

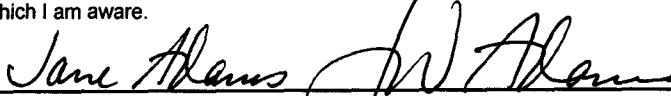
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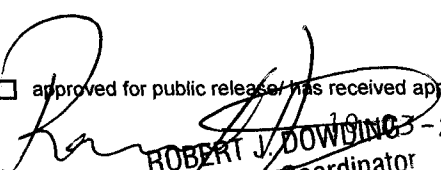


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ENVIRONMENTALLY FRIENDLY BIO-BASED VINYL ESTER RESINS FOR MILITARY COMPOSITE STRUCTURES

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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. These fatty acid vinyl ester resins allow for the formulation of high performance composite resins with no more than 25 wt% styrene. 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. Composite panel validation studies have been performed, showing that the fatty acid-based resins have sufficient modulus, strength, glass transition temperature, and resistance to weathering. Demonstration parts have been prepared and are in the process of being validated for military use.

1. INTRODUCTION

Polymer matrix composites are materials made by combining a polymer with reinforcing fibers, such as fiberglass. 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 reinforcing 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. 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. Yet, reactive diluents in vinyl ester (VE) and unsaturated polyester (UPE) resins, such as styrene and 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 and Reichhold Hydrex 100, which are NESHAP compliant for most composite fabrication applications. However, the viscosity and fracture properties of such resins are poor and unacceptable for most military uses. 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.

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.

The Army Research Laboratory (ARL) in conjunction with Drexel University has developed fatty acid-based vinyl ester (FAVE) resins to significantly reduce the VOC/HAP emissions from VE resins (La Scala, et al., 2004). These resins reduce emissions in composite resins by using fatty acid monomers as styrene replacements to maintain high performance while using low styrene/HAP contents (Fig. 1). These fatty acids monomers are derived from triglycerides/plant oils from various plant sources, such as soybeans. The fatty acid monomers are reactive diluents used to replace all but ~25 wt% of the styrene HAP in the VE or UPE resin (La Scala, et al., 2007). 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.

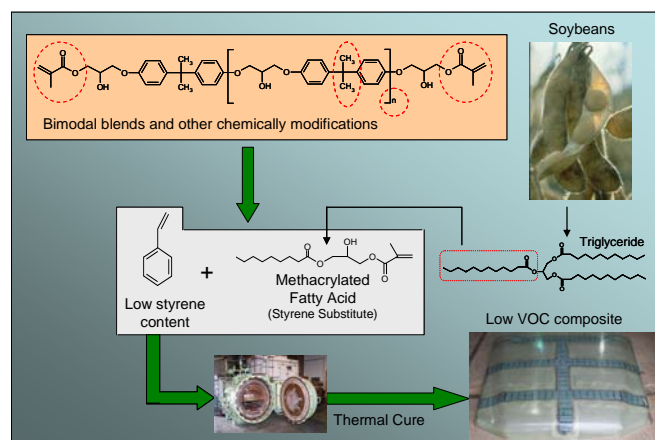


Figure 1: FAVE composites.

This technology would allow DoD facilities to continue manufacturing VE resins using current practices and facilities, while reducing pollution and health risks. However, before it could be used in the military, these FAVE-based composites must be demonstrated/validated on weapons platforms. This work examines the demonstration/validation of FAVE-based composites for (Fig. 2) (a) Marines HMMWV ballistic hardtop, (b) Army HMMWV transmission container (c) Army M35A3 composite replacement hood, (d) Air Force T-38 dorsal cover, (e) navy mine counter measure (MCM) composite rudder, and other platforms.

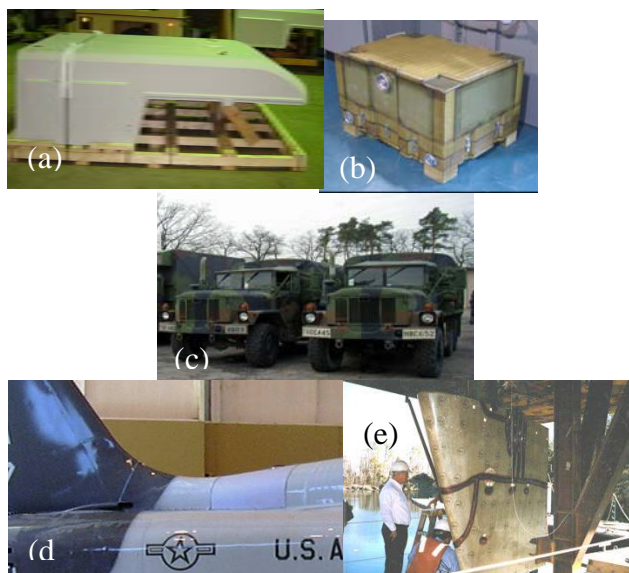


Fig. 2: ARL/Drexel low HAP resins are being demonstrated for (a) HMMWV ballistic hardtop, (b) HMMWV transmission container, (c) M35A3 composite replacement hood, (d) T-38 dorsal cover, and (e) MCM composite rudder.

2. REPLACEMENT RESINS

Various commercial vinyl ester resins are currently used to manufacture of the parts in Fig. 2. Derakane 8084 is a toughened vinyl ester resin containing over 40 wt% styrene, and is currently used in the HMMWV hardtop and transmission container. Corezyn Corve 8100 is a high styrene content resin (50 wt%) and is currently used in the production of the composite rudder. Derakane 510A-40 is used on other Navy composite parts. Hexion Specialty Chemicals 781-2140 is used in the T-38 dorsal cover. Hetron 980/35 is a high temperature vinyl ester used from the M35A3 hood.

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. Thus, 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-L-25S and FAVE-O-25S 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 . These low HAP resin formulations were prepared for DoD use

by Applied Poleramics, Inc. and delivered to the individual laboratories for testing. Table 1 lists the FAVE resins chosen as substitutes for a given commercial resin for each application. Aside from the resin change, there are no other differences in composite preparation, design, etc. from the baseline system to the FAVE composites.

Table 1: Incumbent resins, FAVE replacements, and reinforcing fibers used for each demonstration part.

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-O-HT
M35A3 and M939 Hood	3-Tex 96 oz E-glass	Hetron 980/35 (VE)	FAVE-O-HT
Transmission Container	3-Tex 54 oz E-glass	Derakane 8084	FAVE-O-25S or FAVE-L-25S
T-38 Dorsal Cover and F-22 Canopy Cover	Fibre Glast Developments Corp. 120 3 oz E-Glass and Style 7781 E-glass 9 oz	Hexion 781-2140	FAVE-L-25S or FAVE-O-25S
Rudders	Fiber Glass Ind. 18 oz E-glass	Corezyn Corve 8100 and Derakane 510A-40	FAVE-L

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.

3. DEMONSTRATION PLATFORMS

In this work, the low HAP fatty acid vinyl ester resins will be tested for their ability to replace commercial high HAP vinyl ester resins for Army, AirForce, Navy, and Marines applications.

3.1 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 by ~1800 lbs/month.

3.2 Replacement Parts for Army Tactical Vehicles

The CCM has developed composite replacement hoods for the M35 truck along with Sioux Manufacturing Corp. (SMC). 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 solved the problems associated with the previous hood designs and have excellent performance. The hood could use either a 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 ~200 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 required maintenance 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 would reduce styrene use by 400 lbs/month.

3.3 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 and no covers can be ordered because they are no longer manufactured, and no tooling is available for new manufacture.

The Advanced Composites Office (ACO) at Hill Air Force Base 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 uses similar materials to the original dorsal covers; glass fabrics, room temperature processing with vinyl ester or epoxy resins. The current vinyl ester resin used for this part contains 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.

3.4 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 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 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

4.1 Resin Viscosity Measurement

The viscosity of the resin was measured using a TA Instruments AR2000 rheometer (New Castle, DE) in steady shear flow experiments using parallel plate geometry (40 mm plate) with peltier at a controlled temperature of 25°C. The shear rate was increased from 1 s⁻¹ to 200 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 viscosity stabilized to within 5% tolerance for three consecutive intervals.

4.2 Polymer and Composite Preparation

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.

4.3 Polymer and Composite Properties

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, 1994).

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 while elevated temperature samples were tested at 250°F. 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. Samples were tested at approximately 22°C and 40% relative humidity while elevated temperature samples were tested at 250°F.

4.4 Composite Weathering

Samples were immersed in various liquids to simulate exposure during fielding. First, samples were soaked in de-ionized water until fully saturated (Fig. 3a). Full saturation was determined by removing the samples periodically from the water, superficially drying them, and then weighing them. Once the weight gain for the samples dropped to zero, the samples were considered fully saturated. This usually required approximately 7-10 days. Samples were also freeze-thawed daily in water for 1 week to determine the effect of freezing conditions on composite performance. Sea water immersion was performed for 1 month on selected samples (Fig. 3b) and methyl ethyl ketone (MEK) and JP-8 immersion was

performed for 1 week to determine the effect of these immersions on thermal and mechanical performance.

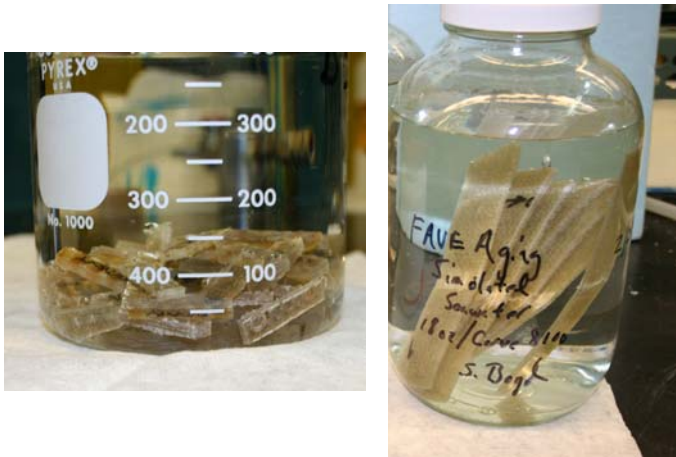


Figure 3: (a) composites samples immersed in de-ionized and (b) Composite samples immersed in sea water.

Xenon weathering was used to artificially weather the composite samples according to ASTM G151-00, MIL-STD-810F-03. Xenon arc lamps most faithfully correlate to actual sunlight exposure (300 – 2400 nm) relative to other accelerated aging techniques. The composite samples were exposed to cyclical weathering of 20 h light followed by 4 h dark cycle at a constant 50°C and 50% RH for 1 month.

5. DEMONSTRATION AND VALIDATION OF FAVE COMPOSITES

5.1 Resin Viscosity

The viscosity of the FAVE resins relative to the commercial VE resins is shown in Fig. 4. The results clearly show that FAVE-L and FAVE-O are more viscous than the commercial resins. However, FAVE-L-25S and FAVE-O-25S have viscosities that match some of the commercial resins. The FAVE-O-HT is more viscous, but should be sufficient for use in the M35A3 application. No shear thinning was observed for any resin.

5.2 Basic Composite Properties

Fig. 5 shows the glass transition temperature (T_g) of the VE composites before water immersion, after water immersion, and dried after water immersion. For all samples, water immersion caused a drop in T_g of 3-5°C. Yet, once the sample is re-dried, the T_g recovers its initial dry T_g . The FAVE-O-HT resin had the highest T_g , which should be sufficient for the higher operating temperatures that truck hoods can experience. However, in general, the FAVE resins had lower T_g s than the commercial resins they was designed to replace. This could be a problem, but T_g is typically oversized for

these systems. Mechanical performance at elevated temperatures is the major deciding factor on whether the resin meets the performance metrics.

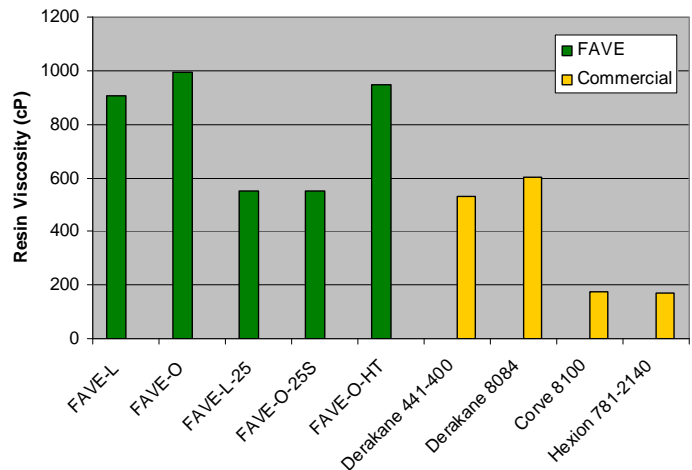


Figure 4: Viscosity of FAVE resins relative to commercial VE resins.

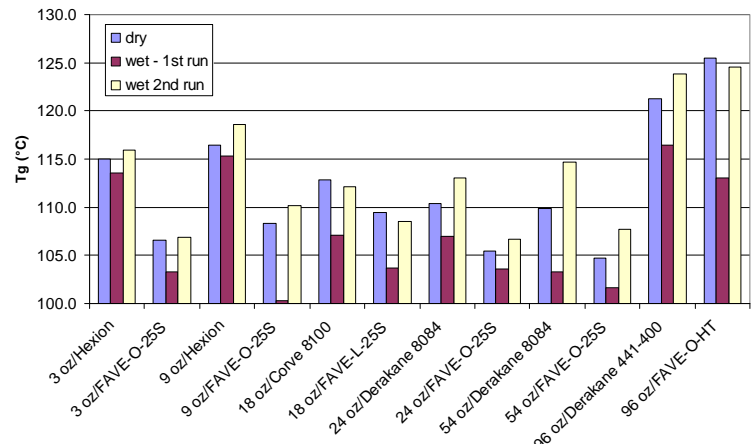


Figure 5: T_g as a function of resin and fiber for samples that are dry, wet, and dried after water immersion.

Room temperature mechanical performance of the fatty acid composites before and after accelerated weathering and fluid immersion was similar or better relative to the commercial resins (Fig. 6). Results clearly showed that Xenon weathering had little impact on composite properties. Salt water immersion caused a slight drop in properties relative to the baseline sample, but the FAVE resin performance was very similar to that of the commercial resin. On the other hand, both JP-8 and MEK caused drops in the properties of some commercial composites while having little effect on the properties of FAVE composites. Freeze thaw properties (not shown) did cause a reduction in T_g and slight reduction in mechanical properties, but had a similar effect on commercial and FAVE resins. These room temperature mechanical results indicate that these composites meet the basic requirements for the

HMMWV hardtop, HMMWV transmission container, T-38 dorsal cover, and composite rudder. Furthermore, these composites should meet the required performance for years during fielding.

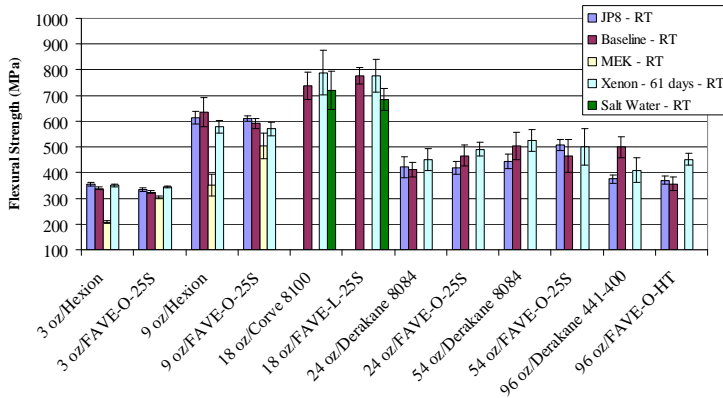


Figure 6: Room temperature properties of composites before and after various accelerated weathering or fluid immersion.

Elevated temperature performance was necessary to validate basic composite performance for M35A3 truck hoods. The properties at 250°F for FAVE-O-HT were above or met the threshold values: strength 36.2 ksi (30 ksi min), modulus 3.0 msi (3.0 msi min), and short-beam shear strength of 3.2 ksi (3.0 min). Therefore, these FAVE resins should have the appropriate performance for this truck hood application.

5.3 Composite Demonstration Parts

The HMMWV transmission container was fabricated using FAVE-O-25S (Fig. 7). The resin performed well in fabricating this part, as there was good wetting of the fibers with an acceptable infusion time of 30 min. This part will soon 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. Furthermore, RRAD will validate its performance in fielding trials.

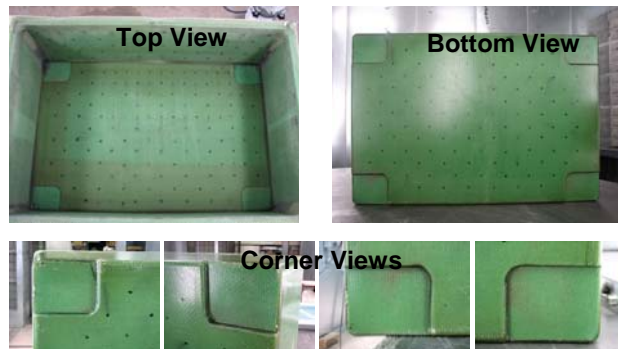


Figure 7: HMMWV transmission container fabricated using FAVE-O-25S resin.

FAVE-O-HT was used to manufacture both the M35A3 truck hood as well as an M939 truck hood (Fig. 8). The resin performed very well in producing these parts. Infusion required only about 30 minutes. Additional hoods are being manufactured by Sioux Manufacturing Corp. to be delivered to RRAD for validation during field trials. In the meantime, 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 M35A3 hood design) will be used to validate the performance of M35A3 and M939 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.

Ballistic panels were prepared for validating the FAVE-L-25S for the HMMWV hardtop application. Ballistic results show that the FAVE resin had far better performance with 44 mag. and M80 threats relative to the commercial resins and matched that of high performance, expensive epoxy resin composites.

Aside from the T-38 dorsal cover, the Air Force demonstrated an F-22 canopy cover (Fig. 9). The purpose of this cover is to allow for painting and other maintenance while protecting the transparent canopy from damage. This canopy cover prepared using FAVE-L-25S meets all required performance specifications, including toughness, strength, and flexibility.



Figure 8: (a) M35A3 hood and (b) M939 hood.



Figure 9: F-22 canopy cover.

The composite rudder will soon be manufactured by Structural Composites, Inc. (SCI). 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 SCI, and will be tested by SCI in conjunction with the Naval Surface Warfare Center, Carderock Division. 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 will

likely be acceptable replacements for the commercial high HAP vinyl ester resins used in the Marines HMMWV helmet hardtop, Army tactical vehicles, T-38 dorsal cover, the MCM composite rudder, and other military applications. Full scale tests and field trials using the low HAP fatty acids-based resins will be completed in the next year to fully validate these parts for military use.

ACKNOWLEDGEMENTS

The authors would like to thank API for preparing the fatty acid monomers and FAVE resins. The authors also thank Ashland, Corezyn, and Hexion Specialty chemicals for supplying the commercial resins. Fiber Glass Industries supplied the 18 oz unidirectional fabric. Funding was provided by ESTCP WP-0617.

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.
- La Scala, J.J., Jeyarajasingam, A., Logan, M.S., Winston, C., Myers, P., Sands, J.M. and Palmese, G.R., 2007: Fatty acid-based vinyl ester composites with low hazardous air pollutant contents, *J. of BioBased Matl. and BioEnergy*, **1**, 409-416.
- 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*.