New Reactive Diluents for an Environmentally Efficient Approach to Composite Repair

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Dr. Michael E. Wright

US NAVY, NAVAIR
Naval Air Warfare Center Weapons Division
Research Division, Chemistry Department
1900 N. Knox Road (Stop 6303)
China Lake, CA 93555-6106
760-939-1640 (phone)
760-939-1617 (fax)
michael.wright@navy.mil

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List of Symbols, Abbreviations, and Acronyms

AIBN	azobis(isobutylnitrile)
ARL	Army Research Laboratory
cP	centipoise
^oC	degrees in centigrade
DoD	DepartmentofDefense
DSC	differential scanning calorimetry
h	hour
LFL	lower flammability limit
MEHQ	4-methoxyphenol
MEKP	methyl ethyl ketone peroxide
MHz	megahertz
min	minute
mL	milliliter
NAWCWD	Navy Air Warfare Center, Weapons Division
NADEP	naval aviation depot
nm	nanometer
NMR	nuclear magnetic resonance
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure limit
PMC	polymer matrix composite
RD	reactive diluent
SAE	Society of Automotive Engineers
SDT	simultaneous differential thermal analyzer
STEL	short term exposure limit
TGA	thermogravimetric analysis
TMA	thermomechanical analysis
T_g	glass transition temperature
UV	ultraviolet
VE	vinyl ester
VOC	volatile organic compound
wt-%	weight percent

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1. Executive Summary

The use of polymer matrix composites (PMCs) to replace metal components is providing DoD with a cost effective path to create lighter, more fuel efficient, and faster vehicles (land, sea, and air). In addition, PMCs do not suffer from the effects of corrosion like their metal counter parts so there is significant savings in maintenance over a component lifetime and DoD can avoid the use of toxic corrosion inhibiting coatings {e.g. chromium (VI)}. One negative aspect to PMC production and repair is that volatile organic compounds (VOCs) are often produced during processing and cure of the PMC. Elimination of VOCs is a critical target and is pivotal for increasing PMC applications while decreasing their environmental footprint. Since repair work is often done in the field where environmental control is difficult, VOC elimination is especially important.

In this limited scope program we were successful in preparing three new reactive diluents for use with vinyl ester resins. The new reactive diluents (RDs), 4-(4'-tributylsilylphenoxy)styrene (**S1**), (3-phenoxyphenyl)methyl methacrylate (**A1**), and 4-phenoxyphenyl methacrylate (**A2**) were prepared in quantities ranging from 12 to 100 g and each RD was fully characterized by analytical and spectroscopic methods. Each of the RDs prepared in this study possessed viscosities at ~100 cP and vapor emissions were reduced by 10,000+ times when compared to styrene. We found that **S1** did not react well with the VE and this led to phase separation. In addition, **S1** was found to be unreactive when exposed to UV light in the presence of 1 wt-% $Ph_3S(CF_3SO_3)$ (a known reagent for the photo-generation of acid). In contrast, both **A1** and **A2** were found to cure well with the VE resin utilizing common free-radical initiators.

Mixtures of **A1** and **A2** from 30 to 60 wt-% with the VE resin were prepared and yielded a homogeneous solution. We selected ~50 wt-% as the most suitable for repair work (i.e. good wet out, self-leveling, easy to pour). Characterization of the resin mixtures and a composite layup (DSC and TMA,) indicated that cured **A1** suffers from a low T_g. TGA data indicate this may be due to a small amount of unreacted **A1**. At this point **A2** appeared as the top candidate to pursue for repairing the engineered defects. *It is noteworthy to mention that this reactive diluentVE repair resin contains **no styrene**.*

Repair of 1" holes were performed using **A2** and styrene as the reactive diluent. Each RD afforded void free repairs as well as providing ample wet-out and layup workability. Mechanical testing for the repaired samples showed no statistical difference in failure mode/strength; however, in both cases the repair recovered only a small portion of the materials original strength.

This program demonstrated that indeed a *styrene free VE repair resin* can be developed based on phenyl ether derivatives. Further testing at a larger scale is needed to more fully evaluate the strength and mechanical properties for this new class of reactive diluents.

2. Objectives

The primary objective of this project is to eliminate VOCs during the repair of composite structures at DoD maintenance facilities, in accordance with SERDP statement of need WP-SON-07-02. In order to do so, the project is intended to demonstrate the feasibility of using phenyl ether-based reactive diluents with extremely low volatility to eliminate or drastically reduce VOCs by replacing the reactive diluent styrene in vinyl polyester resins. In addition, this project will seek to develop a photo-initiated curing system as a first step in increasing DoD's flexibility in composite repair strategies.

Specific goals of the project include the following: 1) reproducible synthesis and purification of phenyl ether-based reactive diluents on a scale sufficient to demonstrate feasibility of commercial production (up to 100 g) 2) physical and chemical characterization of the aforementioned reactive diluents to determine volatility and suitability for use in composite repair processes, including a) melting point b) evaporation rates c) viscosity d) miscibility with vinyl polyester resin and e) ability to cure at temperatures below 100 °C when formulated with small amounts of commercially available initiators 3) formulation of suitable initiators, reactive diluents, and vinyl polyesters into repair resins 4) physical characterization of the repair resins, including their curing characteristics and mechanical properties when cured 5) production and repair of vinyl polyester resin samples with engineered defects, 6) investigation of the ease of making repairs and repair efficiency, along with an evaluation of the overall feasibility of the proposed repair process, and 7) investigation of the feasibility of performing cure by processes other than the application of heat, in order to expand the range of repair applications and limit the generation of volatiles.

3. Introduction & Background

The development and use of composite structures in place of more traditional metals (such as steel or aluminum alloys) in DoD applications have resulted in significant environmental benefits, including 1) an improvement in fuel economy for land, sea, and air vehicles due to reduced system weight, 2) a reduction in the need for corrosion prevention activities, that often involve the application, emission, or disposal of toxic substances (such as hexavalent chromium with aluminum alloys and cadmium on high-strength steel), and 3) decreased energy costs and pollution associated with materials manufacturing activities. These benefits, however, are offset by new environmental challenges. In particular, the repair of composite structures is typically more complex and demanding than the repair of metals, and often requires the use of volatile organic compounds (VOCs) such as styrene at repair locations. As more DoD vehicles (air, land and sea) and weapon platforms move to a composite structure to provide a lighter, faster, smarter, and safer fighting force, the need for better repair methods that do not involve significant VOC levels is gaining visibility and requires attention by research community.

Composite materials currently in use throughout DoD typically include fibers such as E-glass, high strength S-glass, Spectra (polyethylene), Kevlar (polyphenylene terephthalate), and graphite that are embedded in a polymeric resin. By far the most common resins are as polyester, vinyl ester, and epoxies. Polyester and vinyl ester resins play a vital role in the production of low cost composite parts, and are typically utilized in structures on land, at sea, and in less demanding aerospace applications, such as radomes, while epoxies are typically found in more demanding aerospace applications. In order to fabricate a composite part, the resin must start out as a liquid with a viscosity low enough to permit wetting and interpenetration of the fibers. The liquid must then be transformed into a strong solid via a curing reaction triggered by heat or high-energy mechanical or electromagnetic waves. In all cases involving the resins listed above, the curing reaction is irreversible. If the composite part breaks or cracks, the only means of affecting a repair is to introduce a patch consisting of fibers wet with additional uncured liquid resin. The patch must then be cured while maintaining good adhesion to the surrounding undamaged material. As with any repair, one of the most crucial aspects is adhesion of the repair patch to the original part that is being repaired.

The traditional polyester and vinyl ester resin compositions make use of a solid pre-polymer dissolved in a low viscosity, reactive liquid diluent in order to provide an adequate combination of strength and toughness after cure. The most widely used reactive diluent in a large part due to its low cost is styrene. Styrene has significant vapor pressure (~4.5 mm Hg) at ambient temperature and pressure. As a result, OSHA has established PEL and STEL levels at ~100 ppm. With a flash point of 90 ^{o}F and a lower flammability limit (LFL) of 0.9%, styrene can also constitute a significant fire hazard. Numerous regulatory efforts have sought to reduce or eliminate styrene in manufacturing and repair operations, and have resulted in extensive permitting, training, personnel protective equipment, and waste disposal requirements, all of which adversely impact the schedule and cost of repairing composite structures at DoD facilities.[1] Setting aside the clear health risks, styrene fumes can bother workers at levels far below OSHA STEL levels. A typical vinyl ester and styrene resin system is shown in Figure 1.

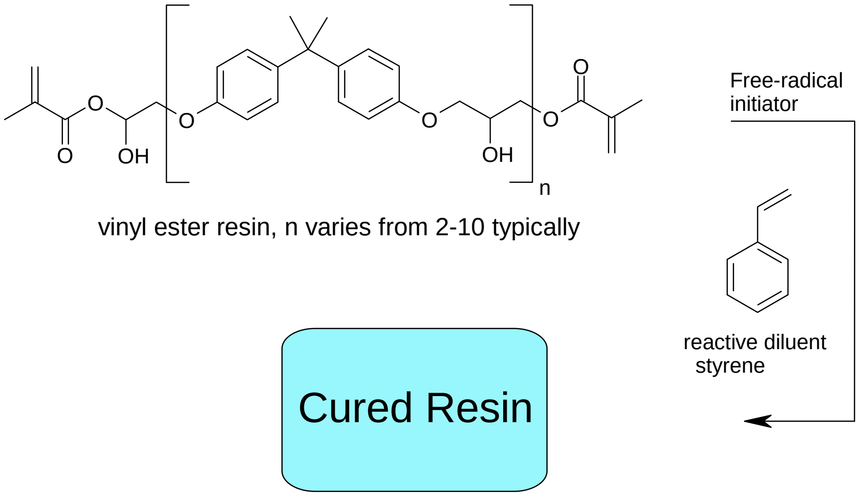

Figure 1. Typical vinyl ester resin and styrene as the reactive diluent.

One approach to mitigating the issues surrounding styrene in polyester resins is simply to substitute an alternate resin material. Epoxy resins are usually the alternative of choice because of their wide availability. In addition to being more expensive, however, epoxy resins have environmental shortcomings of their own. In particular, epoxy resins are most often cured with organic diamine compounds, many of which are toxic. Because of the wide variety of organic diamines available, an epoxy curative with a low volatility can often be selected for the resin formulation. Although doing so reduces the volatility and therefore some of the associated health risk, it does not eliminate the inherent toxicity of the diamines.[2] A typical epoxy resin and curative are illustrated in Figure 2.

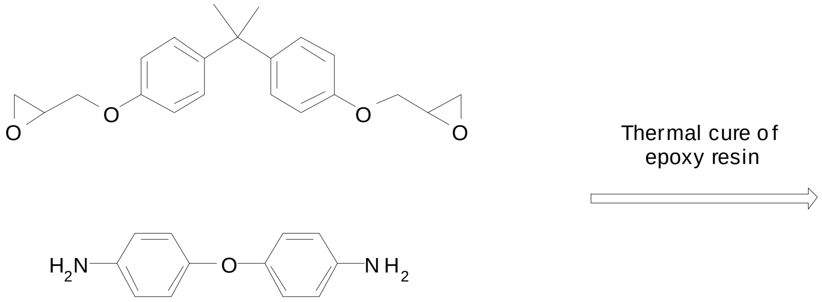

Figure 2. Typical epoxy resin and diamine curative.

Several approaches have been taken to address lowering the VOC levels for polyester resins themselves. The most straightforward is just to decrease the amount of styrene in the formulation.[3] Since styrene thins the formulation significantly, a reduction in the level of styrene results in higher viscosities. Sometimes these higher viscosities are simply tolerated despite the decrease in structural mechanical properties that result; other times, the molecular weight of the solid polyester is reduced, producing a reduction in viscosity that compensates for the lack of styrene. In these cases, the resins often become more brittle. More expensive and time-consuming processes are then put in place to mitigate the loss in mechanical performance. The reduction in styrene content that can be achieved using the aforementioned measures is often limited to between 30% and 70%.

An attractive alternative solution is to find a low VOC, low-viscosity, and low-cost liquid that can directly substitute for styrene. Recently workers at the Army Research Lab (ARL) have led such an effort and demonstrated partial replacement of styrene with fatty-acid based acrylates.[4] An example from the ARL work is displayed in Figure 3 below. The SERDP funded effort succeeded in demonstrating lowered VOC levels while retaining good mechanical properties with a relatively low-cost material. Acrylate systems, as those employed in the ARL effort, confer the advantage of being amenable to very mild cure methods. Since the volatility of styrene decreases rapidly as temperature decreases, the availability of non-thermal curing methods further reduced emission levels. Work has continued at ARL to even further reduce styrene content by utilizing smaller acrylates derived from more traditional organic alcohols (e.g. cyclohexanol).[5]

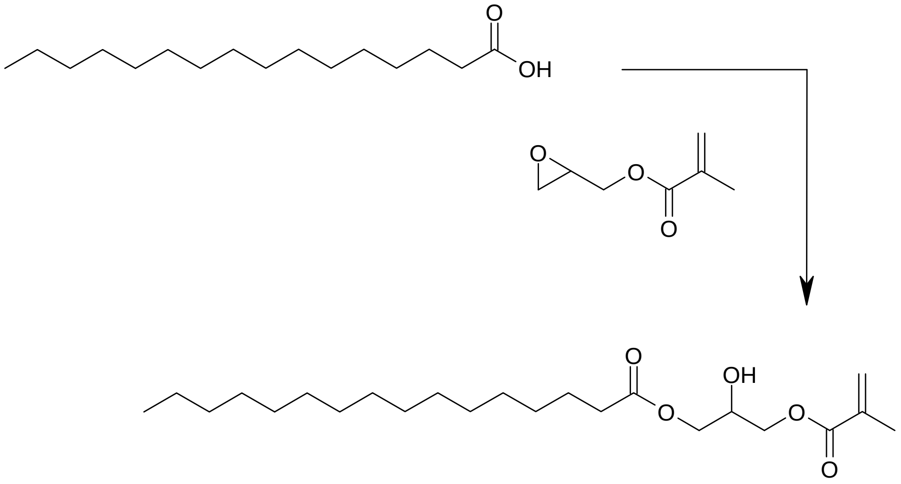

Figure 3. An example taken from a recent and elegant study on VOC reduction utilizing fatty acid glycidyl methacrylate esters led by workers at the Army Research Lab (Sands et al., SERDP PP-1271, final report 2005).

In this project we have investigated the possibility of replacing styrene with reactive diluents based on the diphenyl ether (or often called phenyl ether) core structure. Diphenyl ether itself is commonly found as a low-volatility additive in cosmetics and is available at relatively low cost.[6] If diphenyl ether is functionalized with a reactive moiety, it is likely to retain its low volatility at reasonable cost. Additionally, its overall aromatic character may enhance the mechanical properties of resin formulations as well as imparting properties such as decreased flammability. In a broad chemical sense, phenyl ether can be viewed as a substituted “styrene derivative” (Figure 4) that should have very low VOC emissions.

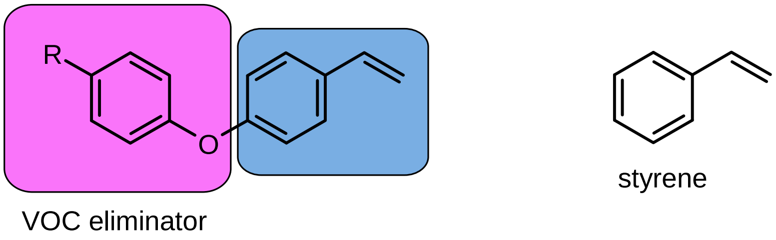

Figure 4. Comparison of phenyl ether with styrene

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4. Experimental Procedures

4.1 Chemical Synthesis

4.1.1 General procedures. All manipulations of compounds and solvents were carried out using standard Schlenk techniques. ^{1}H and ^{13}C NMR measurements were performed using a Bruker AC 200 or Bruker 400 MHz instrument. ^{1}H and ^{13}C NMR chemical shifts are reported versus the deuterated solvent peak (Solvent, ^{1}H, ^{13}C: $CDCl_3$, δ 7.25 ppm, δ 77.0 ppm; MeOH-δ_4, d 3.31 ppm, δ 49.15 ppm. The n-BuLi (2.5 M in hexanes), 4,4'-dibromophenyl ether, vinyl tributyltin, THF (anhydrous, inhibitor-free), N-methyl pyrrolidinone (anhydrous), and tributylchlorosilane, methacryloyl choride, 4-phenoxyphenol, 2,8,9-triisobutyl- 2,5,8,9- tetraaza-1-phosphabicyclo [3.3.3] undecane (phosphatrane ligand), triphenylsulfonium trifluoromethanesulfonate, and 3-(hydroxymethyl)phenyl ether were purchased from Aldrich Chemical Co. and used as received. The $Pd_2(dba)_3$ was purchased from Strem Chemical and used as received. Elemental analyses were performed at Atlantic Microlab, Inc., Norcross, GA.

4.1.2 Preparation of 3-{(4-phenoxyphenyl)}methyl methacrylate (A1). A chilled dichloromethane (60 mL) solution containing 3-phenoxybenzyl alcohol (20.0 mL, 0.11 mol) and NEt_3 (17.2 mL, 0.12 mol) was treated with methacryloyl chloride (12.0 mL, 0.12 mol) via dropwise addition over a period of ~15 min. The reaction was allowed to continue to react with stirring for an additional 5 h. The mixture was allowed to warm and then diluted with H2O and extracted with CH_2Cl_2 (2 x 100 mL). The solvents were removed under reduced pressure (< 40 ºC) and the crude product was initially purified by passing a dichloromethane solution of the monomer through an alumina (neutral, particle size?) and prior to removal of the solvent stabilizer 4-methoxyphenol (MEHQ) was added at various levels (50-200 ppm). This material is of sufficient purity (>98%) for use in preparing resins and other cure chemistries.

Additional purification can be carried out, albeit with significant material loss to afford analytically pure material by flash chromatography on silica gel using 3 % EtOAc/ hexane (v/v) as the eluent. This affords pure 1a as colorless oil (12.8 g, 49 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, overlapping Ph, 3H), 7.10 (m, overlapping Ph, 2H), 7.02 (m, overlapping Ph, 3H), 6.95 (m, Ph, 1H), 6.15 (s, alkenyl, 1H), 5.59 (m, alkenyl, 1H), 5.16 (s, CH_2O, 2H), 1.96 (s, CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 167.2 (C=O), 157.7, 157.1, 138.3, 136.3, 130.0, 129.9, 126.1, 123.7, 122.5, 119.3, 118.4, 118.1, 66.0 (CH_2O), 18.5 (CH_3). Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found C, 76.10; H, 5.98

4.1.3 Preparation of 4-phenoxyphenyl methacrylate (A2). A flask was charged with 4-phenoxyphenol (40 g, 215 mmol), methylene chloride (200 mL), and Et_3N (34.4 mL, 248 mmol) and the mixture chilled to 0 ^{o}C. Over a period of 15 min methacryloyl chloride (24 mL, 244 mmol) was added dropwise to the reaction mixture, then the ice bath removed, and reaction was continued for an additional 2 h with stirring. The mixture was diluted with water and the organic layer separated and washed with water (3 x 100 mL), brine (100 mL), and then dried over $MgSO_4$. Prior to removal of the solvents under reduced pressure, the stabilizer 4-methoxyphenol (MEHQ) was added at the desired level (50-200 ppm). ^{1}H NMR (400 MHz, $CDCl_3$): 7.35 (m, Ph, 2H), 7.10 (m, overlapping Ph, 3H), 7.02 (m, Ph, 4H), 6.36 (m, alkenyl, 1H), 5.76 (m, alkenyl, 1H), 2.07 (s, CH_3, 3H) ^{13}C NMR (100 MHz, $CDCl_3$): 166.1 (C=O), 157.4, 154.8, 146.5, 136.0, 129.9, 127.3, 123.5, 122.9, 119.8, 118.9, 18.5 (CH_3) Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.56. Found C, 75.66; H, 5.53

4.1.4 Preparation of 4-bromophenyl-4'-(tributylsilyl)phenyl ether (2). A RB flask was charged with 4-bromophenyl ether (10.0 g, 30 mmol) and dissolved in THF (120 mL). The reaction mixture was chilled (-78ºC dry ice/acetone bath) and treated with n-BuLi (12.5 mL, 32 mmol) via dropwise addition. After addition was complete the reaction mixture was allowed to stir at -78º C for 1 h and then n-Bu_3SiCl (8.5 mL, 32 mmol) was added dropwise over a period of 15 min. The reaction was diluted with H_2O (100 mL) and extracted with hexanes. The solvents were removed from the organic layer under reduced pressure and the crude product purified by flash chromatography on silica gel using 5% chloroform/hexane (v/v) as eluent to afford pure **2** as a colorless oil (4.86 g, 36 %). ^{1}H NMR (400 MHz, $CDCl_3$): 7.46 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.9 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 1.32 (m, 12H), 0.89 (t, 6.9 Hz, -CH_3, 9H), 0.78 (m, Si-CH_2, 6H); ^{13}C NMR (100MHz, $CDCl_3$): 157.7, 156.4, 136.0, 133.1, 132.9, 121.0, 118.2, 116.0, 27.0, 26.3, 14.0, 12.5 Anal. Calcd for $C_{24}H_{35}BrOSi$: C, 64.41; H, 7.88. Found C, 64.57; H, 7.91

4.1.5 Preparation of 4-styryl-4'-(tributylsilyl)phenyl ether (Diluent S1). A 200 mL Schlenk flask was charged with 4-bromo-4'-tributylsilyldiphenyl ether (34.48 g, 79 mmol), CsF, (25.28 g, 166 mmol), vinyl tributyltin (27.65 g, 87 mmol), $Pd_2(dba)_3$ (3.63 g, 4.0 mmol), and phosphatrane ligand (2.72 g, 7.9 mmol). The flask was removed from the drybox and NMP (80 mL) was added to the reaction vessel and the mixture was allowed react with stirring at ambient temperature for 16 h. Additional $Pd_2(dba)_3$ (0.3 g, 0.33 mmol)) was added and reaction continued for 6 h. The mixture was diluted with 400 mL ether, filtered, and the solvents removed under reduced pressure. The resulting greenish-yellow oil was then purified by flash chromatography with hexane as the eluent to afford **3** as a colorless-oil (12.5 g, 40 %). ^{1}H NMR (400 MHz, $CDCl_3$): 7.45 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 6.71 (dd, J = 17.6 Hz and 10.9 Hz, 1H), 5.68 (d, J = 17.6 Hz, 1H), 5.21 (d, J = 10.9 Hz, 1H), 1.32 (m, 12H), 0.90 (t, J = 7.2 Hz, -CH_3, 9H), 0.78 (m, $SiCH_2$, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.1, 156.8, 136.3, 135.9, 133.2, 132.5, 127.8, 119.5, 118.1, 113.1, 27.0, 26.3, 13.9, 12.5.

4.1.6 Other materials. U-Nyte XM10181 resin was kindly supplied in powder form by Hydrosize Technologies, Inc. Whereas most resins are only available in liquid form, the availability of powder enabled direct comparisons between resin formulated with styrene and with the newly created phenyl ether alternatives created in this program. Due to the limited supply of this material and the need to retain a simple formulation, it was utilized only for formulating repair resins. To ensure maximum reproducibility and to avoid issues with non-optimized resin formulation, the composite samples used for creating engineered defects were laid up from a commercially available formulation (435 Standard Layup Polyester Resin from U.S. Composites). Glass cloth (SAE styles #7781 and #120) were also obtained from U. S. Composites. Methyl ethyl ketone peroxide (MEKP) and azobis(isobutylnitrile) (AIBN) initiators were obtained from Aldrich Chemical Co. and used as received.

4.2 Typical Procedures for Preparing Composite Layups

4.2.1 Standard polyester layup samples. Three layers of SAE style #7781 glass cloth were cut to 24” x 24” and stacked in a +45°, 0°, -45° orientation sequence. A single ply of SAE style #120 glass cloth was cut to 24” x 24” and laid on top (0° orientation). The Standard Layup Resin (having a green color) was mixed with the manufacturer-supplied catalyst (MEKP) according to manufacturer’s instructions (1.25% by weight) and then applied to the cloth. Wet out of the cloth was induced using a compression roller. Within ~15 min, the resin hardened into a semi-translucent, light green panel. These panels were then cut into 1” x 8” or 2” x 8” strips for subsequent use. The cloth styles and lay up are based on composite radome structures that have been used as a basis for testing repair methods at NADEP Jacksonville.

4.2.2 Repair resin layup samples. Repair resin layups were made in a manner analogous to Standard Resin Layup samples, except that the glass cloth was cut to 8” x 8” in order to conserve material, since the formulations were newly developed. For repair resin **A1**, 1 % of MEKP was used as initiator, while for repair resin **A2**, 1.25% of MEKP was used as initiator. The style and orientation of glass cloth, as well as the fabrication procedure, was indentation to that of the Standard Layup Resin.

4.2.3 Engineered defects. The goal in creating defects was to induce a highly reproducible pattern of damage that would significantly, but not completely, degrade the tensile properties of test specimens. Thus, circular template jigs of ½” in diameter or 1” in diameter were used to carefully punch a hole in the Standard Layup Resin strips. The strip width was always maintained at twice the hole diameter. These engineered defects are a smaller version of the 12” diameter round test sections that are used in depot testing. Repairs at the 12” scale would have precluded mechanical testing and would have consumed more than 100 times the amount of synthesized material; therefore, to fit the scope of the project, the scale of the defects was reduced.

4.2.4 Repair procedure. In order to make the most reliable comparisons between material systems, the repair procedure was designed to be as simple and reproducible as possible while generating at least some improvement in mechanical properties to use as a basis for quantification. The edge of the hole in the Standard Layup Resin strip was carefully cleaned, using gentle mechanical abrasion and by wiping with a damp cloth to remove as much dust as possible. A circle of the style #120 glass cloth was cut to a diameter ½” larger than the defect, aligned (center to center) with the defect, and placed under it as a backing. Circular plies of glass cloth (all oriented at 0° to the longitudinal direction of the test strip and of the same diameter as the defect) were then carefully laid in the hole, using three layers of style #7781. A final, covering layer of style #120 glass cloth consisting of a circle ½" larger than the defect diameter (aligned center-to-center with the defect) was then placed atop the stack. This arrangement roughly parallels the repair procedure used for composite radomes at NADEP Jacksonville at a smaller scale, except that the in-service defect uses a step cut into the composite, rather than a covering patch, to achieve overlap.

The repair resin formulations were based mixtures of the U-Nyte polyester with between 30% and 60% by weight of one of the following: styrene, diluent **A1**, or diluent **A2**. At the time of repair, a pre-specified (1% to 2%) level of MEKP or AIBN initiator was added to the repair resin and stirred briefly. The repair formulation was then poured on to the cloth plies at the defect site and squeezed to wet out the fibers. The entire test strip was then carefully turned over, and additional resin was added to the backing cloth, followed by more squeezing. With a total fiber to resin weight ratio of 3 to 2, both dry areas and excessive resin build-up could be avoided. The repaired strips were then cured by placing in an oven for a pre-determined temperature, time, and atmospheric exposure sequence (typically 1 hour at 100°C under nitrogen).

4.3 Characterization Tests

4.3.1 Evaporation rates. Evaporation rates were determined by placing approximately 35 mg of the reactive diluent in a 6 mm diameter aluminum pan in an enclosed micro-balance (precision 0.00001g) and observing changes in weight. For non-volatile diluents, several days of observation were required, necessitating a correction for the small diurnal variation in weight observed due to temperature and humidity changes.

4.3.2 Viscosity. A mark Ubelode viscometer was used to obtain flow time measurements for both reactive diluents and polyester resin solutions incorporating them. Flow times were calibrated using styrene as a standard, since a direct comparison to styrene was of interest. The known value of styrene viscosity was taken to be 0.9 centipoise (cP) at 20 °C based on the literature and this was used to verify our technique.

4.3.3 Density. ~30 mg samples were weighed to 0.0001 g precision using a Mettler Toledo Analytical balance. The volume of each sample was also measured to a precision of typically 0.0001 mL using an AccuPyc 1330 gas pycnometer, with nitrogen as the chamber gas. Nitrogen is often used in place of helium for polymeric samples due to the high permeability of these samples to helium gas.

4.3.4 Estimated Cure Reactivity. The relative cure reactivity of diluents with varying amounts of initiators was examined using a TA Instruments Q100 Series Differential Scanning Calorimeter (DSC), at a heating rate of 10 °C/min under a 40 mL/min nitrogen purge. The DSC produces a heat flow curve, the onset and maximum of which are used as characteristic "cure" temperatures. A less sophisticated test for cure was done with polyester formulations and composite samples. The samples were exposed to a given set of conditions (temperature, time, and atmosphere) and then tested by contact with a clean absorbent paper. If any traces of absorbed liquid, any significant flow or deformation, or any significant tack or adhesion of the paper were observed, then the sample was considered uncured.

4.3.5 Fiber and unreacted monomer content. The relative weight of glass fibers, polymerized resin, and unpolymerized resin were determined using a TA Instruments Q600 Series Simultaneous Differential Thermal Analyzer (SDT) in the Thermogravimetric Analysis (TGA) mode at a heating rate of 5 °C/min under 40 mL/min. nitrogen purge. The TGA mode measures the amount of weight lost as the sample is heated, producing three distinct mass values: an initial weight loss (generally below 300 °C) due to volatilization of unreacted low molecular weight material, a primary weight loss (300-600 °C) due to decomposition of polymerized resin, and a non-volatile residue at temperatures above 600 °C due to inorganic material (the glass fibers). These values are then converted to weight percentages.

4.3.6 Glass transition (T_g) temperatures and dynamic mechanical data. The glass transition temperature, creep rate, and relative storage and loss modulus values were measured on approximately 1 mm thick samples of resin and/or diluent with initiator cast into 6 mm diameter aluminum pans with the aid of a TA Instruments Q400 Series Thermo-mechanical Analyzer (TMA) using a ~4 mm diameter cylindrical quartz probe with a flat penetrating surface. A heating rate of 2 °C/min and a 40 mL/min. nitrogen purge is utilized. Using a compressive force oscillating with amplitude 0.1 N, average value 0.2 N, and frequency 0.01 Hz, the dimensional change of the sample was monitored. The amplitude and phase of the oscillatory dimension change in relation to the force was then used to determine the storage modulus, loss modulus, and ratio of the two (tan delta). The temperature corresponding to the peak value of the loss modulus was considered the glass transition temperature. The non-oscillatory component of the dimensional change was also computed and used to measure the creep rate as a function of temperature.

Tensile tests strips of material were placed into a dogbone template jig and cut to size with a Tensilkut (model 10 78) high speed router using a solid carbide (#40-75) Sieburg Tensilbit. A standard Instron wedge grip was used to hold the samples that were pulled at 0.05 in/min to a 80% drop in load to indicate failure. Load was applied via an Instron 55R1115 universal mechanical testing machine with 20,000 lb capacity in tension or compression by means of electromechanical screws. The resulting force-displacement curve was used in conjunction with the sample geometry to determine the tensile modulus, failure stress, and failure strain of composite samples, both undamaged, with engineered defects, and as-repaired.

5. Results and Discussion

5.1 Reactive Diluent Syntheses.

The initial and significant challenge in the program was to synthesize the new reactive diluents starting from diphenyl ether. The first target was the styrene-like diphenyl ether analog and this ultimately proved to be quite a synthetic challenge (Figure 5). The phenyl ether analog of styrene (diluent **S1**) was successfully synthesized in batch sizes of up to 12.5 g, which provided an ample supply for characterization purposes. Fortunately, all of the diluents were isolated as pourable liquids, even after purification. Since the physical state of these materials could not be predicted beforehand, the successful synthesis of liquid molecules eliminated one of the most significant risks associated with the project.

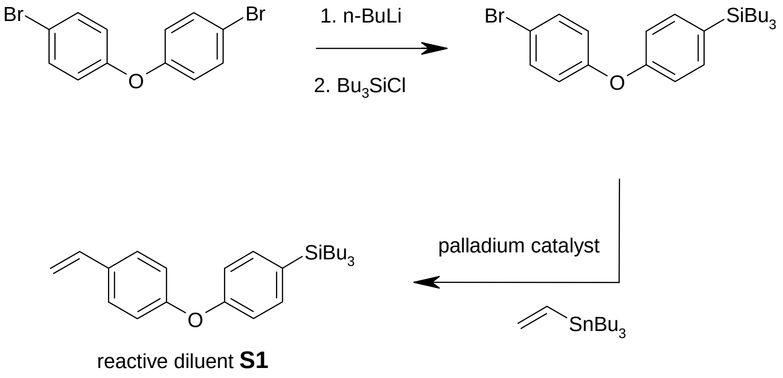
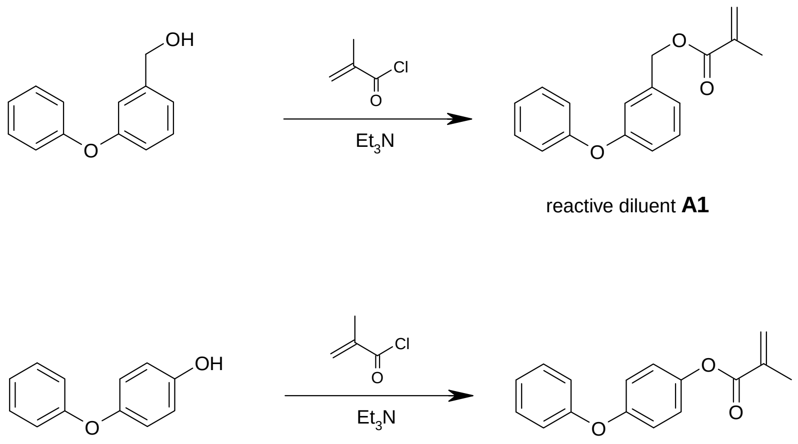


Figure 5. Synthetic scheme for preparing reactive diluent **S1**.

Reactive diluents **A1** and **A2** were accomplished in one step from commercially available phenyl ether derivatives (Figure 6). We did find it more difficult to isolate **A1** in analytically pure form and to do, the final purification required flash chromatography on silica gel. This is somewhat of a drawback to **A1** since column chromatography is difficult to run at large scale (i.e. >100 g).



reactive diluent **A1**

reactive diluent **A2**

Figure 6. Synthetic scheme for the preparation of reactive diluents **A1** and **A2**.

5.2 Physical Properties & Reactivity of Diluents S1, A1, and A2.

With the successful synthesis effort for reactive diluents **S1**, **A1**, and **A2**, we embarked on a set of preliminary evaluations designed to determine their suitability for use in VOC-free composite repair. These evaluations were conducted on a “Pass”/”Fail” basis. A reactive diluent that failed to pass all the tests would not be considered for further study. The test and criteria were as follows: 1) Evaporation rate relative to styrene. This test correlates directly to the expected level of VOC reduction. Any diluent with an evaporation rate more than 10% of styrene (thereby being unlikely to achieve 90% or more reduction in VOC levels) would fail, 2) Viscosity, any diluent with viscosity more than 1,000 cP would fail. Most polyester resin formulations are designed to have viscosities no higher than 1,000 cP prior to cure. Although higher viscosity formulations are useable, a reactive diluent viscosity above 1,000 cP virtually guarantees a resin viscosity at least an order of magnitude larger than current resins, and was therefore considered unacceptable. 3) Self-reaction. Diluents that could not polymerize at a temperature of 100°C or less would fail. 4) Reaction with polyester resin is critical to insure homogeneity of the resin within the repair and it follows that the reactive diluents should cure at a rate comparable to the polyester resin itself.

5.2.1. VOC considerations. In Table 1 we list data that describes the evaporation rates of styrene and our new reactive diluents **S1**, **A1** and **A2**. What is very clear from the data is that the evaporation rates of the diluents are all about four orders of magnitude smaller than for styrene. This quantitative observation was confirmed by experienced gleaned in working with these new reactive diluents. The odor of styrene was noticed immediately whenever samples were briefly removed from laboratory ventilation hoods. On the other hand, essentially no odor could be detected with working with reactive diluents **S1**, **A1**, and **A2**. This was true even when “perfuming” them in still air. All diluents therefore were rated “pass” in this category.

Table 1. Evaporation rates for Water, Styrene and Reactive Diluents.

Reactive Diluent by name/abbreviation	Temperature (^{o}C)	Evaporation rate (mg/min/m^{2})[a]
Water	20	35[b]
Styrene	20	12,600 (500)
S1	20	0.6 (14)
A1	20	1 (1)
A2	20	1 (1)

[a] numbers in parentheses are the standard deviation for the last significant digit(s) reported for the measurement. [b] theoretical evaporation rate given for comparison purposes.

5.2.2 Reactive diluent viscosity. For all three reactive diluents prepared in this study we find viscosities to be ~100 Cp at ambient temperature. There was certainly no surprise we see viscosities ~100 times greater than styrene. With that said, we did find that we could take the solid U-Nyte resin and make homogeneous "solutions" at 30 wt-% of the reactive diluent. These "solutions" were deemed to viscous for use in the composites shop and thus 40 to 50 wt-% reactive diluent was used in making the flat panels. We did not obtain measured viscosities and relied upon the expertise of the composites shop and by qualitative comparisons (ease of wet out and workability during layup) to the commercial styrene based resins.

5.2.3 Self-Reaction of diluents S1, A1, and A2. We conducted cure experiments in a DSC and evaluated the reactive diluents doping samples with AIBN curing agent then heating the samples at 10 ^{o}C/min. If an exothermic event (caused by the polymerization) was detected at an onset temperature of 100 °C or less, the sample was judged as having sufficient polymerization reactivity. We are using the approximation that the onset is roughly correlated to the activation energy required for polymerization (i.e. lower onset temperature indicates a smaller activation energy). For each of the three reactive diluents an exotherm was observed below 100 ^{o}C and in the general terms, each was deemed to pass the self-reaction test by free-radical initiation.

5.2.4 Photo-initiated Cure of S1. We also explored the initiation of polymerization by photo-generated acid in the case of **S1**. Reactive diluent **S1** is the type of styryl monomer that should be susceptible to cationic polymerization based on related electron-rich analogs (e.g. 4-methoxystyrene). Thus, we made films of the reactive diluent on a glass slide and that had been doped with triphenylsulfonium trifluoromethanesulfonate {$Ph_3S(CF_3SO_3)$, ~1 wt-%}, a known photo-acid generator[7] and then irradiated extensively with UV light (254 nm) (Figure 7). After hours of irradiation, no indication of curing/reaction had taken place. At this point we abandoned the idea of photo-curing our reactive diluents.

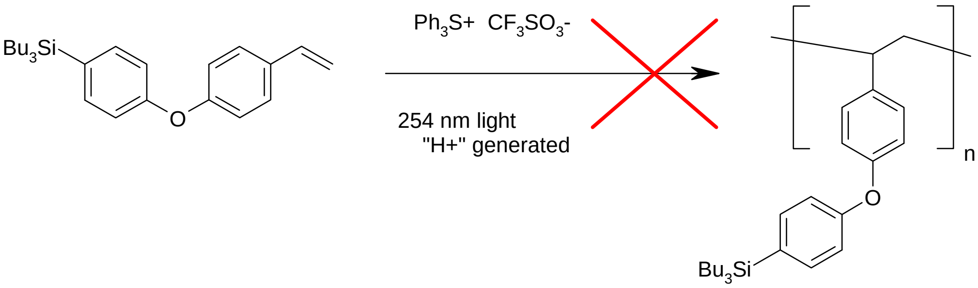


Figure 7. Reaction scheme showing idealized photo-initiated cure of S1. The triphenylsulfonium trifluoromethanesulfonate {$Ph_3S(CF_3SO_3)$} catalyst is a well known and commercially available substrate for the photo-generation of acid (in this case triflic acid).

5.2.5 Reaction (or lack) of reactive diluents with vinyl ester resin. For reactive diluent **S1** we observed that phase separation took place when co-curing with vinyl ester. This phase separation for **S1** took place for a wide variety of initiator types and levels. We verified that indeed the polyester resin was curing and the remaining (i.e. phase separated) material was indeed unreacted **S1** (Figure 8). Although this is most likely dominated by a difference in cure rate, it may also reflect the ability of the reactive diluent to “dissolve” the polyester resin as reaction proceeds. Although the tributylsilyl-group does a very nice job of creating a liquid phenyl ether reactive diluent, it may be promoting phase separation at very early stages of cure. We suspect that other groups in the 4’ or 3’ position could be studied that would still decrease viscosity yet better dissolve the vinyl ester resin.

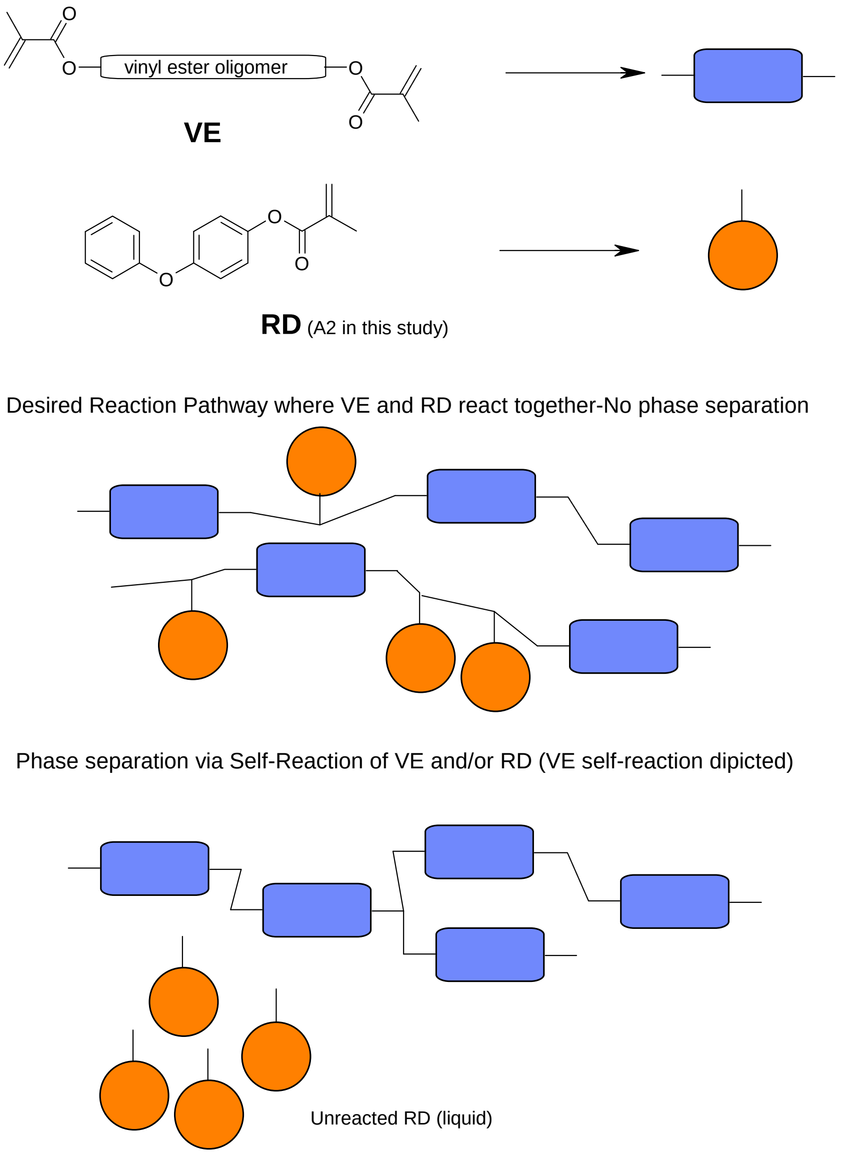


Figure 8. Cartoon showing the desired reaction pathway (as seen for **A2**) and one of self-reaction of VE leading to phase separation of the RD (as seen for **S1**).

We found that reactive diluents **A1** and **A2** did not show phase separation. They formed very nice homogeneous and highly cured materials. Generally, the observation of no phase separation is a reliable indication that the reaction rate with the polyester resin and reactive diluent are similar and that one has a co-cured resin (Figure 8). Given the limited scope of the program, we did not pursue detailed kinetic studies to quantify the reaction rates of the polyester resin with the various reactive diluents. Instead, we simply assigned a “Fail” rating to the mixed reaction test for diluent **S1**, and a “Pass” rating for diluents **A1** and **A2**.

5.3 Physical Data and Reaction Summary.

Table 2 shows a summary of the results for each gate that a reactive diluent must pass through. Diluents **A1** and **A2** passed all tests with either exceptional qualities or acceptable. However, reactive diluent **S1** failed in the mixed reaction test by showing nearly complete phase separation after cure. As a result of these data we down selected to reactive diluents **A1** and **A2** for use in making panels and working repairs. By identifying two diluents that passed the initial series of tests, the risks associated with continued development were greatly reduced.

Table 2. Comparisons and evaluation of styrene and new reactive diluents.

Reactive diluent	Evaporation rate (mg/min/m^2)	Viscosity (cP)	Cure at less than 100 °C	Curable with vinyl ester resin
Styrene	12,600	0.9	Yes	Yes
S1	0.6	~100	Yes	No
A1	1	~100	Yes	Yes
A2	1	~100	Yes	Yes

5.4 Evaluation of A1 and A2/Vinyl Ester Composite Panels

5.4.1 TGA evaluation of composite layups. Samples of the cure glass layups were evaluated using TGA. For **A1** we typically saw a small weight loss above 200 °C and we believe this is a small amount of unreacted **A1** in the composite layup (Figure 9).

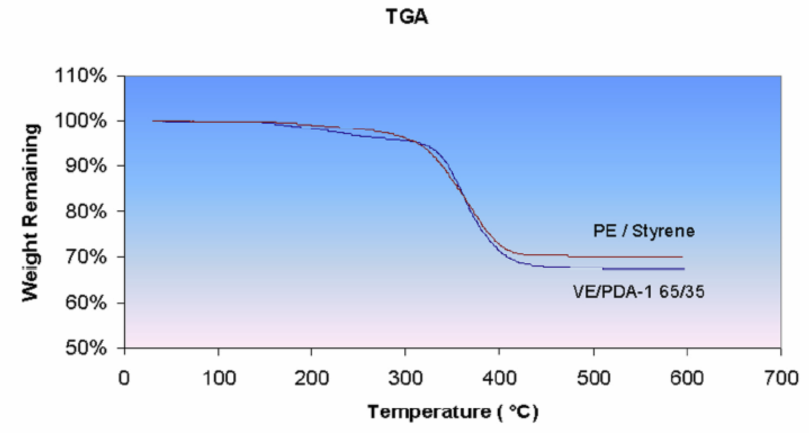


Figure 9. TGA plots for a vinyl ester/styrene and vinyl ester/**A1** layup. Note the weight loss for the **A1** layup starting at ~200 °C.

5.4.2 Stiffness evaluation of reactive diluents A1 and A2. As noted above we seemed to have small amounts of unreacted **A1** in the "cured" composite layups. We investigated changing the mol-% of initiator to search for conditions that would deliver full cure of **A1**. What became very apparent is that regardless of the amount of initiator employed, both the TGA and apparent storage modulus (data below T_g) (Figure 10) indicated that unreacted **A1** remained in the samples. We interpret this as the unreacted **A1** leads to a plasticization of the resin matrix.

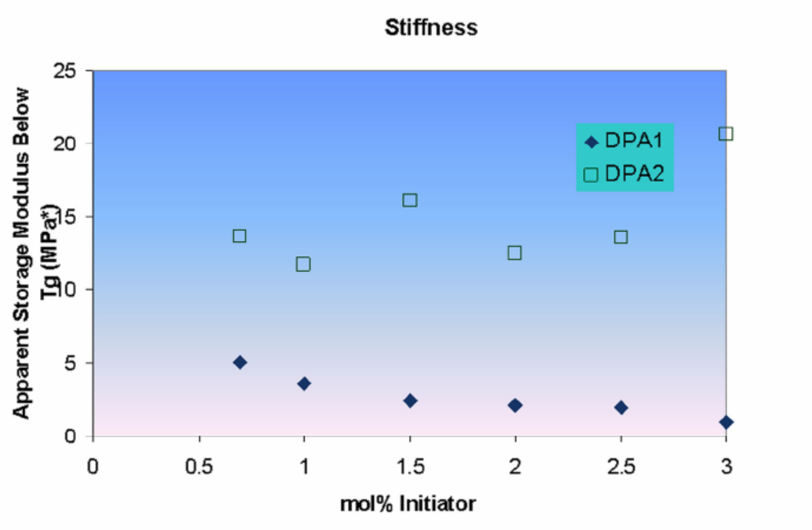


Figure 10. TMA analysis of cured composite resins made from reactive diluent **A1** and **A2** and U-Nyte VE.

This was further confirmed by looking at the Tg for the cured material. In this case we examined only the reactive diluent and samples were cured in the DSC by heating at 100 °C for 1 h and then determining the T_g by a cool down and single ramp up at 10 °C/min. Clearly, no matter what the level of initiator reactive diluent **A1** does not achieve a desirable T_g and/or complete cure (Figure 11).

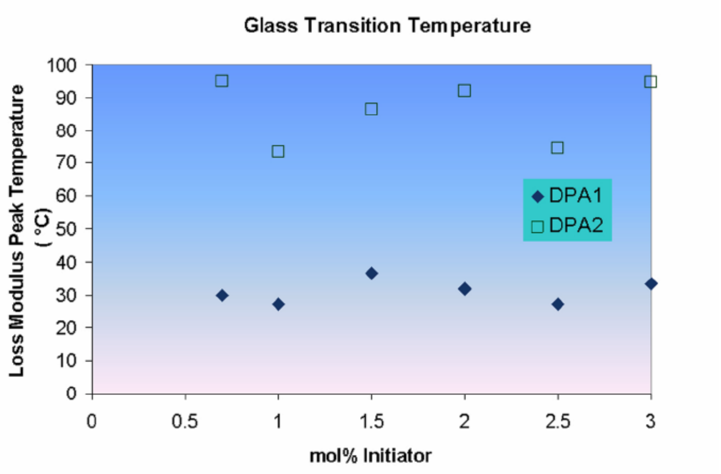


Figure 11. DSC analysis of cured samples for reactive diluents **A1** and **A2** utilizing varying amounts of initiator.

The conclusion from this slight regression in looking at the neat reactive diluents is that **A1** would appear not to be suitable for study in making repairs. Thus, we have further down selected in this study and the remaining work will focus on reactive diluent **A2** for the repair work ahead.

5.5 Initial Repair Studies

5.5.1 Defects and Repair Layout. We initially looked into utilizing 1" wide strips of the composite lay-ups and found that working with and filling the engineered defect far too difficult. Each repair was covered with style #120 E-glass cloth ~1/2" larger than the original defect hole (Figure 12). We choose to use the 2" wide panels with the 1" diameter circular defect placed in the center (Figure 13).

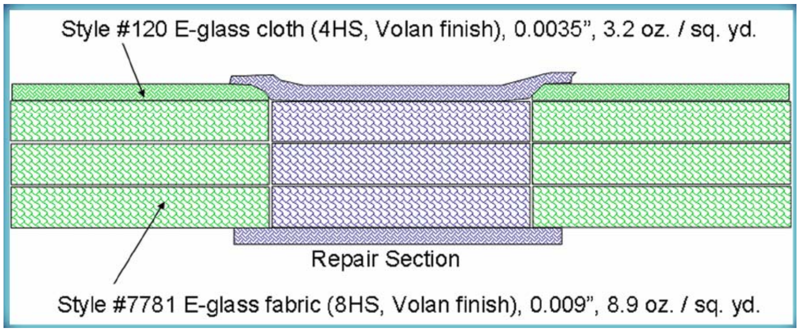


Figure 12. A schematic that illustrates the type and arrangement of E-glass used in our composite repairs.

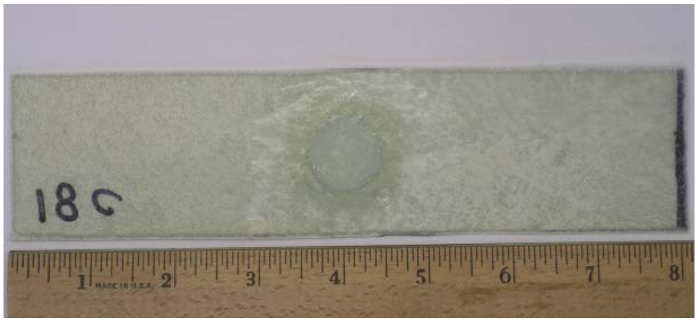


Figure 13. Picture showing a typical 2” x 8” composite layup with a 1” defect hole filled with a repair.

5.5.2 Mechanical testing for repairs made on 2” x 8” panels: A comparison of reactive diluents A2 and Styrene. A typical resin make up for the repairs involved using 50 wt-% of reactive diluent and 50 wt-% of the U-Nyte vinyl ester. The composite repair itself was typically 40 wt-% resin and 60 wt-% E-glass. In general each of the repair resins worked well in terms of wet out, and other than the styrene vapors, it was difficult to distinguish the repair resin characteristics. It is important to note that for repairs, viscosity is important but not at the level scrutinized for resin infusion molding. We do discount or rule out that in fact **A2** could serve in such resin formulations but that is and was beyond the scope of the current proposal.

What was revealed in the mechanical testing is that our repairs were not very effective for both the styrene and **A2** reactive diluents. Certainly some strength was regained by the repair and for each resin they fall within being statistically the same (Figures 14 and 15).

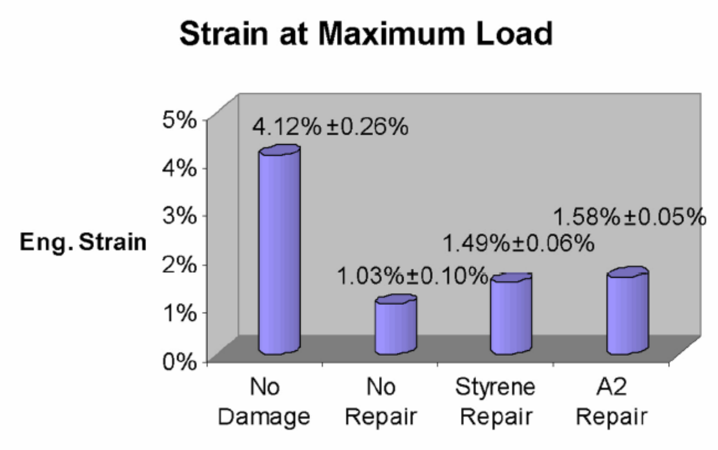


Figure 14. Figure showing elongation at the point of failure.

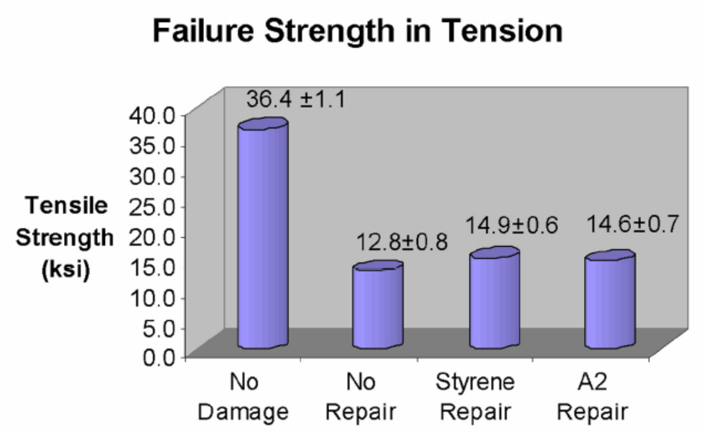


Figure 15. Tensile strength of original panel, open hole, and repairs made with a styrene and **A2** repair resin system.

We measured the density of the repairs as a function of the reactive diluent. For the repairs show above in Figures 14 and 15 we found the densities for the original panel, styrene repair, and **A2** repair to be 1.923(21), 1.647 (32), and 1.874 (4) g/cm^3, respectively. The numbers in parentheses are the estimated error in the last significant digit(s) reported. These data are consistent with the **A2** resin making void-free repairs. Although not shown, micrographs after cutting, polishing, and epoxy modification (dye added to help visualize voids) showed the repairs to be nearly void free.

6. Concluding Remarks

All three reactive diluents prepared in this study were capable of dissolving a relatively high molecular weight VE resin (M_n of ~4000) and the resulting resin solutions (RD + VE) provided excellent wet-out of the glass cloth and workability of the layup. This was all performed in the absence of styrene in what could be referred to as a "VOC free" work environment.

As testing proceeded it was clear that reactive diluent **A2** surfaced as the best candidate for making repairs based on reactivity and mechanical properties. Repairs made with **A2** and the VE resin afforded repairs that behaved nearly identical to the repairs made using styrene as the RD. What became very apparent in this study is that the relatively small engineered defects proved inadequate for truly evaluating the strength & adhesion of the repair resins. This was true regardless of the RD (i.e. styrene or **A2**).

In conclusion, we find that indeed phenyl ether derivatives can form RD that can deliver repair RD/VE resins void of styrene and these resins do cure to form void-free layups with reasonable T_g's (~100 ^oC) based on the VE used in this study. Further work is needed with full scale repair demos (i.e. 12" x 12") and employing the more typical scarfing that can be done at the larger scale. In addition, derivatives of **S1** could be prepared to help promote cationic polymerization (e.g. α-methyl substitution) with little increase in viscosity. And lastly, work should continue to explore other styryl and phenoxy-acrylates based on biofeedstocks such as resorcinol and phloroglucinol. This work has in part demonstrated the value of having an oxygenated aromatic core by providing outstanding solubility of the VE in the RD.

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