

# LIQUID RESINS WITH LOW VOC EMISSIONS

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## ABSTRACT

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. VE resins with no more than 20 wt% styrene were prepared using methacrylate terminated lauric acid. The viscosities of these resins were below 500 cP, allowing the use of vacuum assisted resin transfer molding for composite production. The polymer properties were similar to that of commercial resins, including  $T_g$  greater than 120°C, flex strength greater than 100 MPa, modulus of approximately 3 GPa, and fracture toughness greater than 200 J/m<sup>2</sup>. To prove that these resins can be used to produce large scale structures, a composite hood for an M35-A3 truck was fabricated using a low VOC resin containing 15% fatty acid monomers and only 20% styrene.

Bimodal molecular weight distributions of VE monomers reduce styrene emissions while still maintaining low resin viscosities and high fracture properties. Low molecular weight monomers reduce the resin viscosity while high molecular weight monomers increase the fracture toughness. It was found that resin viscosity decreased exponentially as both the styrene content and the number average molecular weight of the VE monomers increased in the resin. In fact, the viscosity was a predictable function of these variables allowing us to determine the minimum possible styrene content in a given resin. Using bimodal blends, styrene contents as low as 30 wt.% still resulted in similar resin viscosities and fracture properties compared to commercial VE resins with far greater styrene contents.

## 1. INTRODUCTION

Vinyl ester (VE) resins are used to make polymer matrix composites in military and commercial applications because of their good properties, low weight,

and low cost. These resins have superior properties relative to unsaturated polyester (UPE) systems and are less expensive and easier to process than epoxy systems. Vinyl ester resins contain VE monomers and a reactive diluent, such as styrene. The VE monomers have two terminal free-radically polymerizable unsaturation sites, enabling the resin to cross-link. Reactive diluents, such as styrene, have a single vinyl group, and act as linear chain extenders. The reactive diluent is used because it severely reduces the resin viscosity and improves overall polymer properties by allowing for a higher degree of reaction of the monomers by delaying the onset of gelation and reducing diffusion limitations [Flory, 1953]. These properties provided by the reactive diluent also allow for the use of low cost composite fabrication processing methods, such as vacuum assisted resin transfer molding. On the other hand, styrene and other commonly used reactive diluents are volatile organic compounds (VOC) and hazardous air pollutants (HAP).

VOC emissions are liberated during all of the phases of composite fabrication [Fink, et al., 2001]. Unfortunately, even after cure during the lifetime of the part, VOC emissions can be substantial. Past work has shown that up to 50% of the styrene in vinyl ester resins is unreacted after cure [Ziaee and Palmese, 1999]. Because styrene is a HAP and a VOC, the Federal Environmental Protection Agency of the United States of America introduced legislation to limit styrene emissions from composite manufacturing [EPA, 2003]. Therefore, liberation of VOC emissions must be mitigated not only during composite processing, but also during curing and fielding of the composite part. Thus, a means of reducing the styrene emissions from VE resins is desired. Current low VOC VE systems do exist (33% styrene); however, these resins typically have poor performance in general and low fracture toughness in particular.

Unfortunately, decreasing the styrene content in VE resins does not offer an acceptable solution to this problem. As the styrene content is reduced, the fracture toughness decreases and the resin viscosity increases, making it difficult to use inexpensive molding techniques [Huang, 1993]. For example, Dow Derakane 441-400

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uses 27% less styrene than Derakane 411-C50, but has less than half the fracture toughness [Dow, 2000].

Various monomers with volatilities lower than that of styrene have been used as styrene replacements, such as vinyl toluene [Smeal and Brownell, 1994]. First of all, these styrene replacements still produce significant VOC emissions, and are therefore still regulated by the EPA [EPA, 2003]. In addition, few monomers yield resins with properties comparable to styrene based resins, and even fewer can match the low cost of styrene.

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

Simply altering the molecular weight of vinyl ester monomers does not provide a means for both reducing styrene emissions and maintaining resin and polymer properties. Low molecular weight vinyl ester monomers have poor fracture properties because of their high cross-link densities [Huang, 1993]. High molecular weight VE monomers yield resins with high fracture properties via matrix toughening. However, low styrene contents cannot be used because the resin viscosity increases severely and processing becomes unacceptably difficult [Res. Perform. Prod., 2001]. On the other hand, “BM-VE” resins that use a mixture of low and high molecular weight vinyl ester monomers (i.e. bimodal blend) could be used to maintain low resin viscosities and low styrene contents while achieving high fracture toughness.

Fatty acid monomers are excellent alternatives to styrene because of their low cost and low volatility. In addition, fatty acids are renewable resources because they are derived from plant oils. Therefore, not only would the use of fatty acids in liquid molding resins reduce VOC emissions, thereby reducing health and environmental risks, but it also would promote global sustainability. Although plant oil based monomers have been used in a number of polymers, including toughening agents for PVC, plasticizers, interpenetrating polymer networks, and as the cross-linking agent in thermosetting networks, until now, fatty acids have not been used as reactive diluents in thermosetting liquid molding resins.

In this work, we examine the use of fatty acid monomers as styrene replacements and bimodal blends of vinyl ester monomers with reduced styrene content to decrease the emissions from VE and UPE resins. Although it is imperative to reduce styrene emissions from VE and UPE resins, the processing of these resins and their resulting polymer properties must be similar to

that of commercial resins. Therefore, viscometric, thermal, and mechanical characterization of the resulting resins and polymers must be done to assess the ability of these methods reduce styrene emissions from liquid molding resins.

## 2. EXPERIMENTAL

### 2.1 Vinyl Ester Preparation

Vinyl ester monomers were prepared via methacrylation of diglycidyl ether of bisphenol (DGEBA) (Fig. 1) [Malik, et al., 2000]. Epon 828, 1001F, 1004F, 1007F, and 1009F (Miller-Stephenson) were used as the source of DGEBA. To determine the epoxy equivalent weight, epoxy titration was performed as per ASTM D1652-90, Procedure B. The epoxy resin was dissolved in 15 mL methylene chloride (Aldrich) and 10 mL tetraethylammonium bromide solution (Aldrich, 0.4 g/mL). The sample was titrated with the perchloric acid/peracetic acid solution (Aldrich) until the indicator, 0.1% crystal violet in acetic acid (Aldrich), changed color from blue to green. The epoxy titration results agreed well with literature values for the epoxy equivalent weight [Res. Perform. Prod., 2001].

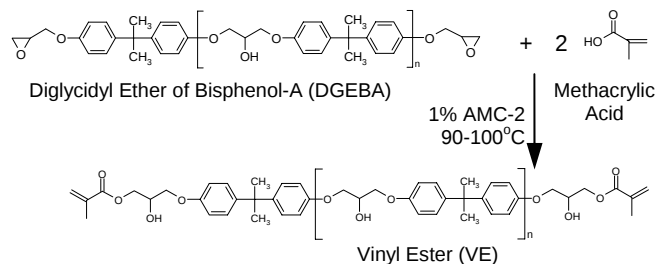


Figure 1: The methacrylation of DGEBA to form vinyl ester monomer.

VE 828 was prepared via methacrylation of Epon 828. Approximately 500 g Epon resin was reacted with 1.01 times the stoichiometric amount of methacrylaic acid (Aldrich) (i.e. as determined through epoxy titration). AMC-2 (Aerojet Chemicals), which is a mixture of 50% trivalent organic chromium complexes and 50% phthalate esters, was used as a catalyst for the reaction and to prevent epoxy homopolymerization [Aerojet Chemicals, 2000] in the amount of 1 wt.%. The reaction was run at 90°C. Acid number titration was used during the course of the reaction to measure the amount of free (unreacted) acid in the VE system. The acid number tests were performed in accordance with ASTM D1980-87. The reaction was run until an acid number (mg NaOH/g VE) of 5, corresponding to ~2% free acid, was achieved.

Bimodal blends of VE monomers were prepared by methacrylation of blends of Epon 828, used as the low

molecular weight DGEBA, and 1001F, 1004F, 1007F, or 1009F as the high molecular weight DGEBA. Approximately 200 g Epon 828 was added to the reactor. Approximately 100 g styrene (20 wt.%) was added to the reaction vessel to help dissolve the Epon 100XF. The reaction vessel was sealed and stirred vigorously with the mechanical mixer. While heating to 100°C, the desired content of Epon 100XF was added to the reactor in aliquots over the course of one hour to prevent excessive clumping of the solid Epon 100XF. In addition, 1.01 times the stoichiometric amount of methacrylic acid along with 1 wt.% AMC-2 catalyst (based on Epon and methacrylic acid masses only) were added to the reactor. Hydroquinone (Aldrich) in the amount of 1000 ppm based on the entire reaction contents was added to prevent gelation. The reaction temperature was kept in the range of 90-95°C. Once the acid number was approximately 5, the reaction was ended.

Fourier transform infrared spectroscopy (FTIR) was used to measure the extent of methacrylation [Brill and Palmese, 2000]. A Thermo Nicolet Nexus 670 FTIR was used in absorbance mode, taking 16 scans per spectrum with a resolution of 4 cm<sup>-1</sup>. The FTIR spectra of these resins indicated that all of the epoxide groups (917 cm<sup>-1</sup>) reacted, and methacrylate groups (942 cm<sup>-1</sup>) were present in the resin.

Size exclusion chromatography (SEC) was run on the VE samples to determine VE molecular weight and styrene content. A Waters 515 GPC was used with two 5 µm styrene-divinyl benzene columns in series. The columns were equilibrated and run at 45°C using tetrahydrofuran (THF) (Aldrich) as the elution solvent at a flow rate of 1 mL/minute. The column effluent was monitored by two detectors operating at 25°C: a Waters 2410 refractive index detector and a Waters 2487 dual absorbance detector operating at 270 nm and 254 nm (absorbed by phenyl rings). Samples were prepared by dissolving 2 mg sample in 1 mL THF.

To measure the molecular weights of VE resins using SEC, the molecular weight as a function of retention time was calibrated using Epon resin samples. The calculated number average molecular weights agreed well with the literature values [Res. Perform. Prod., 2001]. For the bimodal blends, the relative areas of the peaks and the two different number average molecular weights were used to simply calculate the number average and weight average molecular weights. The styrene content was calculated by measuring the area of the low molecular weight peak at 18 min relative to the area of the VE peaks from 12-16 min. VE 828 standards with 30-50 wt.% styrene were prepared and tested to calibrate SEC results. Using this calibration curve, the styrene content in commercial resins was measured. In all cases, the results

agreed within 1% of the initial styrene concentration in the VE (Table 1).

NMR was run on commercial VE resins to verify the styrene content and VE molecular weight. The NMR spectra of VE 828 with known styrene contents were also measured to determine the accuracy of this method. The method used is described in the literature [Ziaee and Palmese, 1999]. The measured values of M<sub>n</sub> and styrene content agreed well with the expected values.

Derakane 411-C50 and 441-400 (Dow) were analyzed in this manner along with the VE 828 and bimodal blends of VE resins. The experimental results for Derakane resins and the VE 828 resin were similar to the literature results (Table 1) [Ziaee and Palmese, 1999; Dow, 2000; Brill and Palmese, 2000]. The styrene mole percent was calculated using the ratio of the methacrylate groups to the ratio of the styrene methylene group. The agreement between literature and experiment was good. Furthermore, VE 828 with 30 wt% styrene was determined to have 29 wt% styrene using NMR, proving the validity of these methods.

Table 1: The VE molecular weights and styrene contents.

| Resin             | VE M <sub>w</sub><br>(g/mol) | VE M <sub>n</sub><br>(g/mol) | Styrene<br>Content<br>(wt.%) |
|-------------------|------------------------------|------------------------------|------------------------------|
| 828 + 30% styrene | 550 ± 50                     | 540 ± 10                     | 29 ± 3                       |
| 1001F             | 1250                         | 1250                         | N.A.                         |
| 1004F             | 1970                         | 1970                         | N.A.                         |
| 1007F             | 4150                         | 4150                         | N.A.                         |
| 1009F             | 5720                         | 5720                         | N.A.                         |
| 828/1001F 29/71   | 867 ± 60                     | 802 ± 20                     | 16.5 ± 2                     |
| 828/1004F 42/58   | 1370 ± 70                    | 933 ± 20                     | 16.5 ± 2                     |
| 828/1007F 53/47   | 2257 ± 90                    | 920 ± 30                     | 19.5 ± 2                     |
| 828/1009F 50/50   | 3130 ± 100                   | 987 ± 20                     | 19.5 ± 2                     |
| Derakane 411-C50  | 1320 ± 60                    | 880 ± 50                     | 45 ± 3                       |
| Derakane 411-350  | 1540 ± 60                    | 960 ± 50                     | 45 ± 3                       |
| Derakane 441-400  | 720 ± 50                     | 700 ± 20                     | 29 ± 3                       |

## 2.2 Fatty Acid Monomer Preparation

Fatty acid (FA) monomers are derived from plant oils, such as soybean oil, which are composed of over 99% triglyceride molecules [Liu, 1997]. Triglycerides are composed of three fatty acids connected by a glycerol center. A number of synthetic procedures have been established for making fatty acid-based monomers to be used as the reactive diluent in VE resins [Palmese, et al., 2004]. Fig. 2 depicts the synthetic route used to form the methacrylated lauric acid (MLau). The carboxylic acid of fatty acids undergoes a simple addition reaction with the epoxide group of glycidyl methacrylate to form a single product. Stoichiometric quantities of lauric acid and glycidyl methacrylate were mixed together and reacted at 70°C for 2.5 hrs using 1 wt% AMC-2 catalyst. FTIR and <sup>1</sup>H-NMR (250.13 MHz, spectral window of ± 2000 Hz,

0.427 Hz/pt digital resolution, 16 scans at 293 K, 90° pulse width) with a Bruker (Billerica, MA) AC250 Spectrometer showed that methacrylation of the fatty acids went to completion. Each MLau 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 MFA is a fairly long hydrocarbon (20 atoms). The effect of fatty acid chain length and unsaturation level are presented elsewhere [La Scala, et al., 2004].

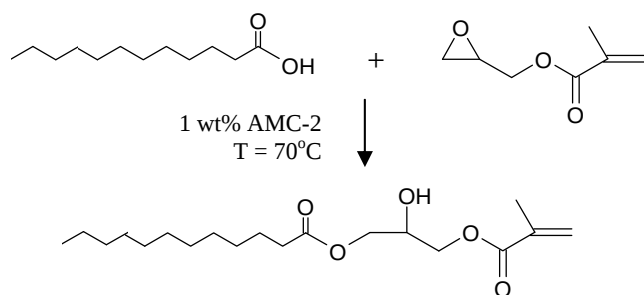


Figure 2: The scheme to produce MFA monomers.

### 2.3 Resin Viscosity

The viscosities of the resins were measured using a Brookfield digital viscometer in Couette geometry (i.e. concentric cylinders). Approximately 8 ml of the sample were placed into the sample holder. The appropriate spindle and shear rate were selected to maximize the allowable torque. All samples were run at 30°C.

### 2.4 Resin Cure

VE resins containing 35 wt% and 45 wt% MLau were prepared. “FA-VE” resins were prepared using VE monomer, MLau, and styrene. These resins contained 65 wt% and 55 wt% vinyl ester monomer. The balances of the resins were made up of MLau and styrene, and the content of each reactive diluent was varied from 0% to 100% of the balance. Various bimodal blends were prepared with styrene contents varying from 30-45 wt%. All resins were initiated using trigonox 239A (Akzo Nobel Chemicals), containing 45% cumene hydroperoxide, and cobalt naphthenate (CoNap) (Aldrich) as a catalyst to promote room temperature cure. The trigonox and CoNap masses used were 1.5% and 0.375%, respectively, of the total resin mass. All resins were allowed to cure at room temperature for 16 hours. Flexural and fracture toughness samples were also post-cured at 130°C for 3 hours prior to testing.

### 2.5 Polymer 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  $\mu$ m while ramping the temperature from 30°C to 200°C at a rate of 5°C/min. Three temperature ramp experiments were run for each sample. The first ramp usually completely post-cured the polymer, but another ramp was performed to ensure this. 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. The point at which the modulus in the rubbery plateau began to increase with increasing temperature was used to calculate the molecular weight between cross-links,  $M_c$ . The theory of Rubber Elasticity was used to calculate  $M_c$  (Eq. 1):

$$E = 3RT\rho/M_c \quad (1)$$

$E$  is the rubbery modulus,  $R$  is the ideal gas constant,  $T$  is the absolute temperature, and  $\rho$  is the sample density [Palmese and McCullough, 1992].

Flexural tests were performed to determine the modulus of elasticity and flexural strength in accordance with ASTM D790-92, Test Method I, Procedure A. The samples had dimensions of 130 x 13 x 3 mm<sup>3</sup> and were tested flat-wise on a support span, resulting in a support-to-depth ratio of 16. The samples were tested using an Instron 5500R at a crosshead speed of 0.5 in/min. All tests were performed at 22°C and 25% relative humidity.

Three-point single-edge notch bend (SENB) specimens were used for fracture toughness measurements. ASTM 5045-93 specifies that the sample dimensions of 2.00 x 0.50 x 0.25 in.<sup>3</sup> to assure plain strain conditions. An initial crack was made by notching the specimens a distance of half their depth. A sharp razor blade was used to initiate a crack at the base of the notches. The samples were tested using an Instron 4505 in flexural mode at a crosshead speed of 0.05 in/min. An un-notched sample was run in the same manner twice during the course of the experiment to account for system compliance, loading pin penetration, and sample compression. All testing was done at ambient conditions.

## 3. RESULTS AND DISCUSSION

### 3.1 Monomer and Resin Viscosity

The viscosity decreased exponentially with styrene content for all bimodal blends (Fig. 3). Styrene is a non-polar small molecule that acts as a solvent and decreases the intermolecular interactions among the larger and more polar vinyl ester monomers. In addition, the viscosity decreased as the molecular weight of the bimodal blend decreased. This result was expected because the viscosity of epoxy resins increases with the molecular weight of the

monomer [Res. Perform. Prod., 2001]. Increased chain entanglements and a decrease in the degrees of freedom of the vinyl ester monomers caused this viscosity increase with molecular weight [Macosko, 1994].

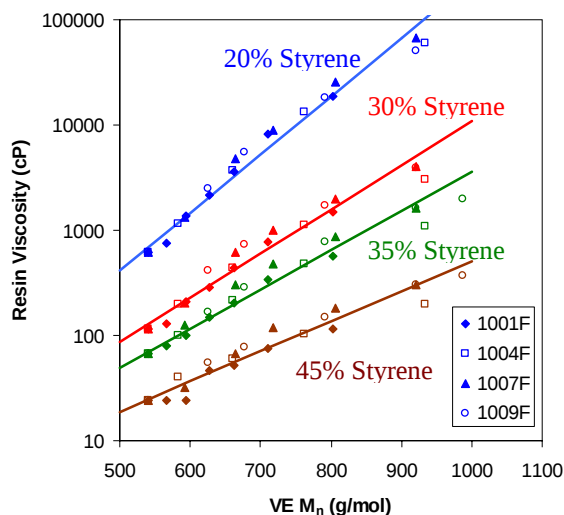


Figure 3: The viscosity of VE bimodal blends as functions of styrene weight percent and  $M_n$  of the vinyl ester monomers.

The number average molecular weight of the VE monomers governs the resin viscosity. For all bimodal blends, the resin viscosity is a single function of the number average molecular weight of the vinyl ester monomers for constant styrene contents (Fig. 3). Therefore,  $M_n$  can be used to normalize the resin viscosity for the particular DGEBA used. Similar results were not found when normalizing with the viscosity average or weight average molecular weight.

The best fit lines in Figure 3 represent a simple expression for the resin viscosity ( $\eta$ ) as a function of number average molecular weight and styrene content. The relationship is (Eq. 2):

$$\eta = \eta_{\text{Styrene}} \cdot \text{Exp} \left[ \frac{M_n}{46.7 \cdot \text{Exp}(2.63 \cdot S)} \right] \quad [\text{cP}] \quad (2)$$

$\eta_{\text{Styrene}}$  is the viscosity of styrene (i.e. 0.7 cP, the viscosity when the vinyl ester molecular weight is zero), and  $S$  is the styrene weight fraction. The form of the relationship implies that we are modeling the effect of the addition of a more viscous, higher molecular weight species on the styrene viscosity. Eq. 2 shows that resin viscosity is proportional to the exponential of the number average molecular weight and proportional to the exponential of the inverse of the exponential of the styrene fraction.

A viscosity of 500 cP is considered about the maximum for most inexpensive liquid molding techniques [Malik, et al., 2000]. Higher viscosities increase the production time and increase the likelihood of voids in the part. Equation 5 can be rearranged to solve for the minimum styrene content required to achieve such a viscosity for given values of  $M_n$ . Table 2 shows that the minimum styrene content increased approximately linearly with the number average molecular weight of the VE monomers. The number average molecular weights can be achieved by mixing certain amounts of VE 828 with a corresponding amount of higher molecular weight VE monomer. For example, to formulate a resin with only 30 wt.% styrene, an  $M_n$  of 675 g/mol can be achieved by blending as much as 78 wt.% VE 828 with 22wt.% VE 1009F or as little as 62 wt.% VE 828 with 38 wt.% 1001F. Table 2 shows that a minimum styrene content of 20 wt.% is necessary to achieve a viscosity of 500 cP for DGEBA-based vinyl ester resins (i.e. the minimum molecular weight of 520 g/mol for DGEBA based vinyl esters occurs when  $n=0$  (Fig. 1)).

Table 2: The minimum allowable styrene content to achieve a viscosity of 500 cP or lower at 30°C for various values of the number average molecular weight of the VE monomers.

| $M_n$ of VE (g/mol) | Minimum Styrene Content (wt.%) |
|---------------------|--------------------------------|
| 520                 | 20.0                           |
| 600                 | 25.5                           |
| 650                 | 28.5                           |
| 700                 | 31.3                           |
| 800                 | 36.4                           |
| 900                 | 40.9                           |

The viscosities of the MLau monomers were approximately 60 cP. This is considerably higher than that of styrene (0.7 cP). The viscosities before cure were 800 cP and 1720 cP for VE resins using 45 wt% and 35 wt% MLau, respectively. Not surprisingly, these viscosities were considerably higher than VE/styrene resins (~50 cP). To reduce the viscosity, blends of MFA and styrene were used as the reactive diluent in VE 828. The viscosity of the FA-VE resins was found to decrease exponentially with styrene content for resins containing 55 wt% and 65 wt% VE 828 resin (Fig. 4). Styrene contents of less than 10% reduced the viscosity of VE resins to the acceptable range. Therefore, only low styrene contents are necessary, from a viscosity point of view.

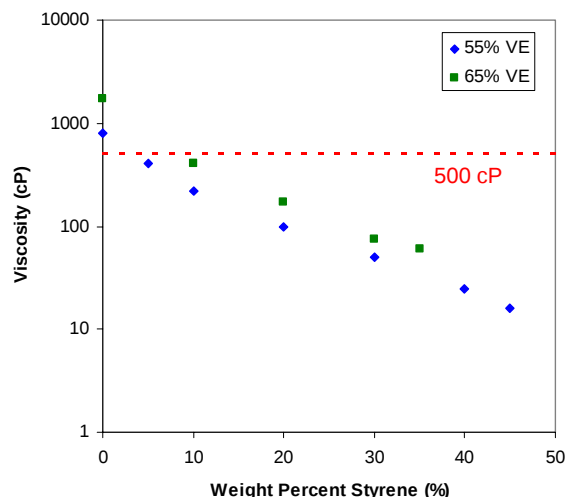


Figure 4: The viscosity of FA-VE resins as functions of vinyl ester monomer and styrene weight percent.

### 3.2 Polymer Properties

Dynamic mechanical properties were affected by the molecular weight of the bimodal blends and the styrene content. As the number average molecular weight of the bimodal resin increased,  $T_g$  decreased because  $M_c$  increased. Samples with the same  $M_n$  and styrene content had  $T_g$  within 3°C of each other. As the molecular weight of the resin increased, the distance between cross-links increased causing the network to become less rigid. However, the effect of bimodal blend molecular weight on polymer properties is fairly small, as  $T_g$  decreased only from 142°C to 125°C as  $M_n$  increased from 540 g/mol to 950 g/mol. For the same reasons,  $T_g$  decreased and  $M_c$  increased as the styrene content increased.  $T_g$  and  $M_c$  were not functions of  $M_w$ . The storage modulus was not significantly affected by the molecular weight of the VE monomers or the styrene content.

The fracture toughness of vinyl ester bimodal blends was measured. Current results show that fracture toughness did not scale with either vinyl ester molecular weight or styrene content. In most cases, the fracture toughness of the blend exceeded that of monodisperse vinyl esters with similar molecular weights. Furthermore, it is evident that very high fracture toughness values can be achieved, even using fairly low styrene contents (Table 3). For example, VE 828/1007F 78/22 with 33 wt% styrene had a  $G_{IC}$  of 350 J/m<sup>2</sup>, which is approximately 3 times that of VE 828 with 45 wt% styrene, while using one-third less styrene. In addition, the fracture toughness of this resin and a few other blends are even higher than that of Derakane 411-C50 (Table 3). All of the blends had higher fracture toughness values than Derakane 441-400 while using similar low styrene contents. When using higher styrene contents similar to that used in

Derakane 411-C50, very high fracture properties are possible (Table 3). Overall, these results show that it is possible to tailor vinyl ester molecular weight to achieve good fracture properties, and maintain resin viscosity while reducing VOC emissions by ~20%.

Table 3: The fracture toughness and viscosities of BM-VE resins relative to monodisperse VE resins and commercial resins.

| Sample             | Styrene Content (wt%) | Viscosity (cP) | $G_{IC}$ (J/m <sup>2</sup> ) |
|--------------------|-----------------------|----------------|------------------------------|
| VE 828             | 35-45                 | 50             | ~80                          |
| Derakane 441-400   | 33                    | 400            | 110                          |
| VE 828/1009F 85/15 | 35                    | 165            | 190                          |
| VE 828/1009F 78/22 | 37                    | 200            | 210                          |
| Derakane 411-C50   | 45                    | 200            | 240                          |
| VE 828/1001F 29/71 | 37                    | 500            | 250                          |
| VE 828/1007F 78/22 | 33                    | 400            | 350                          |
| VE 828/1009F 78/22 | 45                    | 77             | 440                          |
| VE 828/1001F 29/71 | 43                    | 150            | 510                          |

Polymers using MFA monomers produced hard and rigid polymers, similar to that of commercial VE polymers. However,  $T_g$  values and storage moduli were less than 100°C and 2 GPa, respectively. Ternary blends of VE, MFA, and styrene were used to improve the thermo-mechanical properties relative to VE/MFA resins while still having low VOC emissions. The DMA character of these ternary resins improved as the styrene content increased. The storage modulus at a given temperature and the temperature at which the peak in the loss modulus occurred increased as the styrene content in the ternary blend increased. Fig. 5 shows that  $T_g$  improved in a linear fashion with increasing styrene content. These results show that 10%-15% is sufficient for FA-VE resins. Furthermore, at these styrene contents, the resin viscosity is well within the acceptable window for vacuum infusion and other traditional composite infusion methods.

When using MLau as the only reactive diluent, the flexural properties were considerably lower than that of styrene-based vinyl ester resins. Replacing some of the styrene with MFA resulted in properties intermediate between MFA-based and styrene-based resins. For samples with 35% reactive diluent, the flexural strength increased from 83 MPa (VE/MLau) to 134 MPa (VE/styrene), while the flexural modulus increased from 2.59 GPa (VE/MLau) to 4.02 GPa (VE/styrene). This property improvement was larger for samples with 45% reactive diluent as the flexural strength increased from 61 MPa to 139 MPa and the modulus increased from 1.9 GPa to 3.9 GPa as the styrene content in the ternary blend increased. In all cases, the flexural strength and moduli of the ternary systems were slightly greater than a linear increase. This is due to the fact that ternary blends have a higher extent of cure than their binary counterparts [La Scala, 2004]. Only 10% styrene is required in the ternary

blends to increase the flexural modulus to 3 GPa and the flexural strength to 100 MPa or greater. Therefore, using MLau to replace some styrene in VE resins still resulted in good flexural properties, while significantly reducing styrene emissions. In addition, Derakane 411-C50 was found to have similar flexural strength and modulus as found in the literature (3.4 GPa and 145 MPa) [30], and its properties are also similar to VE 828 with 45 wt% styrene.

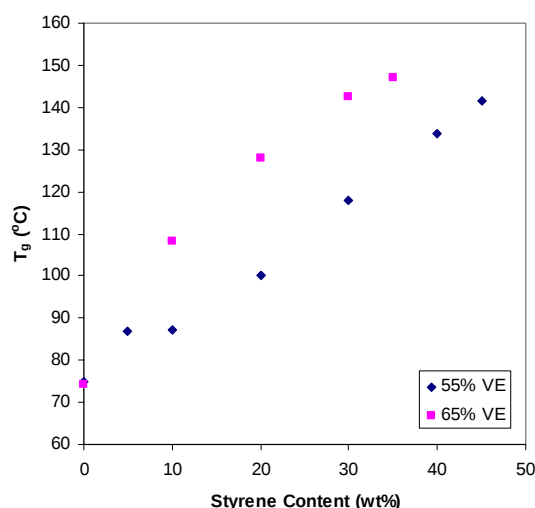


Figure 5:  $T_g$  as a function of styrene content for VE/MLau/styrene blends.

The fracture properties of fatty acid based vinyl esters was also affected by the reactive diluent used (Fig. 6). The fracture properties of fatty acid VE resins ( $148 \text{ J/m}^2 \pm 35 \text{ J/m}^2$ ) were greater than that of styrene-based VE resins ( $G_{IC} = 85 \text{ J/m}^2 \pm 35 \text{ J/m}^2$ ). The reason for this has to do with the fact that vinyl ester monomers react to a fairly low extent (i.e. 70%) with styrene as the reactive diluent relative to when fatty acid monomers are used (i.e. 85%) [La Scala, 2004]. Thus, there were fewer defects, such as dangling chain ends, in fatty acid resins [Wool, 1995]. Furthermore, the fairly high content of unreacted free monomer in fatty acid resins (~35%) acted as a plasticizer and toughened the polymer [La Scala, 2004]. Ternary blends of VE, styrene, and fatty acid monomers produced polymers with better fracture properties than the binary counterparts (Fig. 6). This occurred because of a combination of fewer defects and higher moduli. The fatty acids allowed for high vinyl ester monomer conversion, while the styrene caused a high overall conversion, resulting in a lower content of dangling chain ends relative to the binary blends. Fracture theories, such as vector percolation, show that fracture properties increase with increasing modulus if the connectivity of the polymer is unaffected [Wool, 1995]. As shown previously, increasing the styrene content increased the rigidity of the ternary blends, therefore causing an increase in the fracture properties. Overall, these results

show that it is possible to replace up to 78% of the styrene in VE and UPE resins with fatty acid monomers while still maintaining good polymer performance.

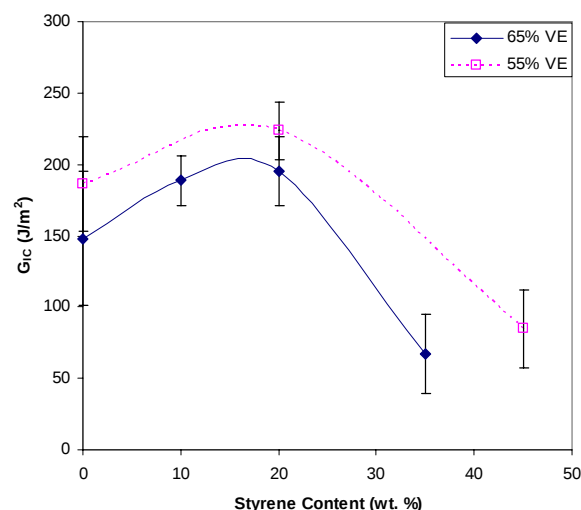


Figure 6: Fracture toughness of VE/MLau/styrene as a function of styrene content in the resin for resins containing 55 wt% and 65 wt% VE 828.



Figure 7: Photographs of (a) the unpainted composite hood and (b) the hood affixed on an M35-A3 truck. The blue stripes are PVC foam stiffeners that are fabricated into the part.

### 3.3 Composites

Composite fabrication and testing is currently underway. Mechanical data is being generated to evaluate fiber-matrix interfacial properties and investigate effectiveness of the new resins in composite laminate enhancements. This on-going research will demonstrate translation of resin properties to mechanical performance of composites with compatible sizing finishes. In addition, the Naval Surface Warfare Center, Carderock, MD is demonstrating the effectiveness of the FA-VE resin as a drop-in replacement for commercial VE resins by producing a hat-stiffened section of the hull structure designed for use in DD(X) style surface ships.

To prove that these resins can be used to produce large scale structures, a composite hood for an M35-A3 truck (Fig. 7) was fabricated using a low VOC resin containing 15% fatty acid monomers and only 20% styrene. The resin completely infused the part in less than 30 minutes, which is very quick for such a large structure (7 ft x 7ft). The part cured well to produce a fine composite structure. Therefore, successful low VOC resins are not merely a concept, but instead are reality.

#### 4. CONCLUSIONS

The military and commercial industry has a large need for high performance thermosetting resins with reduced VOC emissions. Previously developed solutions to the emissions problem are not acceptable because the resins still produce large amounts of VOCs or composite performance is severely reduced. The Army's solutions to these problems involve modifying the molecular structure of the cross-linker molecules and using plant derived fatty acid monomers as styrene substitutes. These solutions allow for emissions reductions of up 78%, while producing resins that have comparable, and in some cases, superior properties to commercial resins. Therefore, these solutions will help enable the Army and the entire military produce the next generation of lighter, more efficient, and environmentally compliant vehicles, ships, and structures.

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