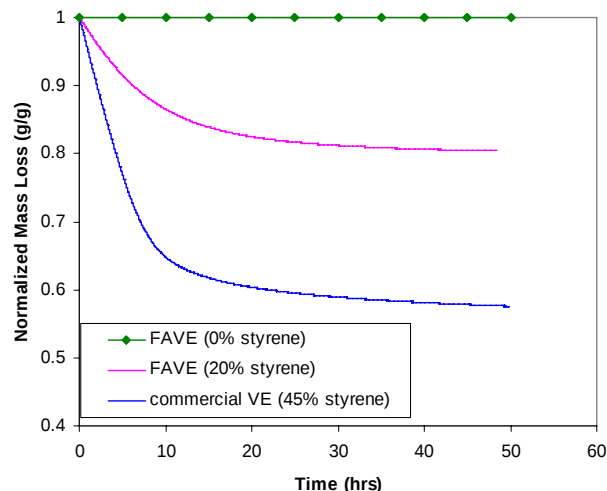


Fig. 2: Thermogravimetric analysis of commercial resins and the fatty acid vinyl ester resins (FAVE) showing that the commercial resins have significantly more mass loss because only the styrene component evaporates.

3. DEMONSTRATION PLATFORMS

In this work, the low HAP fatty acid vinyl ester resins (FAVE) will be tested for its ability to replace commercial high HAP vinyl ester resins in four different military applications. These applications are shown in Figure 3 and represent Army, Marines, Navy, and Air Force applications.

Marines Ballistic Helmet Hardtop for HMMWV

The Marines have been using a non-ballistic HMMWV hard-top for communications platforms that was developed with the Amtech Corporation. Amtech has over 12 years production experience with this part. However, there has been a recent need for added ballistic protection and a new process method. Along with Amtech, the University of Delaware Center for Composite Materials (CCM) recently developed and demonstrated a ballistic helmet HMMWV hardtop. The part exceeds all ballistic and structural requirements and has a relatively low cost. The CCM also improved the process design by making it a vacuum infusion process to reduce emissions. However, the part uses Derakane 8084 as the matrix resin, which is a toughened vinyl ester

containing 40 wt% styrene. Because this resin does not meet NESHAP requirements, this would be an excellent demonstration of the environmentally friendly FAVE technology. Furthermore, because of the high toughness of these low VOC replacements and good properties, we expect successful development of this low VOC/HAP HMMWV ballistic hardtop. Switching to the FAVE resins will enable this process to meet the NESHAP regulations and will reduce styrene HAP use ~1800 lbs/month.

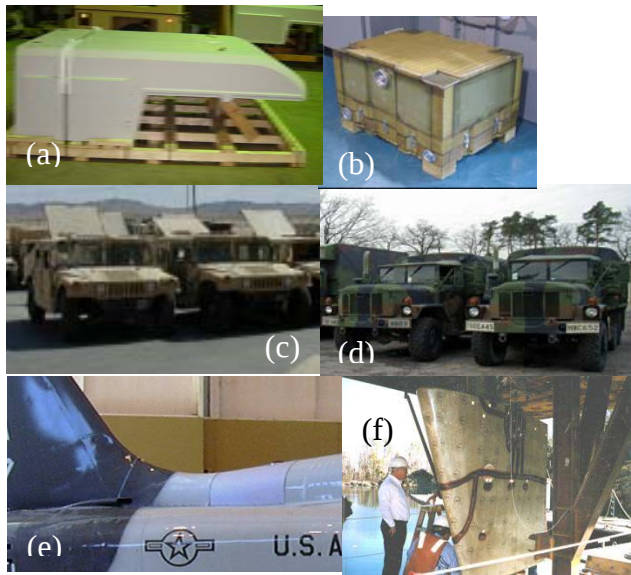


Fig. 3: ARL/Drexel low HAP resins are being demonstrated for (a) HMMWV ballistic hardtop, (b) a HMMWV transmission container, composite replacement hoods for (c) HMMWV, or (d) M35A3, and (e) T-38 dorsal cover, and (f) MCM composite rudder.

Replacement Parts for Army Tactical Vehicles

The CCM has developed composite replacement hoods for the M35 truck along with Sioux Manufacturing Corp. (SMC) and replacement HMMWV hoods with TPI Composites. The SMC HMMWV hoods fracture and fatigue very quickly due to soldiers standing and jumping on them while in battle, or doing surveillance, or maintenance. A few years ago, during a recap/reset, the M35 received a new drive train. Unfortunately, the new power train did not fit within the existing hood. The steel hood was cut, spacer plates were added, and all the parts were riveted back together to fit the new engine. Unfortunately, this led to high corrosion rates of the hood, requiring significant maintenance work. The CCM vacuum infused M35A3 hood and HMMWV hood solved the problems associated with the previous hood designs and have excellent performance. Both hoods use vinyl ester or epoxy resin as the matrix and meet all load, cyclic loading, flexural, thermal, and impact properties. The current vinyl ester resin used has a high styrene content. Using the FAVE resin instead would enable this process to meet NESHAP regulations and reduce styrene

HAP usage in tactical vehicle hoods by ~7000 lbs/month, while meeting all structural and performance requirements.

HMMWV transmissions are shipped into theater using foam and cardboard shipping containers. Due to the poor structural properties of these shipping materials, the transmissions are often damaged during shipping. In most cases, the transmissions are return-shipped from theater on base wood pallets, which further exposes them to significant damage. Red River Army Depot (RRAD) has explored the use of metal shipping containers, but corrosion issues and the maintenance required makes this route unfeasible. The CCM has recently developed a Derakane 8084-based shipping container to meet all of the packaging requirements to prevent transmission damage during shipment. These containers meet the strength, impact, and thermal requirements. Again, using the FAVE resin will make this process NESHAP compliant and will reduce styrene use by 400 lbs/month.

Air Force T-38 Dorsal Cover

An avionics upgrade, which converted 400 aircraft to T-38 "C" model, included a "glass cockpit" and added GPS capability with GPS antenna attached to the dorsal cover. During installation of the GPS antenna many of the dorsal covers were found to be damaged. Some minor damage is repairable but some covers have damage that is beyond repair, so these covers need to be replaced. Spare cover supply was exhausted; no covers can be ordered because they are no longer manufactured, and no tooling is available for new manufacture.

The Advanced Composites Office (ACO) designed and procured tooling for use during repair and remanufacture of T-38 dorsal covers. The part is produced using vacuum assisted resin transfer molding and similar materials to the original dorsal covers; glass fabrics, room temperature processing with vinyl ester or epoxy resins. The current vinyl ester resins used contain high styrene contents and do not meet NESHAP regulations. However, the low HAP ARL/Drexel resin offer an inexpensive drop-in replacement solution to this problem.

NSWCCD Composite Rudder

NSWCCD developed the composite rudder as a solution to the cavitation problems that quickly cause severe damage to metallic rudders. The far smoother composite design allows for much higher speeds before cavitation occurs. Furthermore, removal of paint during cavitation in metal systems accelerates corrosion rates to compound the problem, while this is not the case for composites systems that have negligible corrosion rates. The composite rudder has been manufactured on a small scale for use on the Mine Counter Measure (MCM) ship, and deployed after successful full-scale shock test. PMS

490, John Edwards, reported that “the composite rudder on MCM-9 is looking good after 5+ years on the ship,” and he would like all MCM class rudders to be the same composite design.

The composite twisted rudder (CTR) was designed to minimize cavitation/erosion problems associated with standard rudders. This rudder designs allow for even higher speeds before cavitation occurs. However, the twisted design is difficult to fabricate in steel and the composite version weighs significantly less. The intent for this low HAP rudder is to use it on Navy Destroyers DDG 103-109. If this rudder is successful for DDG, a similar design and the same materials will be used for the future class of Destroyers, DDX. The low VOC/HAP resin developed by ARL/Drexel should be a drop-in replacement for current vinyl ester resins used for the production of the rudder and significantly reduce VOC/HAP emissions that could affect the fabrication and repair of composite rudders for the Navy through the NESHAP regulations.

4. EXPERIMENTAL PROCEDURE

The initial work required for validating the low HAP resins was that we match FAVE resin formulation properties as closely as possible to that of the commercial resins for the given applications. Derakane 8084 is a toughened vinyl ester resin containing over 40 wt% styrene, and is currently used in the HMMWV hardtop and all Army applications. Corezyn Corve 8100 is a high styrene content resin (50 wt%) and is currently used in the production of the composite rudder. Hexion Specialty Chemicals 781-2140 is used in the T-38 dorsal cover.

A number of FAVE formulations have been developed. The FAVE-L resin uses 65% Bisphenol A vinyl ester monomer, 20 wt% styrene, and 15 wt% methacrylated lauric acid (MLau). FAVE-O resin is the same formulation, but uses methacrylated octanoic acid (MOct) instead of the MLau. FAVE-L25 and FAVE-O25 are similar to FAVE-L and FAVE-O, but use 25 wt% styrene and only 10 wt% fatty acid monomer. These formulations were developed to further reduce the viscosity of FAVE resins. Lastly, the formulation FAVE-O-HT with a high glass transition temperature (T_g) was developed that uses 51% Novolac, VE 14% Bisphenol A VE, 25 wt% styrene, and 10% MOct. The Novolac component was used to improve the T_g .

Acid number of the MFA monomers and resins was measured in accordance with ASTM D1980-87 to determine the amount of unreacted free acid in the system. Nuclear magnetic resonance spectroscopy (NMR) was run to ensure that no epoxy functionality was remaining in the fatty acid monomer and that the

VE, styrene, and MFA concentrations were within 2% of what was required. Viscosity was measured using a TA instruments AR2000 rheometer in steady shear flow experiments. The shear rate was increased from 1 s^{-1} to 3000 s^{-1} and then decreased back to 1 s^{-1} , and 10 measurements were taken per decade. At a given shear rate, the shear stress was measured every two seconds. The shear rate and viscosity were recorded when the shear rate stabilized to within 5% tolerance for three consecutive points.

To cure the resins, cobalt naphthenate (CoNap) was used to promote room temperature breakdown of the initiator, Trigonox 239A, which initiated free radical polymerization of the resin. Neat resin panels were prepared for the FAVE resins and commercial resins using 0.375 wt% CoNap and 1.5 wt% Trigonox. Composite panels were prepared with the fibers used in the various demonstration articles and the FAVE and commercial resins. Composites were prepared using the vacuum assisted resin transfer molding (VARTM) process and cured using 1 wt% Trigonox and ~0.2 wt% CoNap. All composite panels used E-glass fibers but had different fabric weights, fiber orientations. 3-Tex 54 oz and 96 oz fibers were used for Army and Marines applications. Fibre Glast Developments Corporation Style 120 3 oz E-glass and Style 7781 E-glass 9 oz fabric are used in the dorsal cover, and an 18 oz unidirectional fiber with stitched mat from Fiber Glass Industries is used in the rudder.

The thermo-mechanical properties of vinyl esters were measured using dynamic mechanical analysis (DMA). Rectangular samples with approximate dimensions of 25 mm x 9 mm x 3 mm were tested using a TA Instruments 2980 DMA in single cantilever geometry. The samples were tested at 1 Hz with a deflection of 15 μm while ramping the temperature from 30°C to 200°C at a rate of 2°C/min. Three temperature ramp experiments were run for each sample. The first ramp completely post-cured the polymer, as verified using infrared spectroscopy. Furthermore, the DMA traces for the second and third ramps were nearly identical, showing that the resulting polymers are thermally stable at least for limited durations up to 200°C. The temperature at which the peak in the loss modulus occurred in the fully post-cured polymer was considered the glass transition temperature of the material (Nielsen and Landel, 2004).

Flexural tests, in accordance with ASTM 790M, were performed to determine the modulus of elasticity and flexural strength. The samples had approximate dimensions of 10 mm x 80 mm x 64 mm and were measured prior to testing. The samples were tested flat-wise on a support span, resulting in a support-to-depth ratio of 16. All tests were performed at ambient

conditions, which were approximately 22°C and 40% relative humidity. The samples were tested using an Instron at a crosshead speed of 0.17 mm/min. The flexural modulus, elongation at failure, and flexural strength were calculated according to the ASTM standard.

Short beam shear tests were performed to determine the shear strength of the composites in accordance with the ASTM D2344-84. Rectangular samples with width-to-thickness and length-to-thickness ratios of 2 and 7, respectively, were tested using an Instron 4505. The samples were tested flat-wise with a span-to-depth ratio of 5 at a crosshead rate of movement of 0.05 in/min.

5. RESIN DEMONSTRATION AND VALIDATION

These low HAP resin formulations were prepared for DoD use by Applied Poleramics, Inc. The fatty acid monomer and resin were prepared in 5 gallon batches. Each resin batch was rigorously tested to ensure it met required specifications. As such, the monomer and resin viscosities were measured and found to be lower than 80 cP and 1200 cP at 25°C, respectively. The acid number was measured to determine the concentration of free acid and was found to be below 20 and 10 for the MFA and FAVE, respectively. NMR showed that there was no epoxy functionality remaining in the fatty acid monomer, and that the VE, styrene, and MFA concentrations were within 2% of what was required.

Current results are very promising. The viscosities of Derakane 8084 and Derakane 441-400 were approximately 1000 cP at 25°C, as were the viscosities of FAVE-L and FAVE-O (Fig. 4). On the other hand, Corve 8100 had a significantly lower viscosity of 600 cP, which was similar to that of FAVE-O25 (650 cP) and FAVE-L25 (700 cP). The viscosity of the FAVE-O-HT was 800 cP, and intermediate of the commercial resins.

The T_g of the Derakane 8084 and Corve 8100 neat resins were approximately 120°C, which was quite similar to that of the FAVE-L, FAVE-O, FAVE-L25, and FAVE-O25 (Fig 5). The Derakane 8084 had a significantly higher T_g of 135°C. The FAVE-O-25HT had an even higher T_g of 145°C. The T_g of the composites for these resins were slightly higher than that of the neat resins, but had the same trends. The strength and modulus were nearly identical for the resins and composites of the low HAP FAVE resins relative to the commercial resins. The neat resin strengths were approximately 130 MPa and moduli were ~3.5 GPa. Composite properties were dependent of fabric type, but had similar properties for all resin types. Furthermore, the short-beam shear strength, which measures fiber-matrix adhesion, was dependant on the fabric type, and

was on the order of 30-100 MPa. However, for the same fabric type, the short beam shear strength differed by 5% or less from one resin formulation to another.

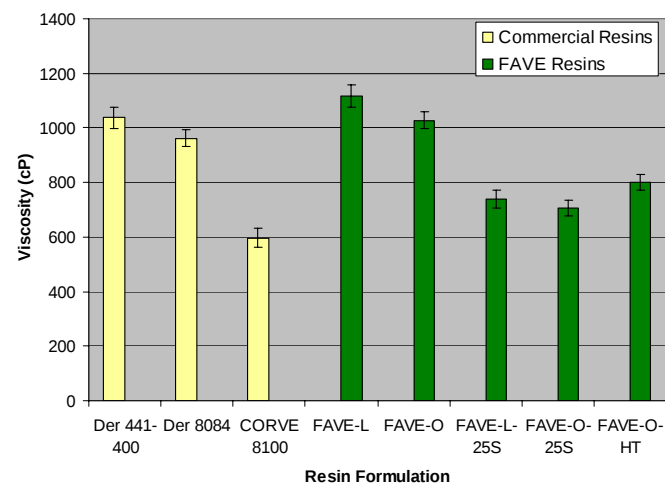


Fig. 4: The viscosity of the fatty acid-based vinyl ester formulations and commercial resins used in this work.

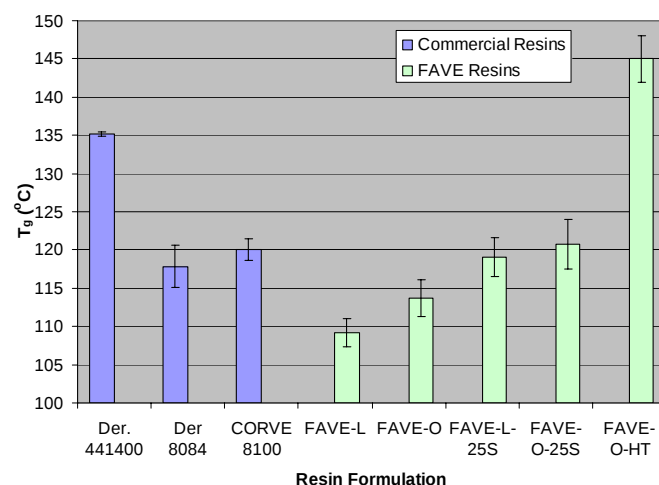


Fig. 5: T_g for the fatty acid-based vinyl ester formulations and commercial resins used in this work.

These results indicate that the low HAP FAVE resins can likely be used to replace the high HAP commercial resins used in various military applications. If higher viscosities can be tolerated for the HMMWV transmission container, T-38 dorsal cover, and composite rudder, the FAVE-L resin will be an appropriate replacement. If not, the FAVE-L25 should provide the appropriate properties. The FAVE-O formulations have slightly improved T_g and viscosities, and could be used for the above applications if slightly better performance is required. The Army truck hood applications and the Marines HMMWV hardtop require a high performance resin with excellent thermal properties. As such, the

FAVE-O-HT would be an excellent candidate to replace the Derakane 8084 and Derakane 441-400.

For all application, the properties and performance of panels and full-scale parts (Fig. 3) will soon be rigorously tested to properly demonstrate this alternative resin technology. As such, various properties will be measured, including wet and dry T_g , stiffness, modulus, strength, and short beam shear strength will be measured for composites fabricated using the low HAP resins relative to composites made using the commercial resins. These properties will be measured at all partner locations to reduce bias.

It was demonstrated that the FAVE resin can be used to make large scale parts (Fig. 6). An M35A3 hood was fabricated using this resin, as well as a hat-stiffened structure for DD(X) advanced sail program. The resin did an excellent job of wetting the fibers and produced qualitatively good parts. However, for this program, much more rigorous testing is required.



Fig. 6: (a) M35A3 hood and (b) hat stiffened structure for Advanced Sail Program and DDX prepared using FAVE-L resin.

In addition, the HMMWV ballistic hardtop will be demonstrated/validated at APG to ensure it meets the required ballistic performance criteria. Basically, small round fire should not penetrate the hardtop according to existing Marines requirements. In addition, the hardtop must undergo full mobility testing on a HMMWV, as well as a minimum 3000 mile off-road durability test to ensure its structural integrity.

For the truck hoods, the ability of these structures to withstand static load, cyclic load, high service temperatures, and impact will be demonstrated to simulate the forces the structure would be exposed to in

the field. A custom designed and built test fixture at the CCM (previously used to test the HMMWV and M35A3 hood designs) will be used to validate the performance of M35A3 and/or HMMWV hoods. In the static load experiments, a 250 lb weight will be placed over a 3" x 3" area at the center of the hood to simulate a soldier standing on the hood. The hood is required to deflect no more than 0.25" at -50°F and 0.5" at 250°F. The impact resistance will be quantified by dropping a 2 lb chrome plated steel ball with 2-3/8" diameter from six feet onto the hood. The ball will be dropped on six different locations to ensure toughness across the structure, as only insignificant cosmetic damage is considered acceptable. The flexural properties must be such that an upward force of 50 lbf at the right and left corners will not cause any damage to the part and not result in greater than 0.5" deflection. The structure must withstand cyclic load of 50 lbf at the left and right corner handles in an alternating fashion for 8 hrs at 10 cycles per minute. These tests simulate a lifetime of lifting the corners of the hood. The durability requirement is for the hood to resist all damage from a 250 lb force downward at the center of the hood, followed by 100,000 cycles at 1 cycle per second to simulate a cyclic soldier load on the hood for the lifetime of the vehicle.

The transmission container will be tested to validate the structure for field use. Critical tests will simulate impact, low service temperatures, and assembly, cargo, and storage loads typical during fielding. The box will be tested under static load conditions to determine the load that it can take before permanently deforming. In addition, stock test, drop tests, and "drag" tests will be performed.

These manufactured parts will be demonstrated under field conditions at RRAD for durability and the performance of the parts will be assessed. The ability of the parts to withstand damage during operation will be measured relative to current parts used in tactical vehicles. After fielding, CCM will re-measure the mechanical performance of the parts to assure that the required performance has been maintained.

The T-38 dorsal cover will be validated at Hill Air Force Base. The dorsal cover will be attached to the T-38 just as the original dorsal cover is attached. The plane/part will be fielded to study the effects of fielding on structural integrity and performance. Specifically, the damage as a function of time will be compared to the standard vinyl ester dorsal covers and their ability to shield electronics from the environment will be assessed.

The low HAP rudder will be tested in the same manner previous MCM composite rudders have been tested. This testing includes resistance to flexing, torsion, and impact damage. The test fixtures are located

at Structural Composites, Inc. (SCI), and will be tested by SCI in conjunction with NSWCCD. If successful, full scale low HAP composite rudders will be produced and delivered to the Navy for a two year at sea evaluation.

6. CONCLUSIONS

Low HAP fatty acid vinyl ester resins have properties similar to that of commercial vinyl ester resins, while producing ~50% less emissions. Current testing has also shown that these resin formulations could be appropriate replacements for the commercial high HAP vinyl ester resins used in the Marines HMMWV helmet hardtop, Army tactical vehicles, T-38 dorsal cover, and the MCM composite rudder. However, full scale testing using the low HAP fatty acids-based resins must be completed before these resins can be validated for these applications.

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REFERENCES

- Environmental Protection Agency, 2003: National Emission Standards for Hazardous Air Pollutants: Reinforced Plastic Composites Production, *Federal Register*, **68**, 19375-19443.
- La Scala, J.J., Sands, J.M., Orlicki, J.A., Robinette, E.J., and Palmese, G.R., 2004: Fatty Acid-Based Monomers as Styrene Replacements for Liquid Molding Resins, *Polymer*, **45**, 7729-7737.
- Lacovara, B., 1999: Reducing Emissions with Styrene Suppressants, CFA.
- Nielsen, L.E. and Landel, R.F., 1994: *Mechanical Properties of Polymers and Composites*, Marcel Dekker: New York, pp. 140-142.
- Palmese, G.R., La Scala, J.J., and Sands, J.M. 2005: Fatty Acid Monomers to Reduce Emissions and Toughen Polymers, U.S. Patent Application, 60/569,379.
- Sands, J.M., Fink, B.K., McKnight, S.H., Newton, C.H., Gillespie, J.W., and Palmese, G.R., 2001: Environmental Issues for Polymer Matrix Composites and Structural Adhesives, *Clean Products and Processing*, **2**, 228-235.
- Smeal, T.W. and Brownell, G.L., 1994: Laminating Resins Having Low Organic Emissions, U.S. Patent 5,292,841.

Vallone, J, 2004: NESHAP Requirements Assessment for Miscellaneous Coatings, Adhesives, Sealers, Etc., *Final Report to ARL, Sustainable Painting Operations for the Total Army*.



Demonstration of Military Composites with Low Hazardous Air Pollutant Contents

John J. La Scala, Ph.D.

U.S. Army Research Laboratory
Multifunctional Materials Branch

APG, MD 21005-5069

jlascala@arl.army.mil

Phone: 410-306-0687

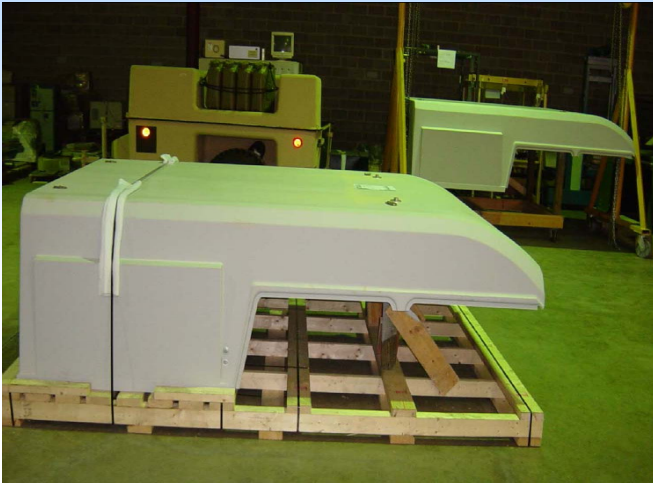
Fax: 410-306-0829



Army Science Conference - 2006



Demonstrations



HMMWV ballistic hardtop



HMMWV transmission container



M35A3 hood



HMMWV hood



T-38 dorsal cover



MCM composite rudder

Acknowledgements

- **Army Research Laboratory**
 - J.M. Sands, Terri Glodek, Caroline Glodek, Phil Myers, Felicia Levine, Kevin Andrews, Daniel De Bonis, R.E. Jensen, M. Maher



- **Drexel University**
 - Palmese research group



- **CCM, University of Delaware**
 - S. Anderson, M. Logan, N. Shevchenko, A. Quabili
 - Jack Gillespie, Wool Research Group



- **NSWC, Carderock Division**
 - R. Crane



- **Advanced Composite Office, Hill AFB and Air Force Research Lab**
 - Larry Coulter, Ken Patterson, Lt. Eric Uhle



- **Applied Poleramics, Inc – Rich Moulton**

- **Funding**
 - SERDP PP-1271, ESTCP WP-0617

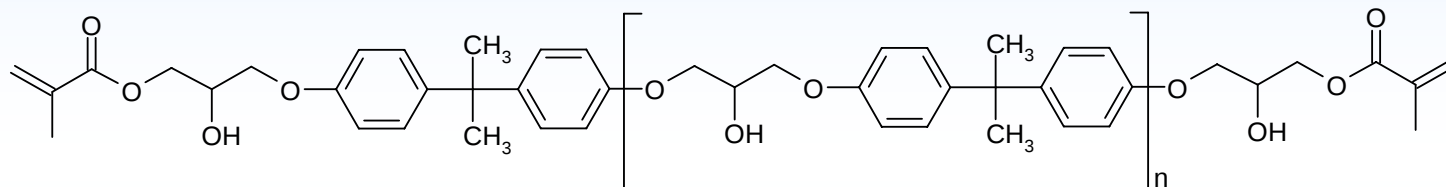
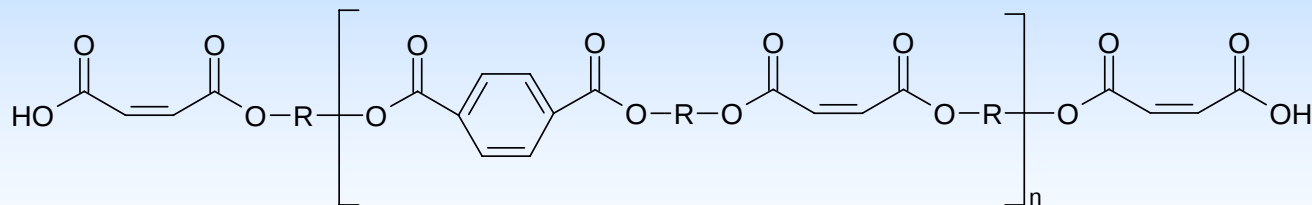


Outline

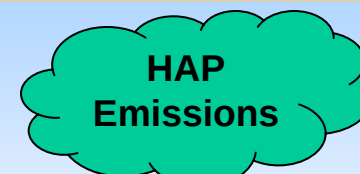
- **Reducing HAP emissions from composite resins**
- **Demonstration Platforms**
- **Validation of Resin Production and Neat Resin Properties**
- **Validation of Composite Properties**

UPE and VE Resins

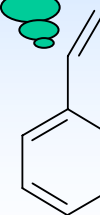
Unsaturated Polyester



Vinyl Ester



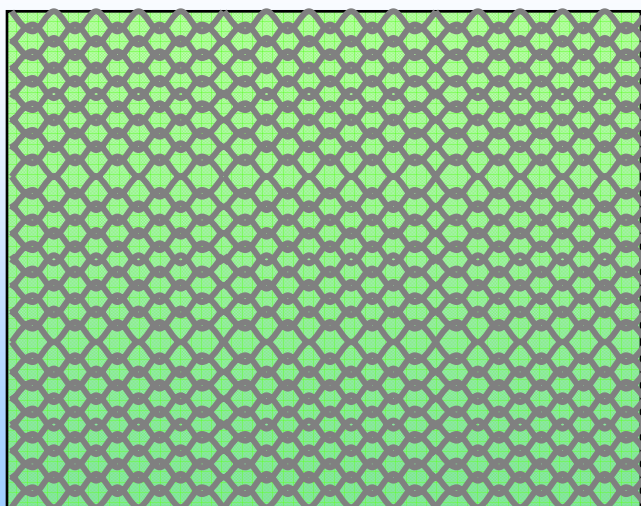
+



Styrene

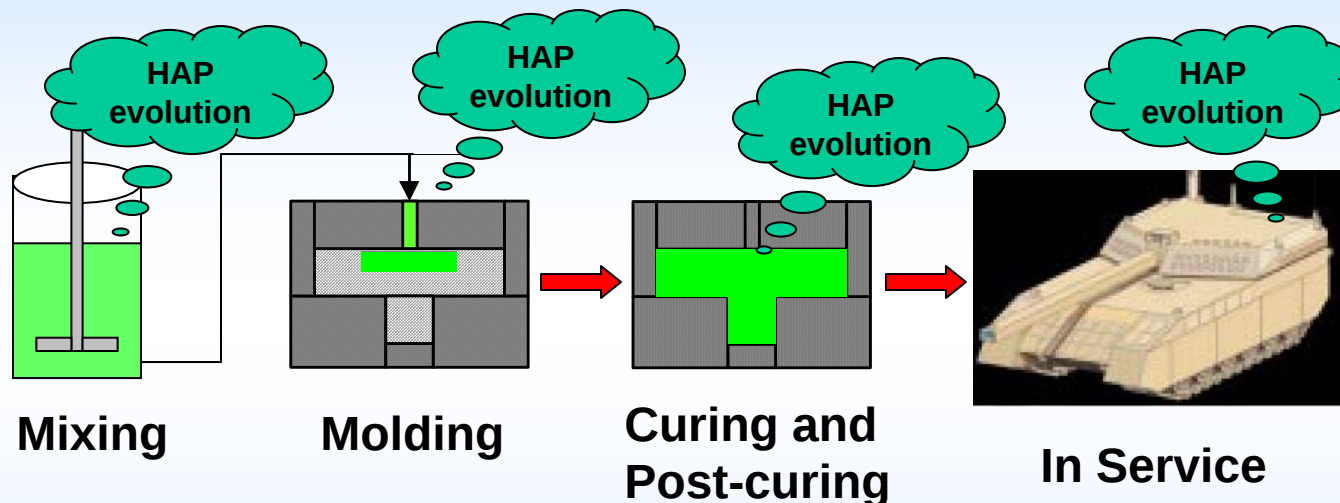
Initiator + Heat

Thermosetting
Polymer



VOC/HAP Emissions

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



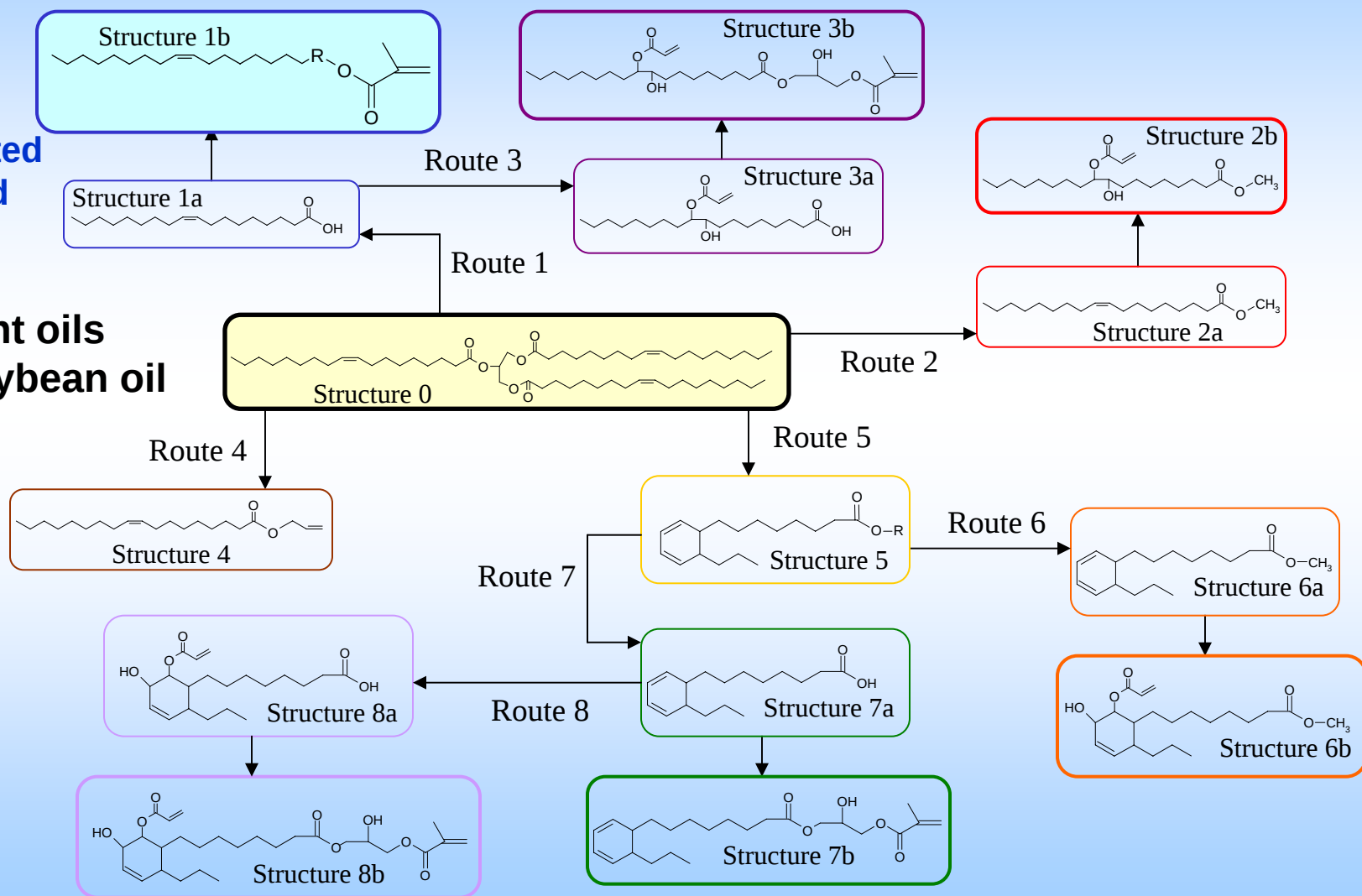
Composites industry consumes 9% of the styrene, but accounts for 79% of styrene emissions

- EPA - Reinforced Plastic Composites National Emissions Standards for Hazardous Air Pollutants (NESHAP)
 - Executed and legally enforceable as of April 28, 2003

Fatty Acid Based Monomers

(MFA)
Methacrylated
Fatty Acid

Plant oils
e.g. soybean oil



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

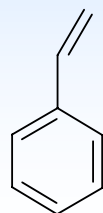
Fatty Acid Vinyl Ester Resins (FAVE)



Commercial Resins

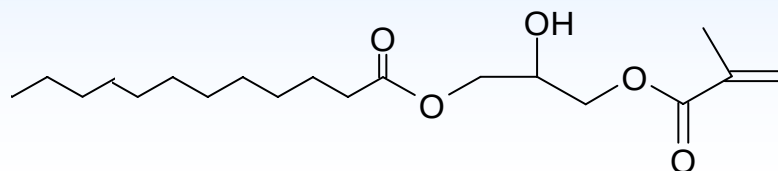
Low VOC ~ 33 wt% Sty

Standard ~ 40-50 wt% Sty



Styrene

10-20 wt%

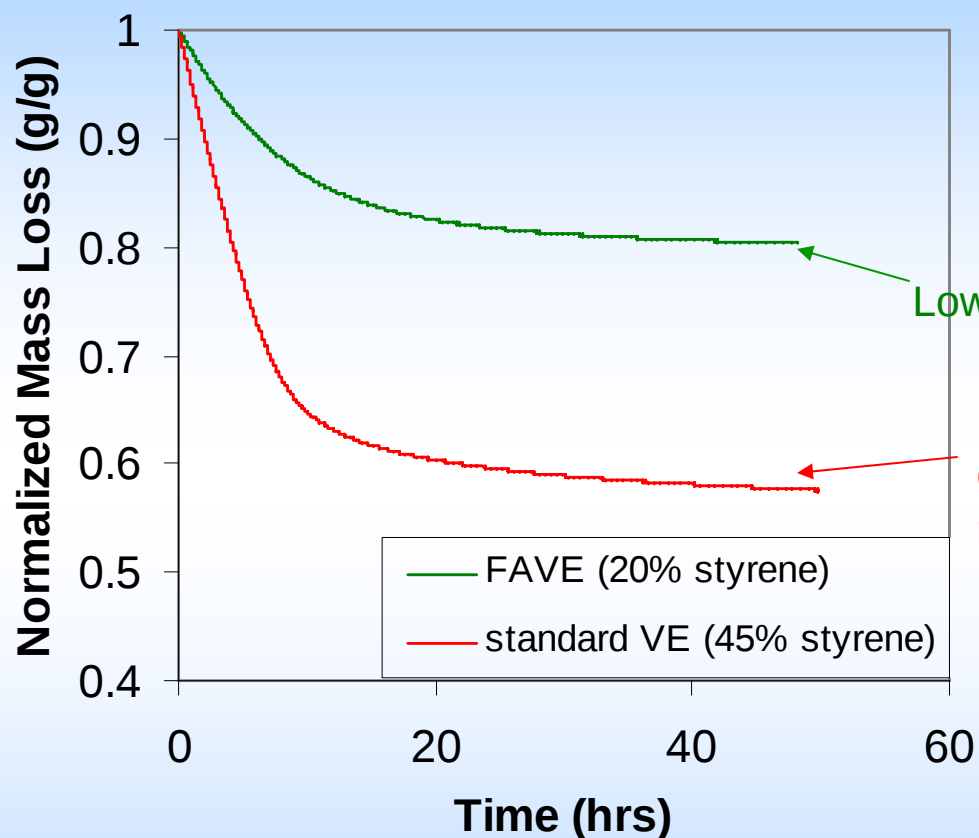


MFA – methacrylated
fatty acid

- **VE**
 - Bisphenol A
 - Novolac
- **MFA**
 - 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%



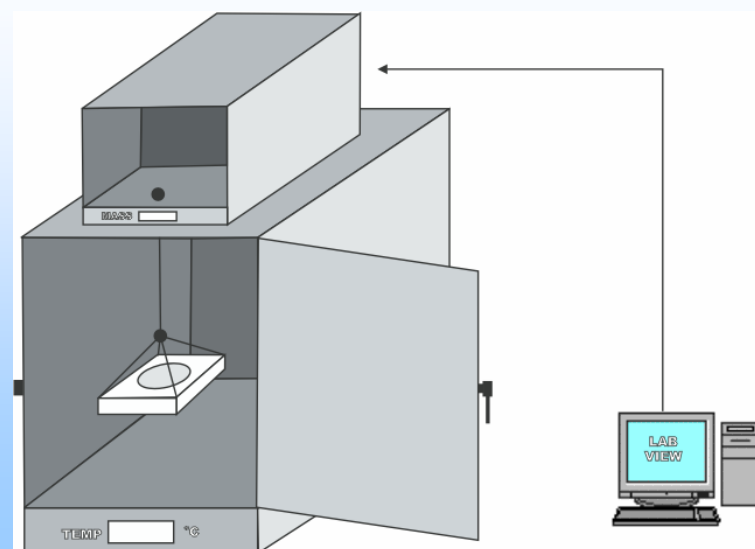
Low Volatile Contents



- Low VOC resin systems reduce emissions by **33-78%**

- MFA monomers themselves produce **no emissions**

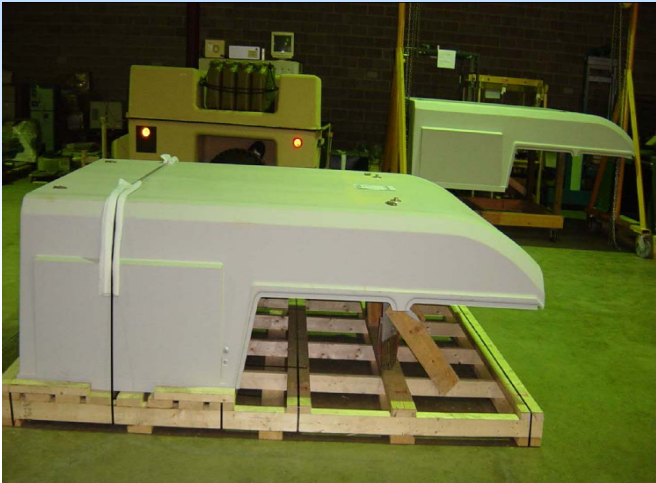
Macro TGA



Outline

- Reducing HAP emissions from composite resins
- **Demonstration Platforms**
- Validation of Resin Production and Neat Resin Properties
- Validation of Composite Properties

Demonstrations



HMMWV ballistic hardtop



HMMWV transmission container



M35A3 hood



HMMWV hood



T-38 dorsal cover

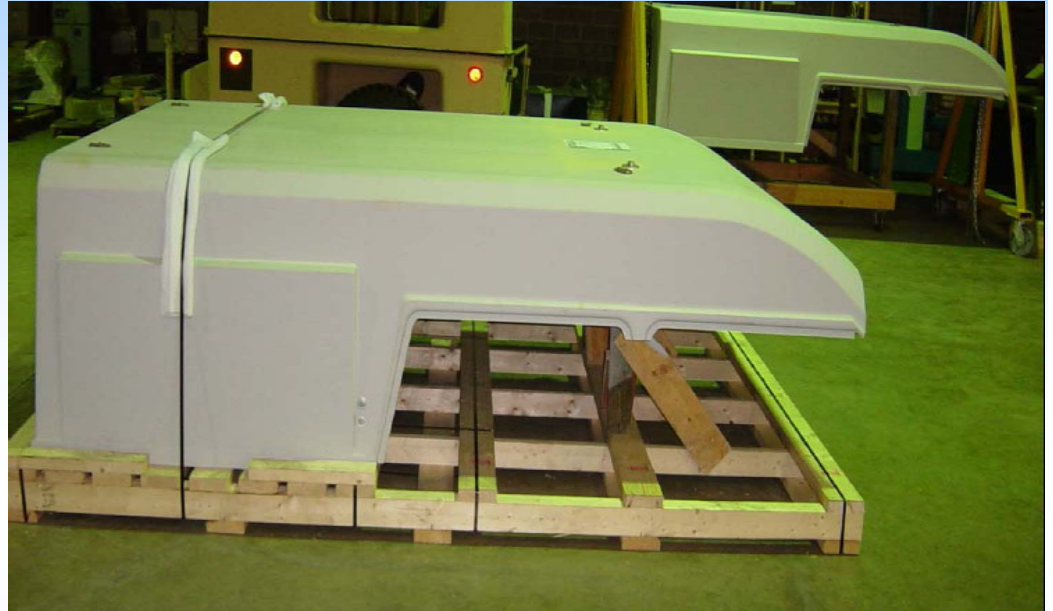


MCM composite rudder

Marines Demo: Amtech Ballistic Helmet Hardtop®

- Need for added ballistic protection and closed molding process
- New Ballistic Hardtop
 - 3-Tex materials (54 oz) used
 - Toughened Derakane 8084 vinyl ester resin (~40% styrene)

**Demonstrate/Validate low
VOC/HAP formulations for
HMMWV hardtop**



- Testing of demo
 - Meets demanding structural requirements
 - Exceeds all ballistic requirements
 - 3000 mile off-road durability

Army Demo: Tactical Vehicle Replacement Parts

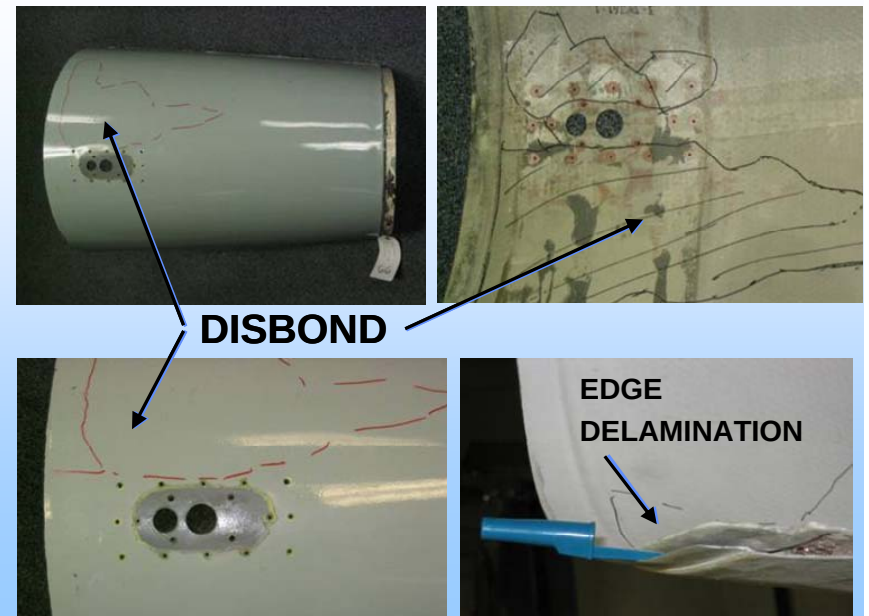
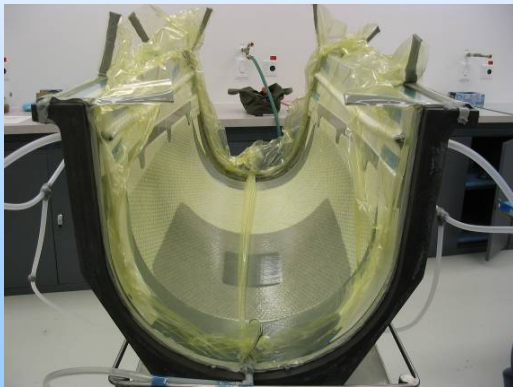
- Corrosion issues with M35A3
- SMC HMMWV hood has poor performance
- Transmissions damaged in shipment without good packaging
- Test demo parts
 - Flexural, impact, cyclic load, High T, etc.



Air Force Demo: T-38 Dorsal Cover

- 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**



Navy Demo: Rudders for MCM, DDG, and DDX

- **Straight rudder (MCM)**
- **Composite twisted rudder (CTR) – DDG and DDX**
- **Easier to fabricate and less cavitation than steel twisted rudders**
- **Composite rudder on MCM-9 has good success after 5 year fielding trial**

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



Benefit to the Soldier

- **Enable composite resins to meet EPA regulations**
- **Allows continued use of VE/UPE resins for the fabrication of current and future composites for the military**
 - **Lighter, faster, and more maneuverable**
 - **Less maintenance – less corrosion, higher durability**
 - **Improved design**

Navy Demo:

Rudders for MCM, DDG, and DDX

Application	Fabric	Resin	Resin Replacement
Amtech Helmet Hardtop	3-Tex 54 oz E-glass	Derekane 8084	FAVE-O
HMMWV Hood	Mahogany 24 oz E-glass	SMC	FAVE-O-HT
M35A3 Hood	3-Tex 96 oz E-glass	Epoxy/Derakane 441-400	FAVE-O-HT
Transmission Container	Mahogany 24 oz E-glass	Derekane 8084	FAVE-L
T-38 Dorsal Cover	Fibre Glast Developments Corp. 120 3 oz E-glass and Style 7781 E-glass 9 oz	Hexion 781-2140	FAVE-L
Rudder	Fiber Glass Ind. 18 oz E-glass	Corezyn Corve 8100	FAVE-L

- **Derakane 8084:** ~40 wt% styrene
- **Hexion 781-2140:** 47 wt% styrene
- **Corve 8100:** 50 wt% styrene
- **Derakane 441-400:** 33 wt% styrene (low HAP resin)
- **FAVE-L/FAVE-O:** 20 wt% styrene, L – Meth. lauric acid
O – Meth. Octanoic acid
- **FAVE-L(O)25S:** 25 wt% styrene
- **FAVE-O-HT:** 25 wt% styrene, Novolac VE

Outline

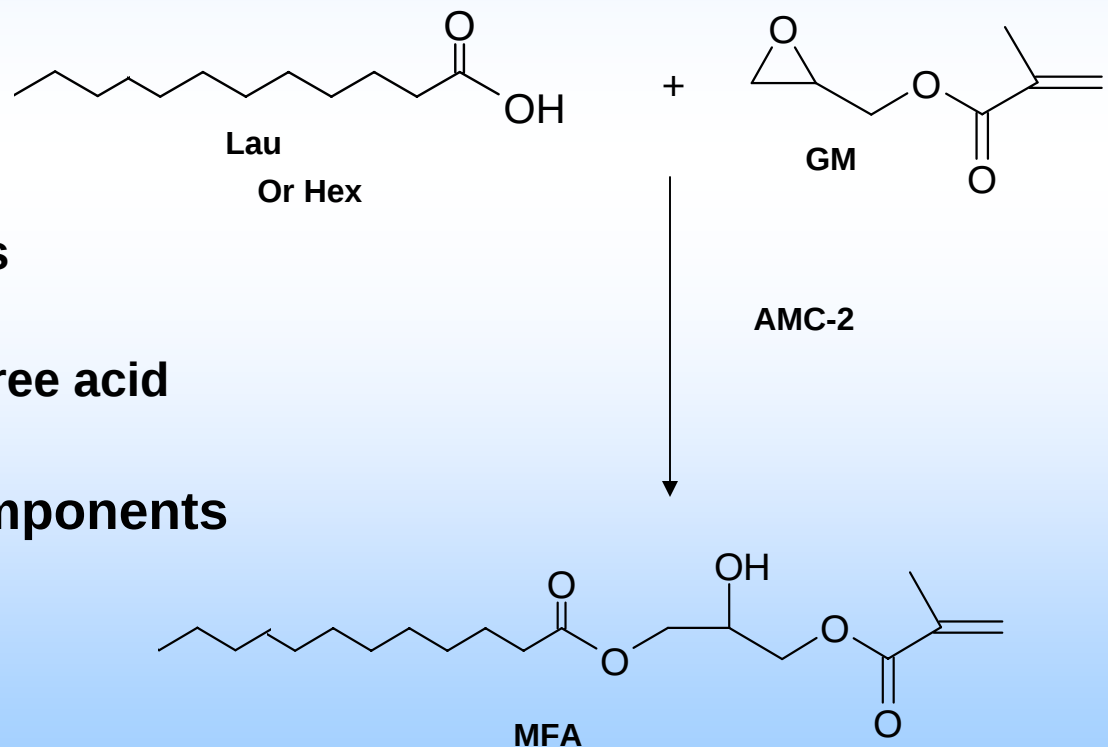
- Reducing HAP emissions from composite resins
- Demonstration Platforms
- **Validation of Resin Production and Neat Resin Properties**
- Validation of Composite Properties

Resin Validation

- Applied Poleramics, Inc. in Benicia, CA
 - Production of MFA monomers
 - Blending of VE, styrene, and MFA to produce resins

- **Must validate:**

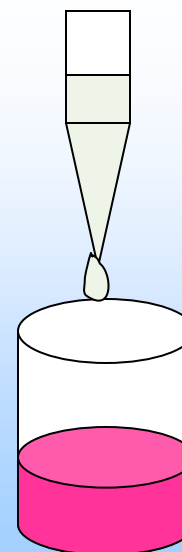
- MFA chemistry
 - No epoxy groups remaining
 - Low amount of free acid remaining
- Proper ratio of components



Acid Number

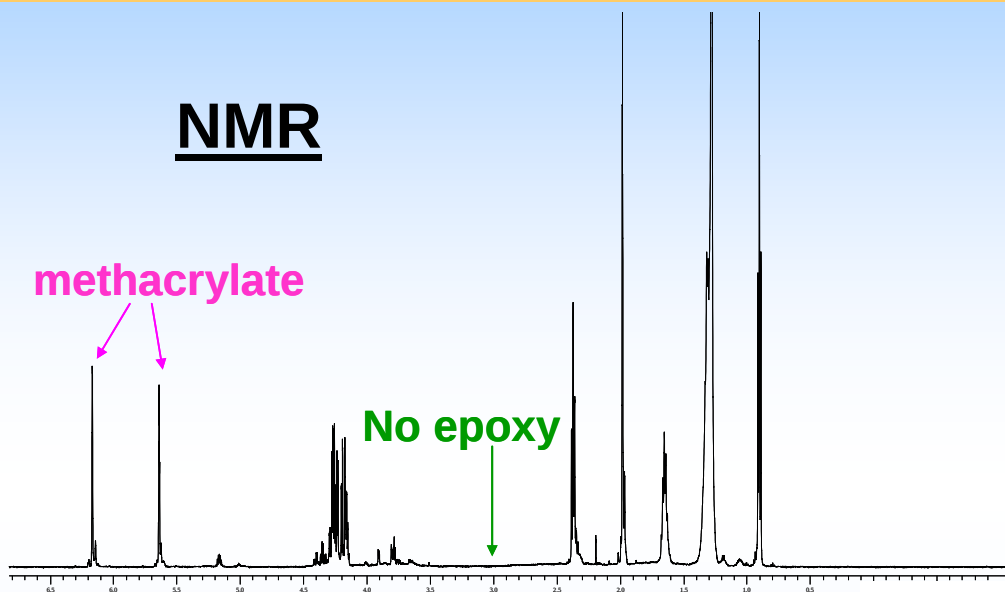
- To determine the amount of unreacted acid in the resin
- Acid number is mass of NaOH required to neutralize 1g of a substance
 - 1 gram of the resin was dissolved in 5 grams of acetone
 - Indicator: 2 drops of 0.5 wt% phenolphthalein in 50% ethanol
 - Titrated with 0.5 N sodium hydroxide
 - Endpoint: when the solution remained pink for 30 seconds

Material	Acid Number	Max Value
MLau	17.5	20
MOct	16.0	20
FAVE-L	8.8	10
FAVE-O	9.0	10

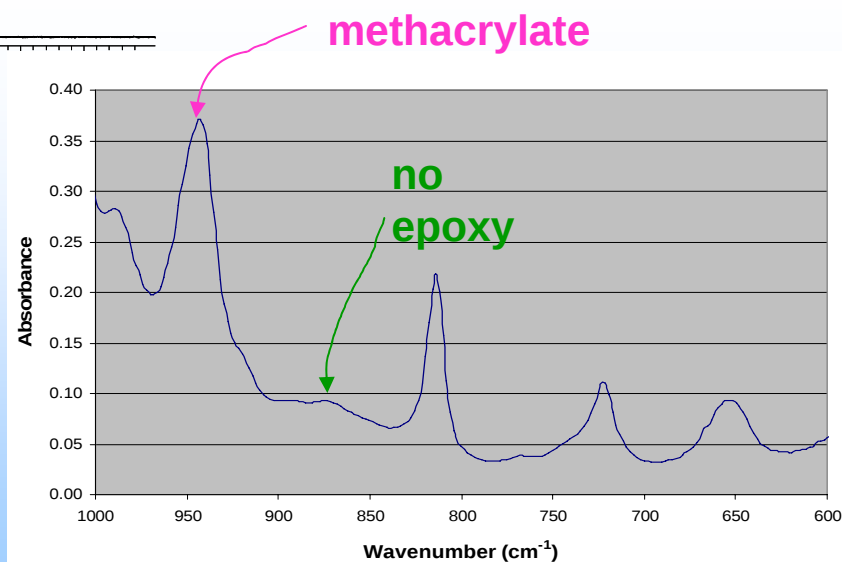


MFA Chemistry

NMR



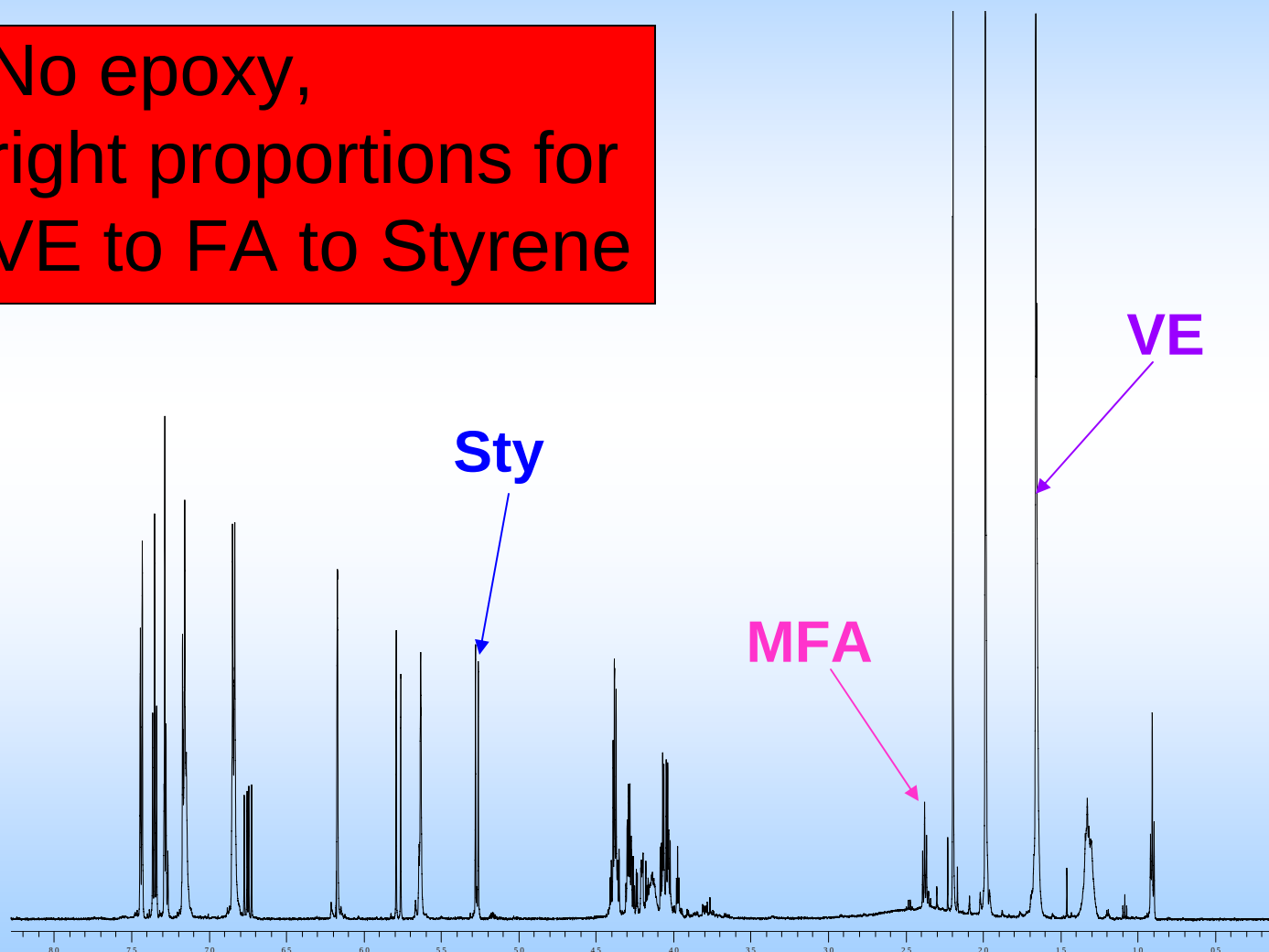
FTIR



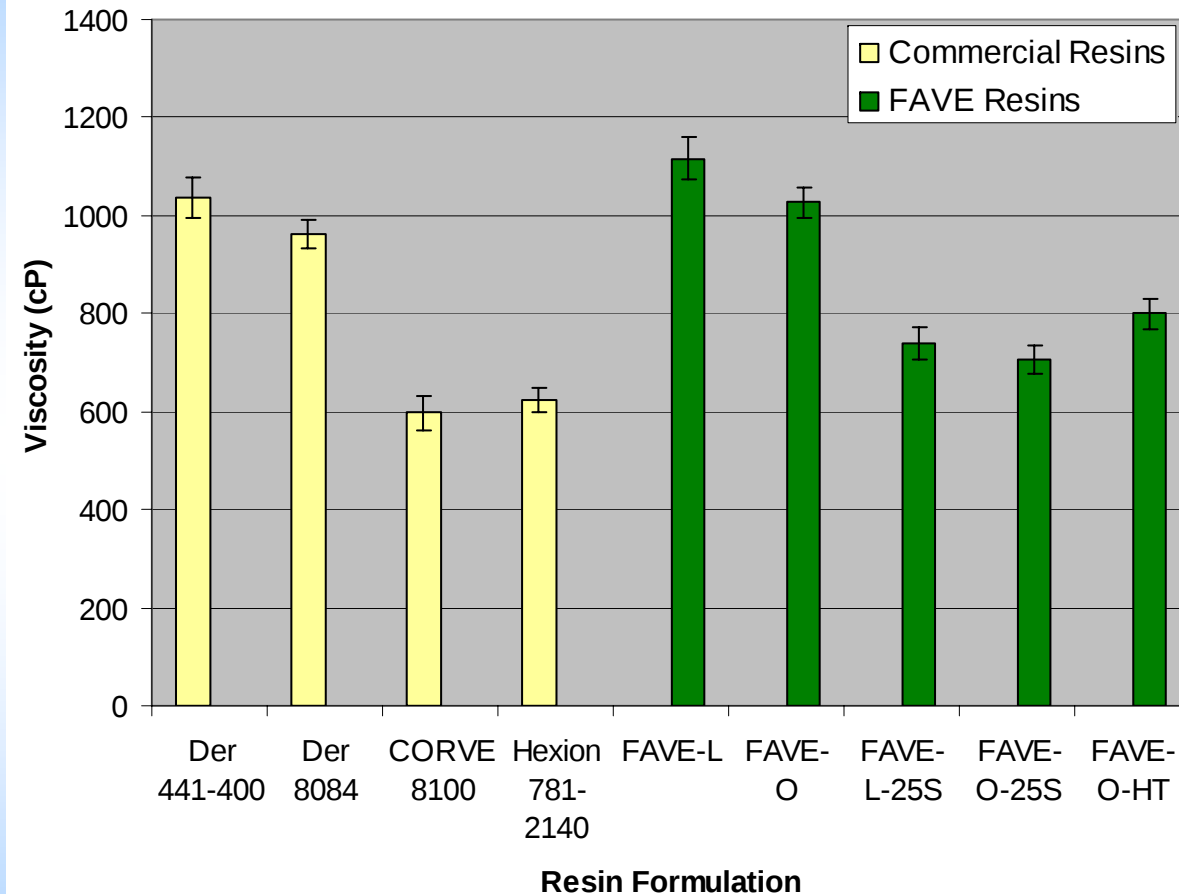
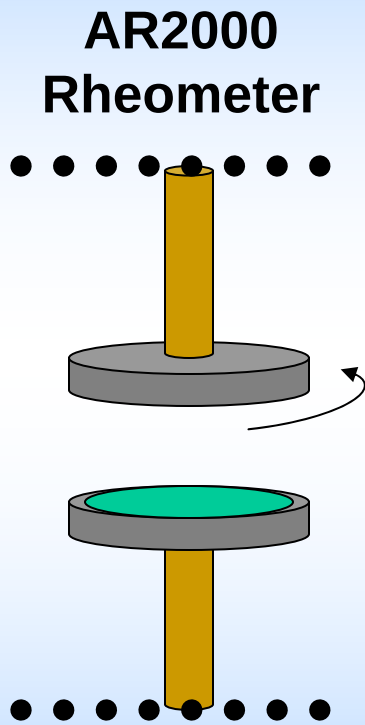
- No epoxy
- Good methacrylate peaks

H-NMR: Component Ratios

No epoxy,
right proportions for
VE to FA to Styrene

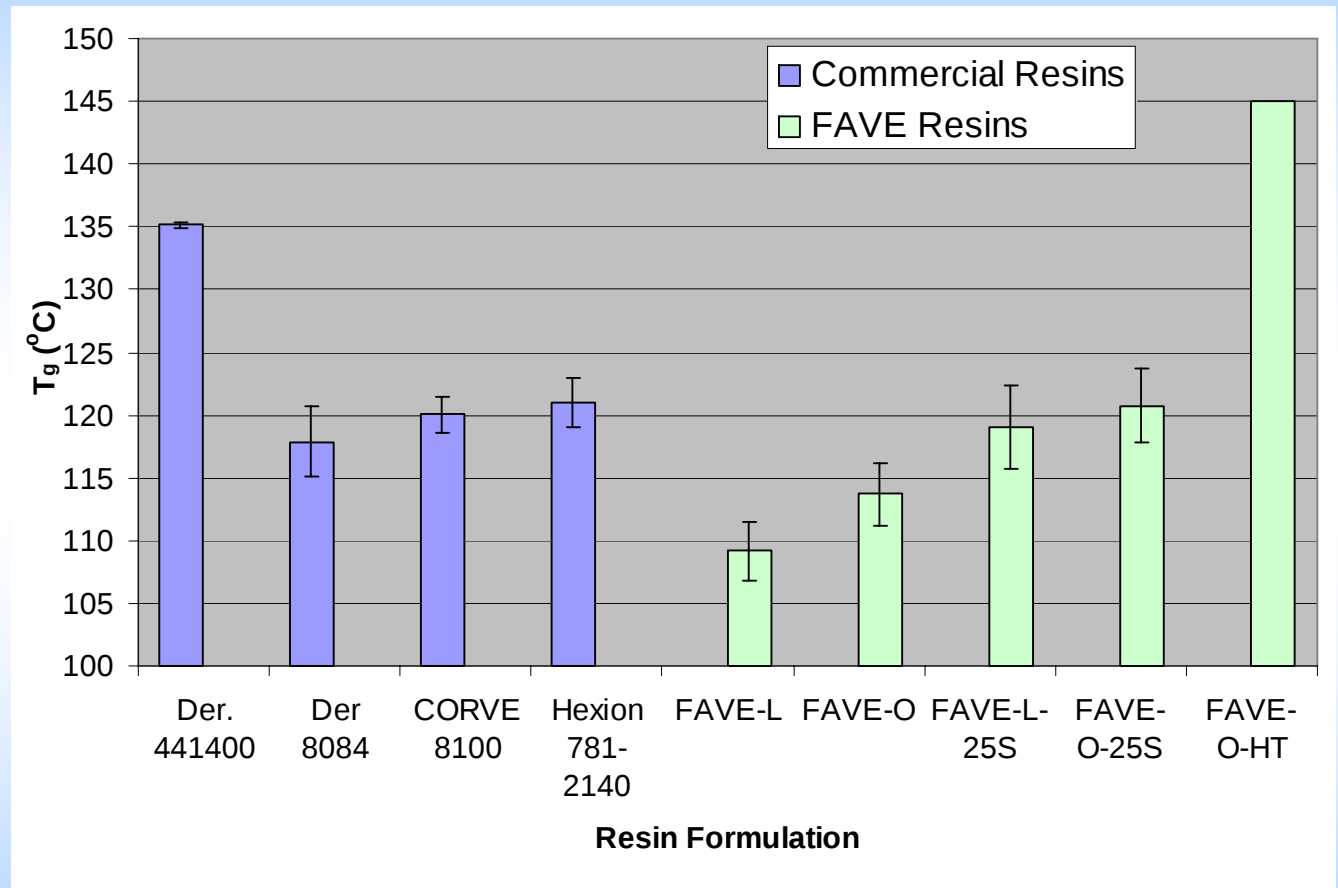
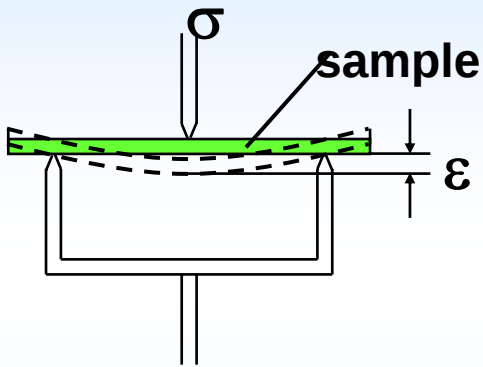


Neat Resin Properties - Viscosity



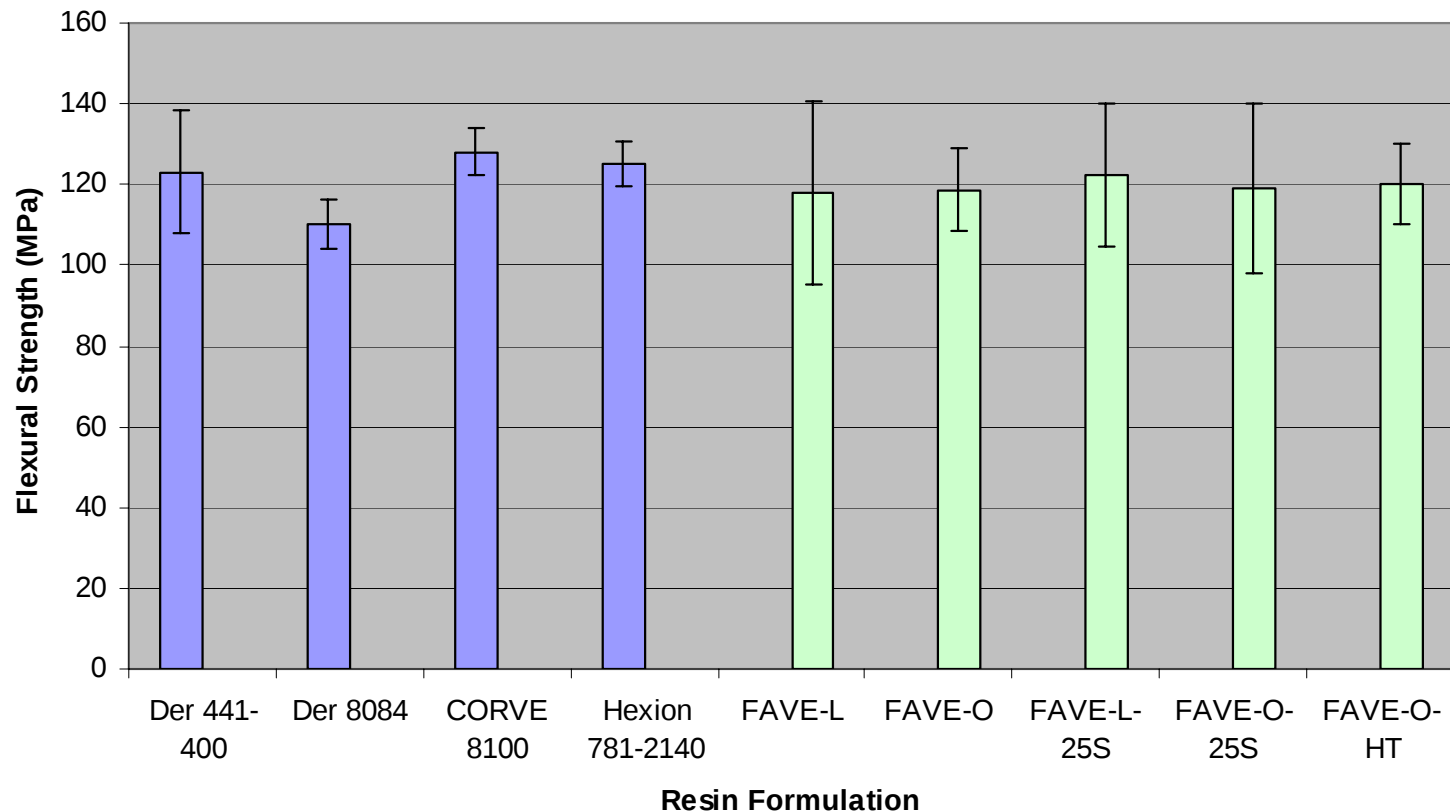
- Fatty acid resins have similar viscosity relative to commercial resins

Neat Resin Properties - Tg



- Fatty acid resins have similar T_g relative to commercial resins

Neat Resin Properties – Flexural



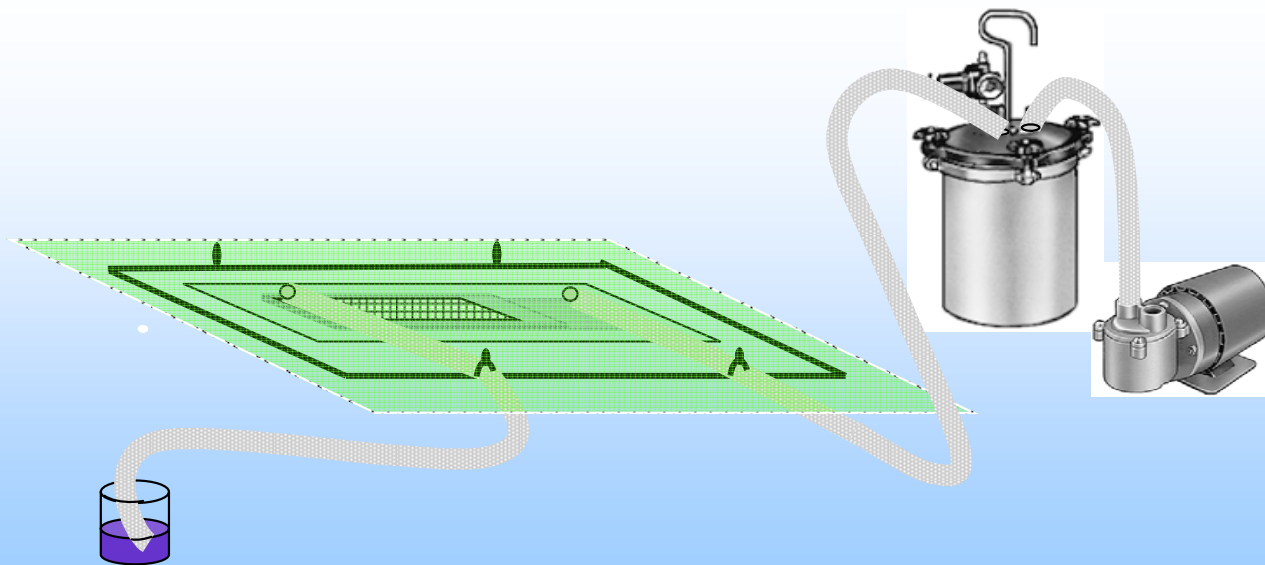
- **Modulus: 3.5 ± 0.2 GPa for all resins**
- **Fatty acid resins have similar strength and modulus relative to commercial resins**

Outline

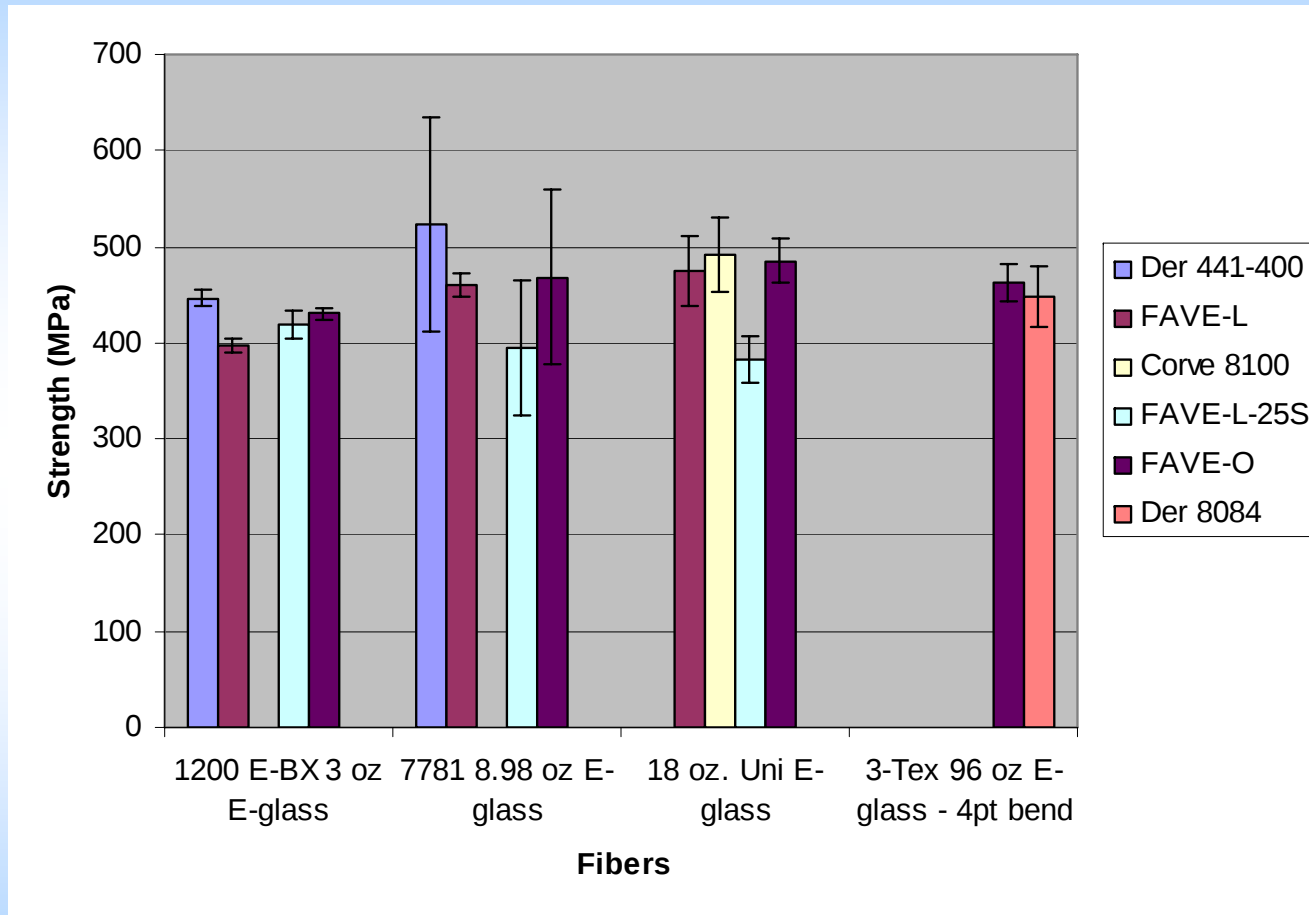
- Reducing HAP emissions from composite resins
- Demonstration Platforms
- Validation of Resin Production and Neat Resin Properties
- **Validation of Composite Properties**

Composite Manufacturing

- Vacuum Assisted Resin Transfer Molding (VARTM)
 - 12 in. x 12 in. x 1/8 in panels
 - Cured at room temperature using CoNap catalyst (0.1 wt%) and Trigonox initiator (1 wt%)
 - Post-cured for 4 hours at 120°C

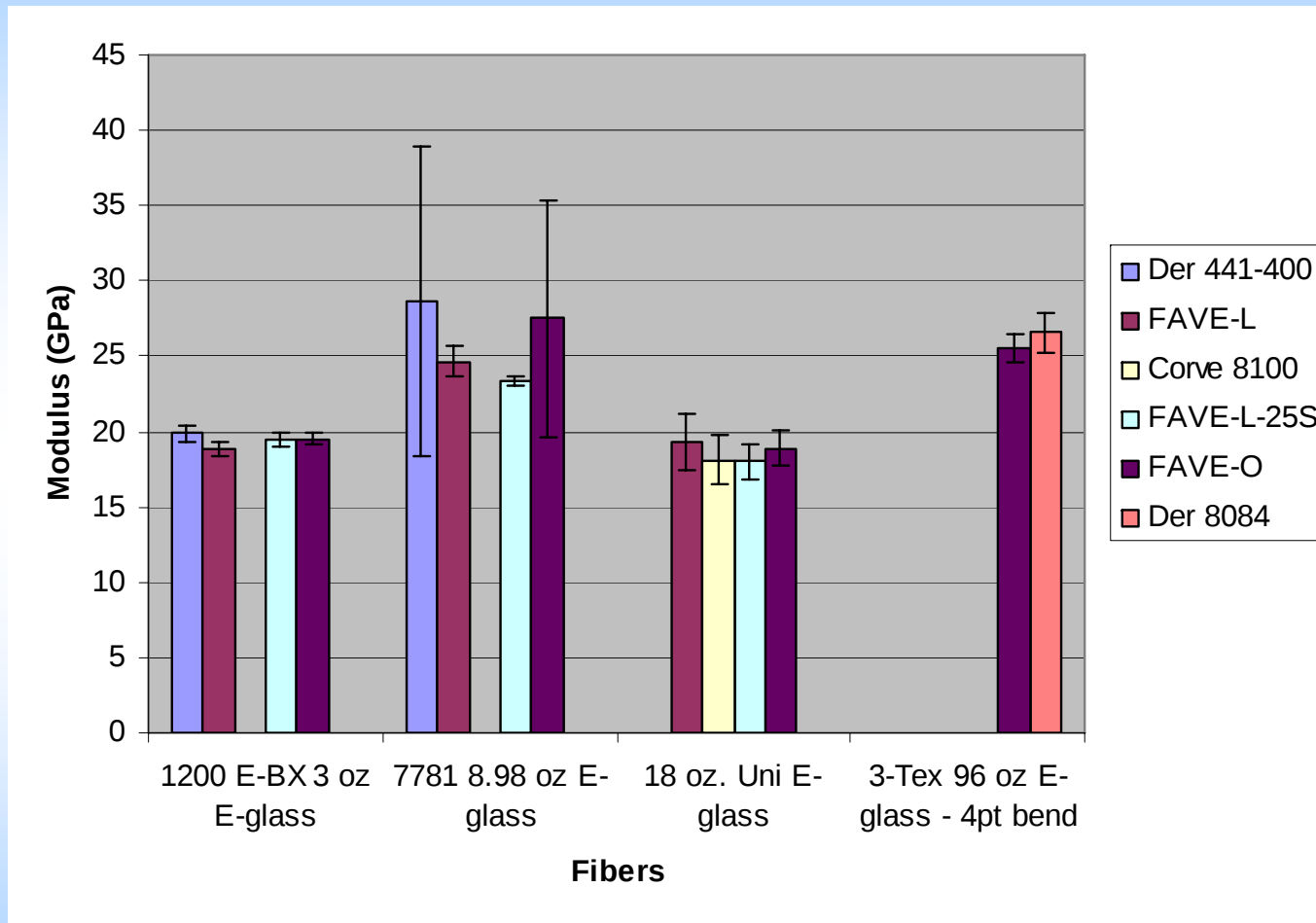


Composite Properties: Flexural Strength



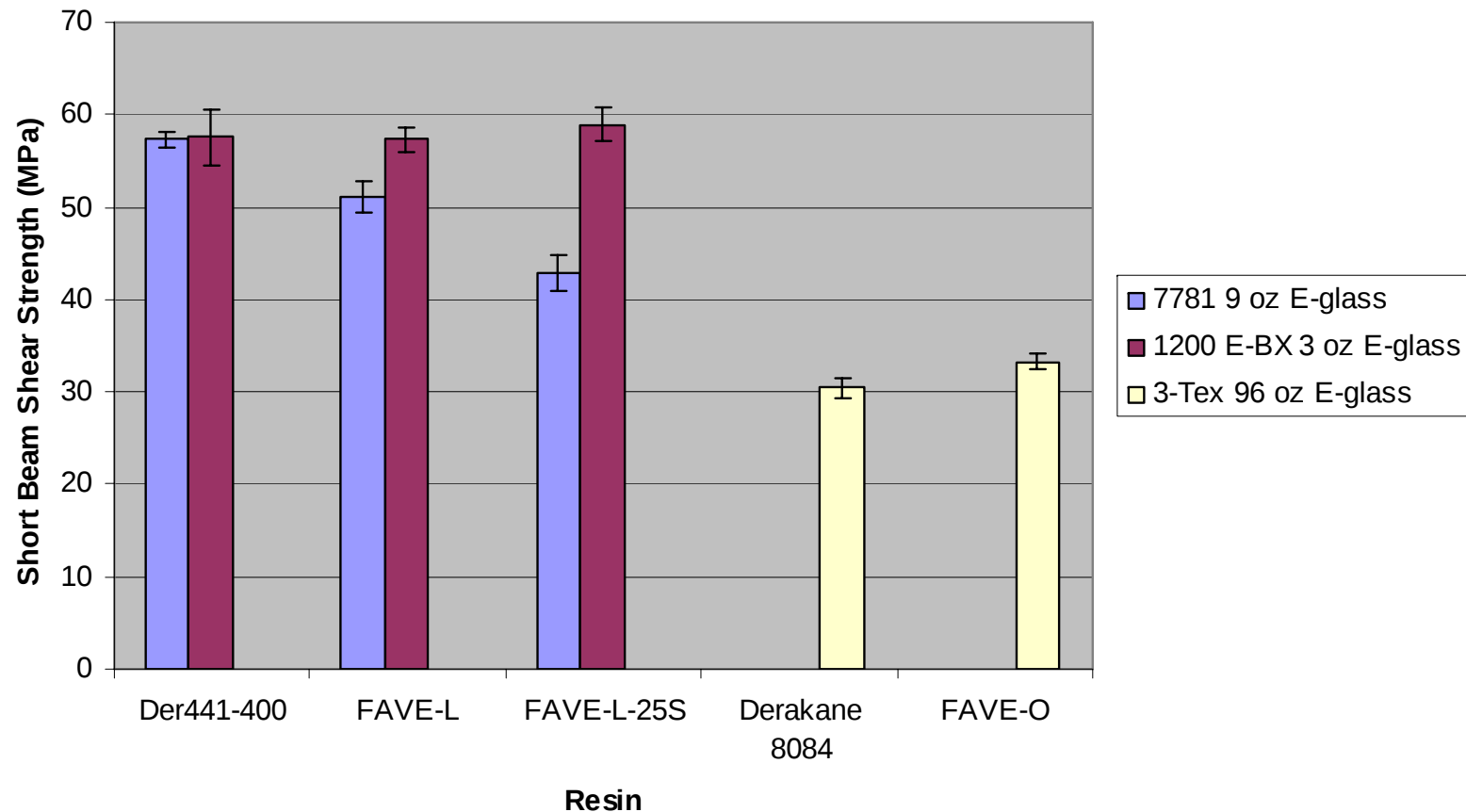
- Fatty acid resins have similar strength relative to commercial resins

Composite Properties: Flexural Modulus



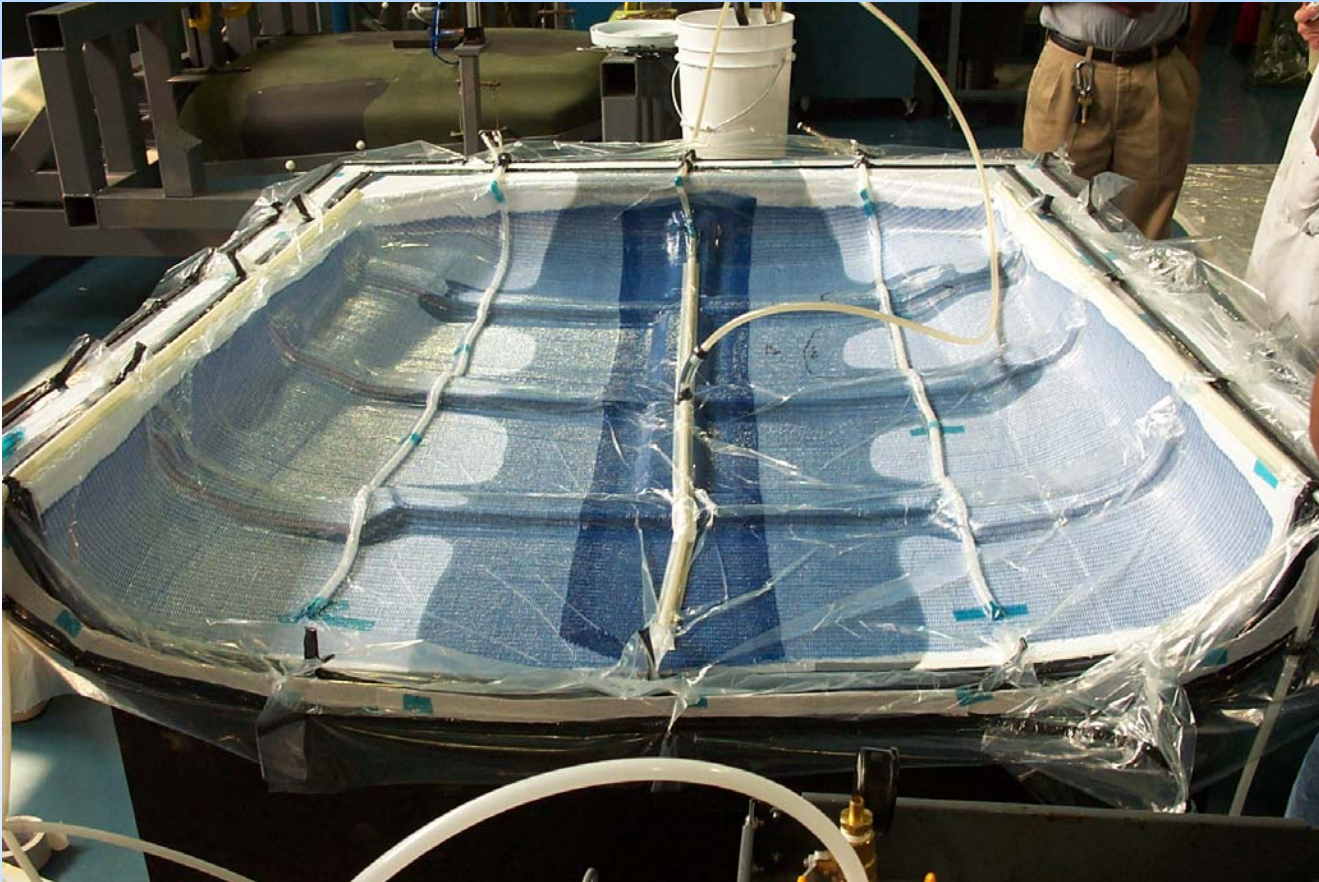
- Fatty acid resins have similar modulus relative to commercial resins

Composite Properties: Short Beam Shear



Short beam shear strength of FAVE and BMVE are similar or better than that of commercial resins.

Resin Infusion

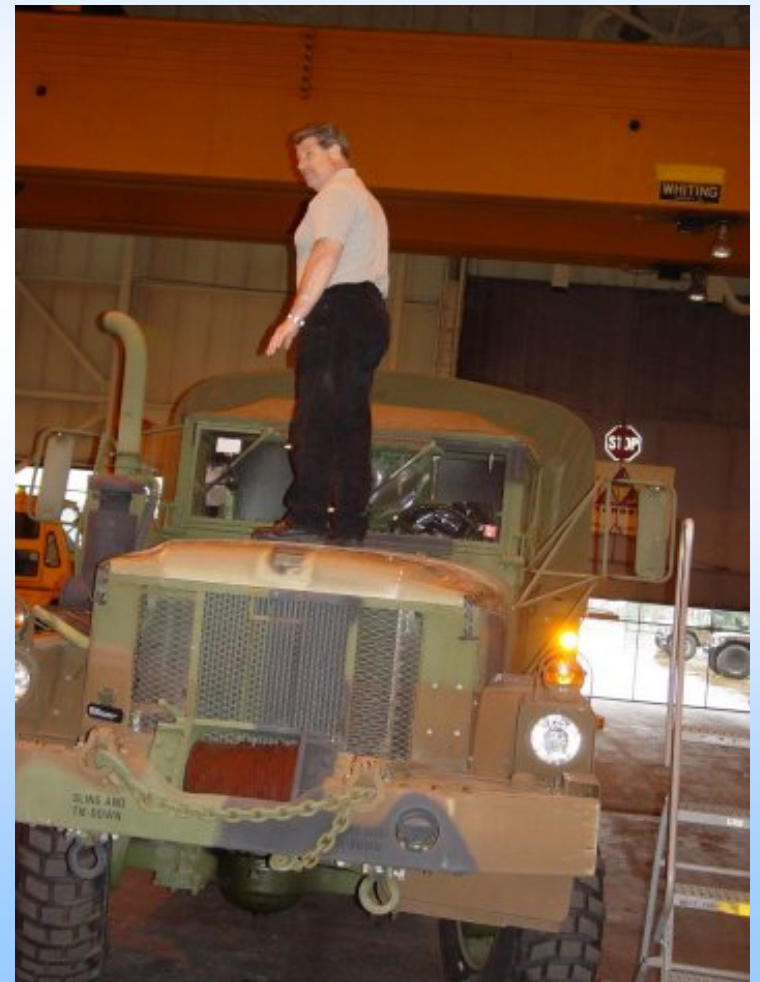


- FAVE-L Resin

- Infusion time: ~30 min → Fast Infusion
- Resin accumulated at foam stiffeners

Final Part

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



Future Directions

- **Less cure shrinkage and lower exotherm**
 - Can make thicker laminates
 - Large Navy radome structures
- **Vertachem is a start-up company commercializing this resin**
- **Drexel student design team working on plant design and economics**



Publications and Awards

- **Patent applications:**

- G.R. Palmese, J.J. La Scala, J.M. Sands, “**Fatty Acid Monomers to Reduce Emissions and Toughen Polymers,**” U.S. Patent Application, May 6, 2005, DREX-1014US.
- G.R. Palmese, J.J. La Scala, J.M. Sands, “**Multi-Modal Vinyl Ester Resins,**” PCT Patent Application, May 2005.

- **Awards:**

- **Army Research and Development Award**, Army Research Laboratory (2005)
- **SERDP Weapons Platform Project of the Year**, SERDP 2005.
- **Best Technical Paper Award, Composites 2004**, American Composites Manufacturers Association (2004).

- **Publications:**

- J.J. La Scala, J.A. Orlicki, C. Winston, E.J. Robinette, J.M. Sands, and G.R. Palmese, “The Use of Bimodal Blends of Vinyl Ester Monomers to Improve Resin Processing and Toughen Polymer Properties,” *Polymer*, 46, 2908-2921 (2005)
- J.J. La Scala, J.M. Sands, and G.R. Palmese, “Clearing the Air: Army Composites Research Reduces Harmful Emissions,” *The AMPTIAC Quarterly*, 8, 118-125 (2004).
- J.J. La Scala, J.M. Sands, J.A. Orlicki, E.J. Robinette, and G.R. Palmese, “Fatty Acid-Based Monomers as Styrene Replacements for Liquid Molding Resins,” *Polymer*, 45, 7729-7737 (2004).

Summary

- Overall properties of **FAVE** resin, polymers, and composites are similar to that of commercial resins.
- Developed formulations with **50-78% reduction in HAP emissions**
- Demonstrated the ability of these resins for making large-scale composite structures
- Future work – validate performance of structures using low HAP fatty acid-based resins

Thank you!!!

Questions or Comments?

jlascala@arl.army.mil

410-306-0687

**Army Research Labs, AMSRD-ARL-WM-MC, Bldg. 4600,
Aberdeen Proving Grounds, MD 21005**



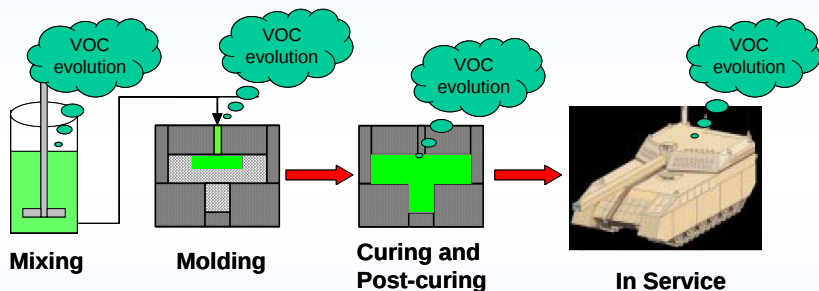
Low VOC Resin Technology

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

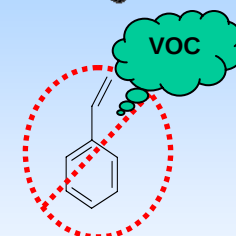
Applicable to all uses of unsaturated polyesters and vinyl esters, including all methods of manufacture.

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

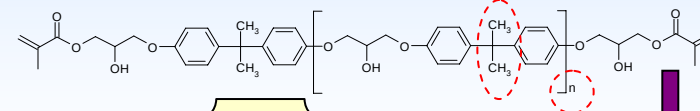


Solutions

- 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



Backup Slides

Neat Resin Properties

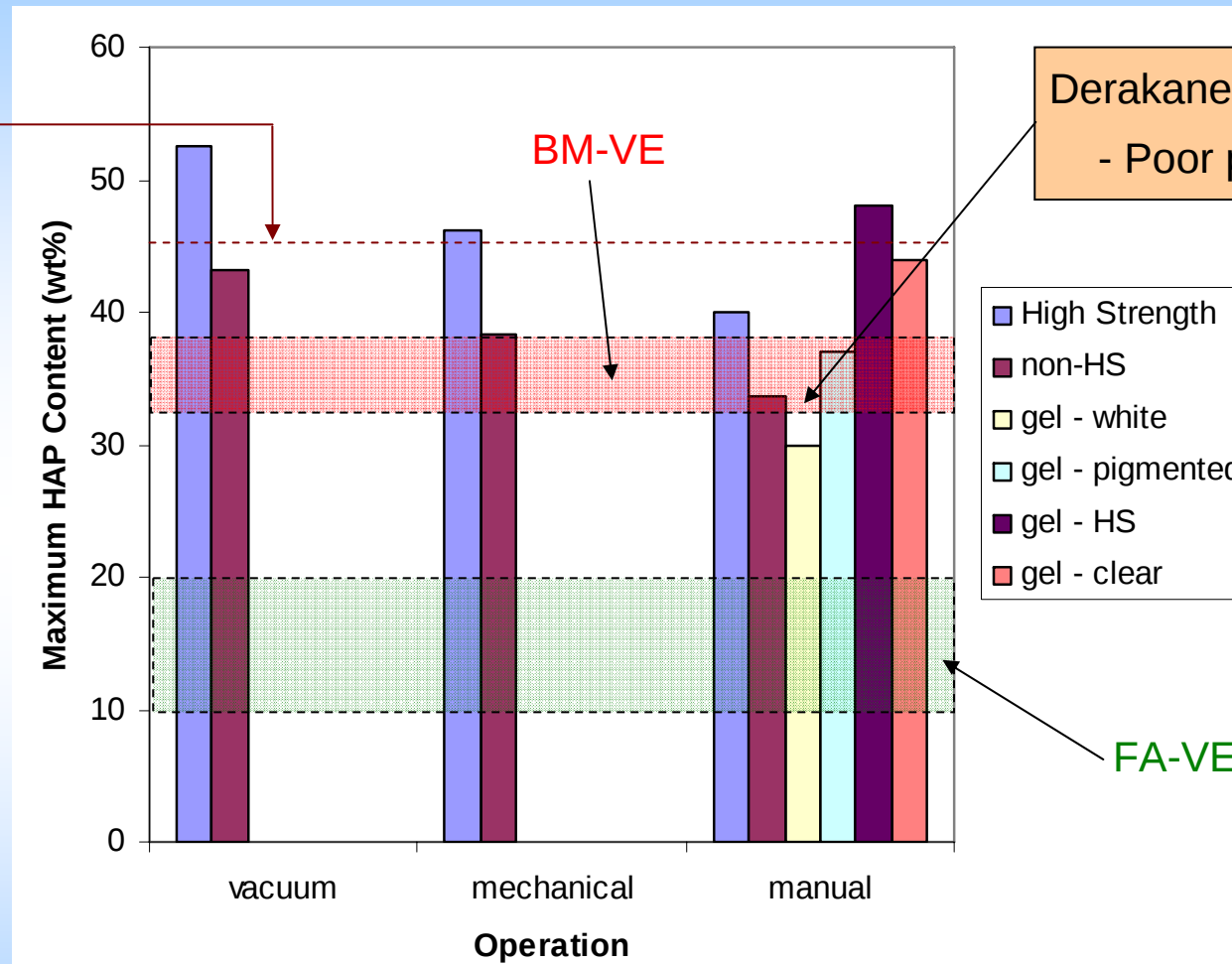
Property	FA-VE Resin	BM-VE Resin	Derakane 441-400	Derakane 411-350
			Low VOC Commercial Resins	Standard Commercial Resins
Styrene Content (wt%)	10-20	28-38	33	45
T _g (°C)	120-130	130-140	140	125
Flexural Strength (MPa)	120	130	130	130
Flexural Modulus (GPa)	3.0	3.5	3.5	3.4
Toughness (J/m ²)	200	200-300	110	240
Viscosity at 30°C (cP)	100-400	150-400	312	270
Gel times	5 min-7 hrs	Not tested	Various	Various
Shrinkage	Low	Moderate	Moderate	High
Renewable	Partly	No	No	No
Biodegradable	No	No	No	No
Cost	~\$4/lb (low size-scale)	>\$2.24/lb	~\$2.24/lb	~\$2.15/lb

- BM-VE resins have low VOC and good toughness
- FA-VE resins have ultra low VOC and high toughness, but have lower strength and modulus

NESHAP

Small Businesses (< 100 tpy HAP)

Derakane 411-C50
 - Does not meet standards for manual ops.
 - Barely meets other standards



Derakane 441-400
 - Poor performance

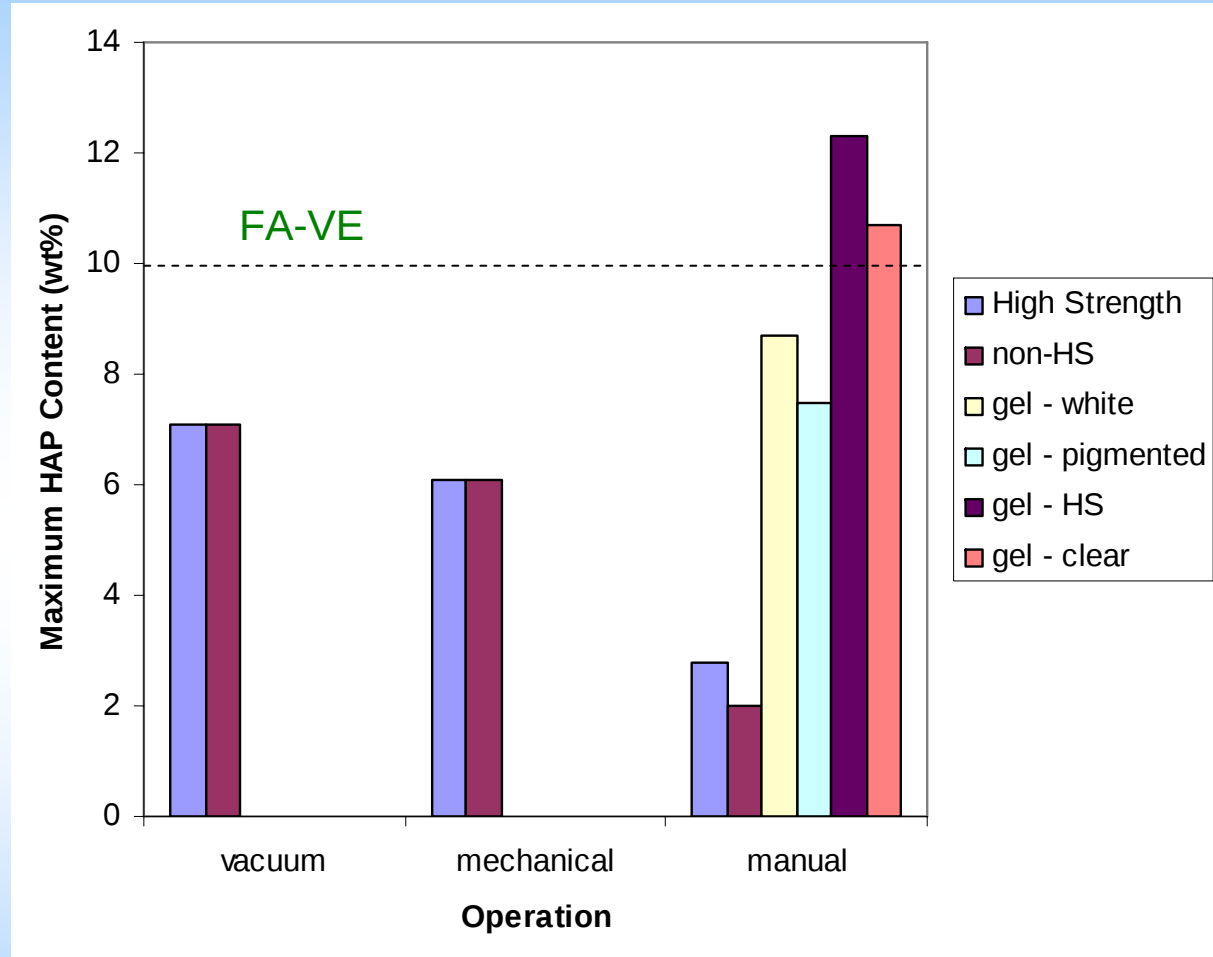
FA-VE

- Bimodal blends meet most NESHAPs
 - Fatty acid-based resins exceed all NESHAPs
- } Including gel coats

NESHAP

Large Businesses (> 100 tpy HAP)

Derakane resins
do not come close
to meeting these
standards



- Fatty acid-based resins meets standards for clear and HS gel coats
- Fatty acid-based resins are close to meeting other NESHAPs
 - Combination of styrene suppressants and bimodal blends
 - Add-on control devices