ARMY RESEARCH LABORATORY

Demonstration of Military Composites With Low Hazardous Air Pollutant Content

by John J. La Scala, Theresa Glodek, Caroline Lochner, Xing Geng, Ashiq Quabili, Ken Patterson, Frank Bruce, Edward Bartling, Charlie Johnson, Philip Myers, Steven Boyd, Stephen Andersen, Lawrence Coulter, Roger Crane, John Gillespie, Jr., James M. Sands, Michael Starks, Jorge Gomez, and Giuseppe R. Palmese

ARL-RP-185 **July 2007**

A reprint from the *Proceedings of the SAMPE 2007 Conference*, Baltimore, MD, 3–7 June 2007.

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

ARL-RP-185 **July 2007**

Demonstration of Military Composites With Low Hazardous Air Pollutant Content

John J. La Scala, Theresa Glodek, Caroline Lochner, Philip Myers, Steven Boyd, and James M. Sands
Weapons and Materials Research Directorate, ARL

Xing Geng and Giuseppe R. Palmese
Drexel University

Ashiq Quabili, Stephen Andersen, and John Gillespie, Jr.
University of Delaware

Ken Patterson, Frank Bruce, Edward Bartling, Charlie Johnson, and Lawrence Coulter
Hill AFB

Roger Crane
Naval Surface Warfare Center Carderock

Michael Starks and Jorge Gomez
Red River Army Depot

A reprint from the *Proceedings of the SAMPE 2007 Conference*, Baltimore, MD, 3–7 June 2007.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
July 2007	Reprint	January 2006–Feburary 2007

4. TITLE AND SUBTITLE
Demonstration of Military Composites With Low Hazardous Air Pollutant Content

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
John J. La Scala, Theresa Glodek, Caroline Lochner, Xing Geng,[*] Ashiq Quabili,[†] Ken Patterson,[‡] Frank Bruce,[‡] Edward Bartling,[‡] Charlie Johnson,[‡] Philip Myers, Steven Boyd, Stephen Andersen,[†] Lawrence Coulter,[‡] Roger Crane,[§] John Gillespie, Jr.,[†] James M. Sands, Michael Starks,[**] Jorge Gomez,[**] and Giuseppe R. Palmese[*]

5d. PROJECT NUMBER
789531

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: AMSRD-ARL-WM-MC
Aberdeen Proving Ground, MD 21005-5066

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-RP-185

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
A reprint from the *Proceedings of the SAMPE 2007 Conference*, Baltimore, MD, 3–7 June 2007.
[*]Department of Chemical and Biological Engineering, Drexel University, 3141 Chestnut St., Philadelphia, PA 19104
[†]University of Delaware, Center for Composite Materials, Newark, DE 19716
[‡]AFRL/MLS-OL, Hill Air Force Base, UT 84506
[§] Naval Surface Warfare Center Carderock, West Bethesda, MD 20817
[**]Red River Army Depot, U.S. Army TACOM, Texarkana, TX 75507-5000

14. 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.

15. SUBJECT TERMS
resins/materials – polyester/vinyl ester, fiber reinforcement – glass, styrene emission

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			John J. La Scala
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL	22	19b. TELEPHONE NUMBER (*Include area code*) 410-306-0687

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

DEMONSTRATION OF MILITARY COMPOSITES WITH LOW HAZARDOUS AIR POLLUTANT CONTENT

John J. La Scala[1]*, Theresa Glodek[1], Caroline Lochner[1], Xing Geng[2], Ashiq Quabili[3], Ken Patterson[4], Frank Bruce[4], Edward Bartling[4], Charlie Johnson[4], Philip Myers[1], Steven Boyd[1], Stephen Andersen[3], Lawrence Coulter[4], Roger Crane[5], John Gillespie, Jr. [3], James M. Sands[1], Michael Starks[6], Jorge Gomez[6], and Giuseppe R. Palmese[2]

[1] - Army Research Laboratory
Aberdeen Proving Grounds, MD 21005-5069

[2] - Department of Chemical and Biological Engineering, Drexel University, 3141 Chestnut St. Philadelphia, PA 19104

[3] - University of Delaware, Center for Composite Materials
Newark, DE 19716

[4] - AFRL/MLS-OL
Hill AFB, UT 84056

[5] - Naval Surface Warfare Center Carderock
West Bethesda, MD 20817

[6] - Red River Army Depot, US Army TACOM
Texarkana, TX 75507-5000

* To whom all correspondence should be addressed

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.

KEY WORDS: Resins/Materials – Polyester/Vinyl Ester, Fiber Reinforcement – Glass, Styrene Emission

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 (1).

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) (2). 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 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 (3). 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 (4). However, these styrene replacements still produce significant emissions, and are therefore still regulated by the EPA (2). 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 (5). 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 (6) as a reactive diluent to replace all but

~20 wt% of the styrene HAP in the VE or UPE resin (7). The solution, which is in the process of being patented (6), 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 (6). 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 (6).

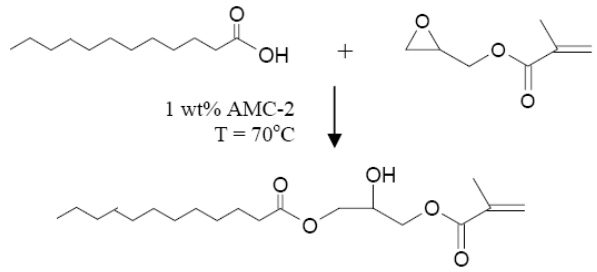

Fig. 1: Reaction scheme to produce MFA monomers.

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).

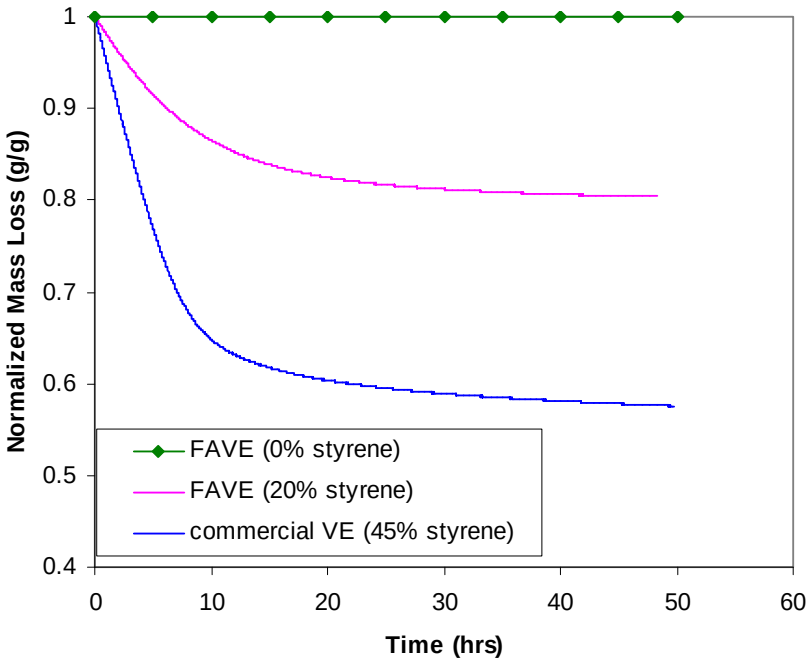

Fig. 2: Thermogravimetric analysis of commercial resins and the fatty acid vinyl ester resins (FAVE) showing that the commercial resins have significantly more mass loss because only the styrene component evaporates.

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.

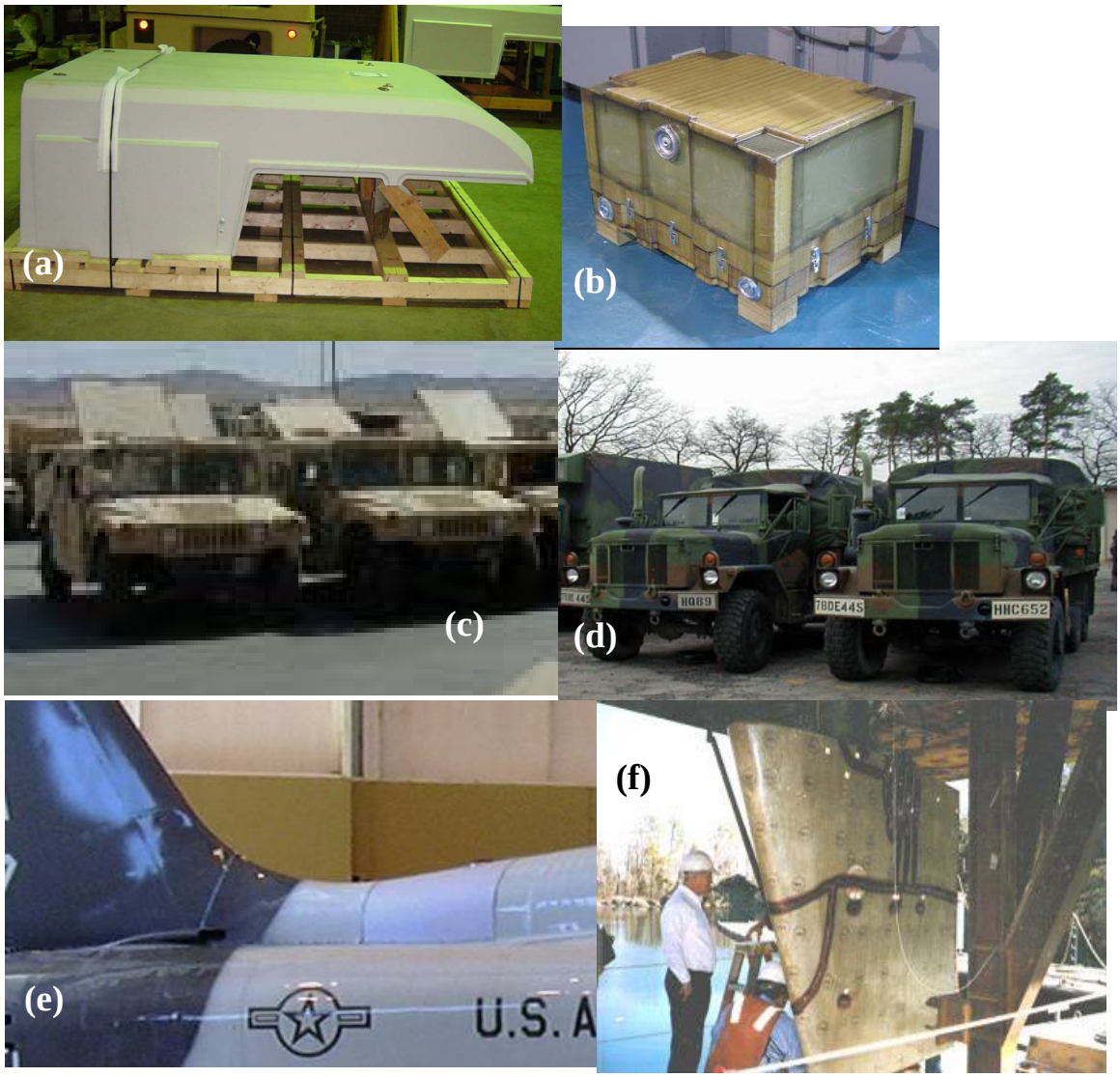

Fig. 3: ARL/Drexel low HAP resins are being demonstrated for (a) HMMWV ballistic hardtop, (b) a HMMWV transmission container, composite replacement hoods for (c) HMMWV, or (d) M35A3, and (e) T-38 dorsal cover, and (f) MCM composite rudder.

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 ~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) 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.

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

The Advanced Composites Office 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.

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 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

4.1 Composite Fibers and Resins 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 (Table 1). Derakane 8084 is a toughened vinyl ester resin containing over 40 wt% styrene, and is currently used in the HMMWV hardtop, and HMMWV transmission container applications. Mahogany 24 oz E-glass fibers are currently used got the HMMWV transmission container applications, whereas 3-Tex 54 oz fibers are used for the HMMWV hardtop. Higher Tg VE resins, such as Derakane 441-400 with 33 wt% styrene are necessary for the HMMWV hood and M35A3 truck hood applications. The HMMWV hood uses Mahogany 24 oz E-glass fibers. A single layer of 3-Tex 96 oz fibers are used for all but the edges of the M35A3 hood. Corezyn Corve 8100 is a high styrene content resin (50 wt%) and is currently used in the production of the composite rudder. Fiber glass Industries 18 oz E-glass uni-directional with stitched mat is used as reinforcement for the composite rudder. Hexion Specialty Chemicals 781-2140 is used in the T-38 dorsal cover and contains 47 wt% styrene. 120 3 oz E-glass and 7781 9 oz E-glass are layered along with a core material to reinforce 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.

There are various resin possibilities that could replace the current commercial resin systems (Table 1). Based on previous results and the technical demonstration packages for these parts, we expect the Tg of most FAVE resin systems to be too low to meet the Army M35A3 and HMMWV hood applications. For that reason, the FAVE-O25S and FAVE-O-HT resins will likely be the only candidate resins for these parts. In addition, we expect FAVE-L and FAVE-O to have too low a Tg for the HMMWV transmission container and hardtop. We are confident that the FAVE-O-25S will have sufficient Tg for these applications, and thus will

not consider the FAVE-O-HT a potential alternative unless the FAVE-O-25S proves inadequate. Because of the low performance requirements for the Navy and Air Force applications, the lower performing resins (FAVE-L and FAVE-O) are being considered first. If these prove inadequate (too high of a viscosity or too low of a Tg), the FAVE-L-25S and FAVE-O-25S will be considered.

Table 1: The current resin and fibers systems used for the demonstration platforms and the proposed low HAP replacement resins.

Application	Service	Baseline Resin	Fibers	Proposed Replacement Resin
HMMWV Transmission Container	Army	Derakane 8084 (40 wt% styrene)	Mahogany 24 oz	FAVE-O-25S
HMMWV hood	Army	Derakane 441-400 (33 wt% styrene)	Mahogany 24 oz	FAVE-O-25S or FAVE-O-HT
M35A3 hood	Army	Derakane 441-400 (33 wt% styrene)	3-Tex 96 oz	FAVE-O-25S or FAVE-O-HT
Amtech HMMWV hardtop	Marines	Derakane 8084 (40 wt% styrene)	3-Tex 54 oz	FAVE-O-25S
T-38 Dorsal Cover	Air Force	Hexion 781-2140 (47 wt% styrene)	120 3 oz E-glass, and 7781 9 oz E-glass	FAVE-L, FAVE-O, FAVE-L-25S, or FAVE-O-25S
MCM Rudder	Navy	Corve 8100 (50 wt% styrene)	Fiber glass Industries 18 oz E-glass (uni- with stitched mat)	FAVE-L, FAVE-O, FAVE-L-25S, or FAVE-O-25S

4.2 Resin Validation 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.

4.3 Resin 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. 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 panels made using the fibers for Air Force and Navy applications were cured using 1 wt% Trigonox and ~0.2

wt% CoNap. These panels were cured overnight at room temperature and postcured at 120°C for 2 hrs. For Army and Marines applications, 2 wt% Trigonox, 0.3 wt% CoNap, 0.2 wt% N,N-dimethylaniline (another promoter), and 0.08 wt% 2,4-pentanedione (a free radical inhibitor) were added to either Derakane 8084 or FAVE-O-25S. These samples were cured overnight at room temperature and postcured for 3 hrs at 135°C.

4.4 Resin 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 30ºC to 200ºC at a rate of 2ºC/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 200ºC. 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 (8).

Flexural tests, in accordance with ASTM 790M, were performed to determine the modulus of elasticity and flexural strength for the Air Force and Navy parts. 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.

For Army and Marines applications, 4 point test were performed following ASTM D 6272 in order to determine the flexural properties. The specimens for this experiment were cut in the lengthwise (fabric wrap) direction of the panel. Each specimen was tested by resting on two supports and loading at two loading noses. The tool side of the specimen was placed on the supports. The distance between the loading noses was one third of the support span. 24:1 Span to depth ratio was used due the loading nose structure. The load span length, Support Span Length, and support span-to-depth ratio were 1.6 in, 4.8 in, and 24:1, respectively. The rate of crosshead motion was 0.09 in/min. The samples were tested at 72°F to determine room temperature properties. In addition, Derakane 8084 and FAVE-O-25S reinforced with the 3-Tex 96 oz fibers were tested at 250°F in an Instron environmental chamber to assess elevated temperature performance. The samples were conditioned at 250°F for at least 2 hrs prior to testing.

Short beam shear (SBS) 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. All samples were tested at 72°F. In addition, for Army and Marines applications, short beam shear testing was also performed on Derakane 8084 and FAVE-O-25S reinforced with the 3-Tex 96 oz fibers at 250°F to assess elevated temperature performance.

5. RESULTS AND DISCUSSION

5.1 Resin Validation Results 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.

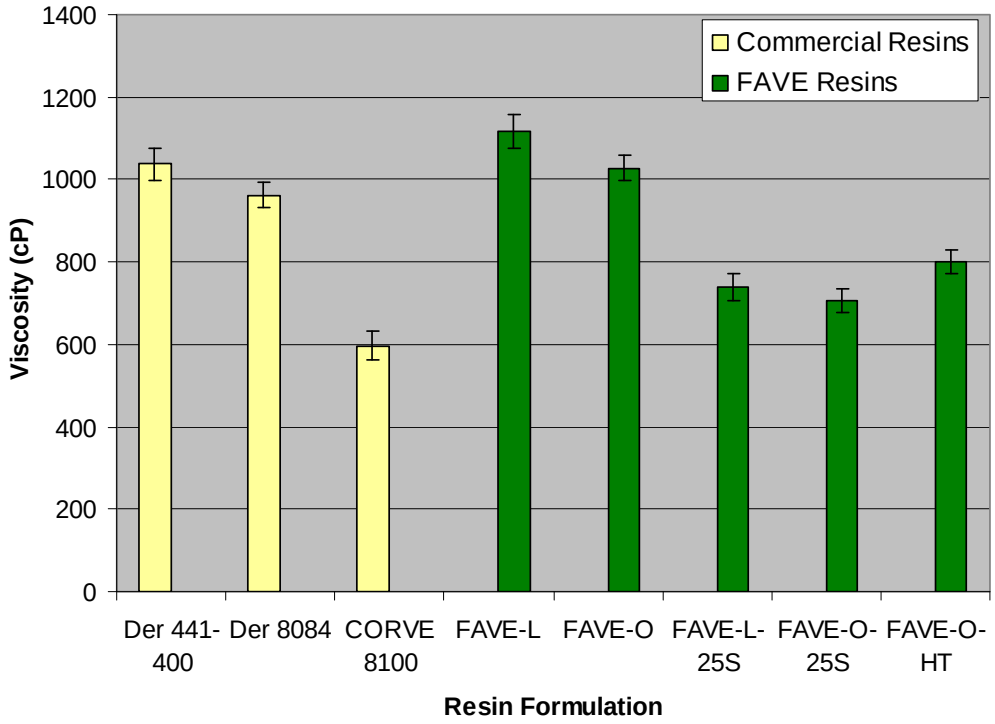

Fig. 4: The viscosity of the fatty acid-based vinyl ester formulations and commercial resins used in this work.

5.2 Glass Transition Temperature 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.

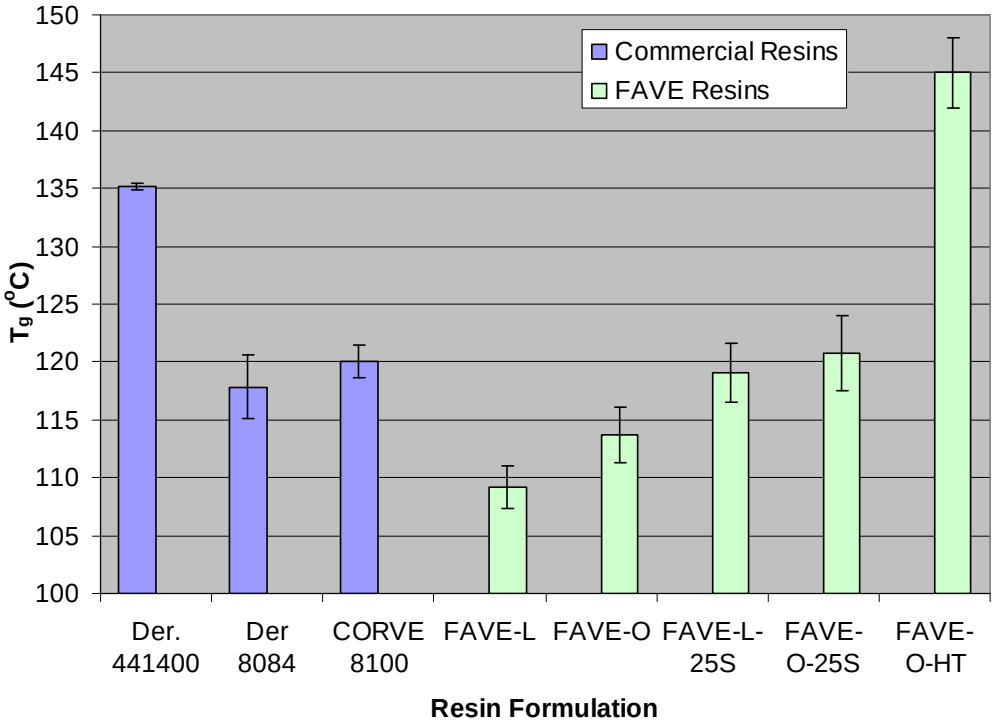

Fig. 5: T_g for the fatty acid-based vinyl ester formulations and commercial resins used in this work.

5.3 Mechanical Properties 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 at room temperature. 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 at room temperature from one resin formulation to another. Even at elevated temperatures, the properties of the FAVE-O-25S were not significantly different from those of the Derakane 8084 composites (Fig. 6). As a result, it is clear that the FAVE-O-25S is a potential candidate to replace Derakane 8084 for the Marines HMMWV hardtop and HMMWV transmission container applications. Despite that, the FAVE-O-25S does not have sufficient properties at 250°F for the HMMWV hood and M35A3 hood applications. These applications allow for only a 20% reduction in modulus and a 33% reduction in SBS. The FAVE-O-25S composites had a 43% reduction in modulus and an 80% reduction in SBS.

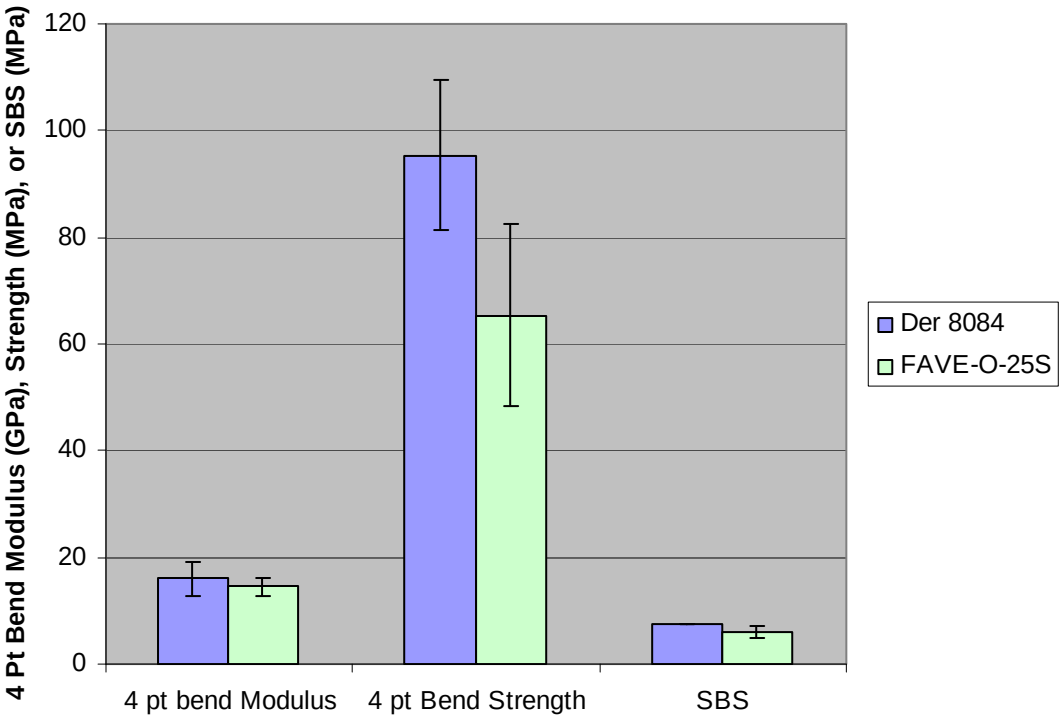

Figure 6: Comparison of the composite mechanical properties measured at 250°F for Derakane 8084 resin and FAVE-O-25S using 96 oz 3-Tex E-glass reinforcement.

5.4 Large Scale Composite Fabrication It was demonstrated that the FAVE resin can be used to make large scale parts (Fig. 7). 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 or wetting the fibers and produced qualitatively good parts. However, for this program, much more rigorous testing is required. Gel time and injection experiments done by the Navy indicate that the FAVE-L is acceptable for the composite rudder. On the other hand, FAVE-L was used to inject a T-38 dorsal cover composite. The high viscosity resulted in a short-shot. The reason for this is the high viscosity of FAVE-L coupled with the fact that distribution media is not used in the production of the part, although a core material with flow channels is used. Regardless, the viscosity of FAVE-L is too high for this application. Lower viscosity resins, such as FAVE-L-25S will be tried shortly.

5.5 Resin Selection Discussion 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. The FAVE-O-25S appears to be an appropriate choice for the Marines hardtop and HMMWV transmission container applications. Based on thermal requirements, the FAVE-O-HT is the only fatty acid vinyl ester resin that will meet the requirements for the M35A# hood and the HMMWV hood. The FAVE-L so far appears to have sufficient performance for the composite rudder application. Yet, the FAVE-L has too high of a viscosity FAVE for the T-38 dorsal cover application, and lower viscosity resins such as FAVE-L-25S will be validated instead.

Fig. 7: M35A3 hood (left) and hat stiffened structure (right) for Advanced Sail Program and DDX prepared using FAVE-L resin.

5.6 Future Demonstration/Validation Testing 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.

The HMMWV ballistic hardtop will be demonstrated/validated at Aberdeen Proving Grounds 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.

7. ACKNOWLEDGEMENTS

The authors would like to thank API for preparing the fatty acid monomers and FAVE resins for this work. 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 and SERDP WP-1271.

8. REFERENCES

1. J.M. Sands, B.K. Fink, S.H. McKnight, C.H. Newton, J.W. Gillespie, and G.R Palmese, Clean Products and Processing, **2**, 228 (2001).
2. Environmental Protection Agency, Federal Register, **68**, 19375 (2003).

3. J. Vallone, “NESHAP Requirements Assessment for Miscellaneous Coatings, Adhesives, Sealers, Etc.,” Final Report to ARL, Sustainable Painting Operations for the Total Army, 2004.
4. U.S. Patent 5,292,841 (1994) T.W. Smeal and G.L. Brownell.
5. B. Lacovara, “Reducing Emissions with Styrene Suppressants,” CFA, 1999.
6. U.S. Patent Application, 60/569,379 (2005) G.R. Palmese, J.J. La Scala, and J.M. Sands.
7. J.J. La Scala, J.M. Sands, J.A. Orlicki, E.J. Robinette, and G.R. Palmese, Polymer, **45**, 7729 (2004).
8. L.E. Nielsen and R.F. Landel, Mechanical Properties of Polymers and Composites, Marcel Dekker, New York, 1994, pp. 140-142.

NO. OF COPIES	ORGANIZATION
1 (PDF ONLY)	DEFENSE TECHNICAL INFORMATION CTR DTIC OCA 8725 JOHN J KINGMAN RD STE 0944 FORT BELVOIR VA 22060-6218
1	US ARMY RSRCH DEV & ENGRG CMD SYSTEMS OF SYSTEMS INTEGRATION AMSRD SS T 6000 6TH ST STE 100 FORT BELVOIR VA 22060-5608
1	DIRECTOR US ARMY RESEARCH LAB IMNE ALC IMS 2800 POWDER MILL RD ADELPHI MD 20783-1197
3	DIRECTOR US ARMY RESEARCH LAB AMSRD ARL CI OK TL 2800 POWDER MILL RD ADELPHI MD 20783-1197

ABERDEEN PROVING GROUND

1	DIR USARL AMSRD ARL CI OK TP (BLDG 4600)

NO. OF
COPIES ORGANIZATION

1 SERDP & ESTCP PROGRAM OFC
J MARQUSEE
901 N STUART STREET
STE 303
ARLINGTON VA 22203