



Successful Initial Development of Styrene Substitutes and Suppressants for Vinyl Ester Resin Formulations

**by John J. La Scala, Eric J. Robinette, Giuseppe R. Palmese,
James M. Sands, Joshua A. Orlicki, and Matthew S. Bratcher**

ARL-TR-3023

August 2003

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Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) August 2003		2. REPORT TYPE Final		3. DATES COVERED (From - To) FY 2002	
4. TITLE AND SUBTITLE Successful Initial Development of Styrene Substitutes and Suppressants for Vinyl Ester Resin Formulations				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) John J. La Scala,* Eric J. Robinette,* Giuseppe R. Palmese,* James M. Sands, Joshua A. Orlicki, and Matthew S. Bratcher				5d. PROJECT NUMBER 622618.H80	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Strategic Environmental Research and Development Program 901 N. Stuart St., Ste. 303 Arlington, VA 22203				8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-3023	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRL-WM-MB Aberdeen Proving Ground, MD 21005-5069				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 * Drexel University, Department of Chemical Engineering, Philadelphia, PA 19104					
14. ABSTRACT Recently, the U.S. Environmental Protection Agency increased legislation to address hazardous emissions from composite manufacturing and repair by enacting new emission standards through the "National Emission Standards for Hazardous Air Pollutants: Reinforced Plastic Composites Production," which specifically targets styrene as a regulated hazardous air pollutant. Volatile organic compound emissions are liberated during all phases of composite fabrication. Three means of reducing the styrene emissions are proposed and investigated in this report, including using a bimodal blend of vinyl ester (VE) monomers to reduce viscosities, replacing styrene with low-volatile petroleum or fatty acid (FA)-based monomers, and incorporating self-assembling vapor barriers using surface-active dendritic polymers to suppress styrene emissions. Each approach for reducing styrene emission shows considerable promise, bimodal VE monomer formulations to petroleum-based substitutes, such as cyclohexyl methacrylate, to renewable organic monomers based on FA derivatives proved successful at reducing styrene emission rates. The least progress was achieved in determining dendritic monomers capable of remaining intermixed in the resin and still actively sealing the surface against vapor losses. The specific formulation details and the approaches necessary to meet cost restrictions are also considered.					
15. SUBJECT TERMS vinyl ester, styrene monomer, substitute monomers, fatty acid, VARTM, composite					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES 62	19a. NAME OF RESPONSIBLE PERSON James M. Sands
a. REPORT UNCLASSIFIED	b. ABSTRACT UNCLASSIFIED	c. THIS PAGE UNCLASSIFIED			19b. TELEPHONE NUMBER (Include area code) 410-306-0878

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1. Introduction

Recently, the U.S. Environmental Protection Agency (EPA) increased legislation to address hazardous emissions from composite manufacturing and repair by enacting new emission standards through the “National Emission Standards for Hazardous Air Pollutants: Reinforced Plastic Composites Production,” which specifically targets styrene, methyl methacrylate, and methylene chloride as regulated hazardous air pollutants (HAP). Volatile organic compound (VOC) emissions are liberated during all phases of composite fabrication (Figure 1). Styrene emissions occur during the mixing of diluents, catalysts, and initiators into the system. Composite parts typically have very large surface-to-volume ratios, which allow up to 20% of the styrene content to be lost during the molding stage. During cure, elevated temperatures increase the vapor pressure of styrene and thus increase the rate of VOC emissions. Unfortunately, even after cure during the lifetime of the part, styrene emissions can be substantial. Past work has shown that up to 50% of the styrene is unreacted after cure (1). Therefore, liberation of VOC emissions must be mitigated not only during composite processing, but also during curing and fielding of the composite part.

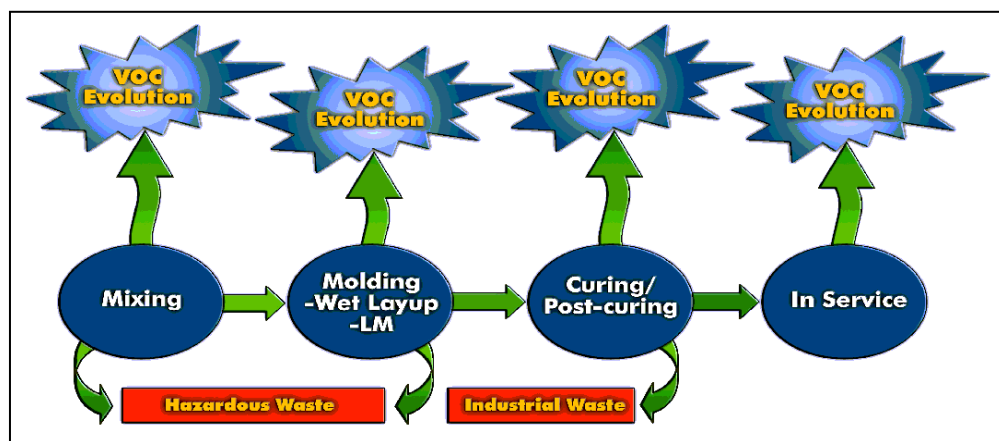


Figure 1. Life cycle sources of pollution associated with composite materials processing. Impact originates from initial fabrication, repair, and potential during service.

The technical objective of the program is to research, develop, and demonstrate low VOC emission, high-performance vinyl ester (VE) resins to comply with the new EPA regulations. Three methods have been formulated for reducing VOC emissions in VE resins (Figure 2):

- Reduction of styrene content by use of bimodal molecular weight distribution of VE monomers,
- Substitution of styrene with low molecular weight alternatives, and
- Suppression of emissions with in situ formed vapor barrier.

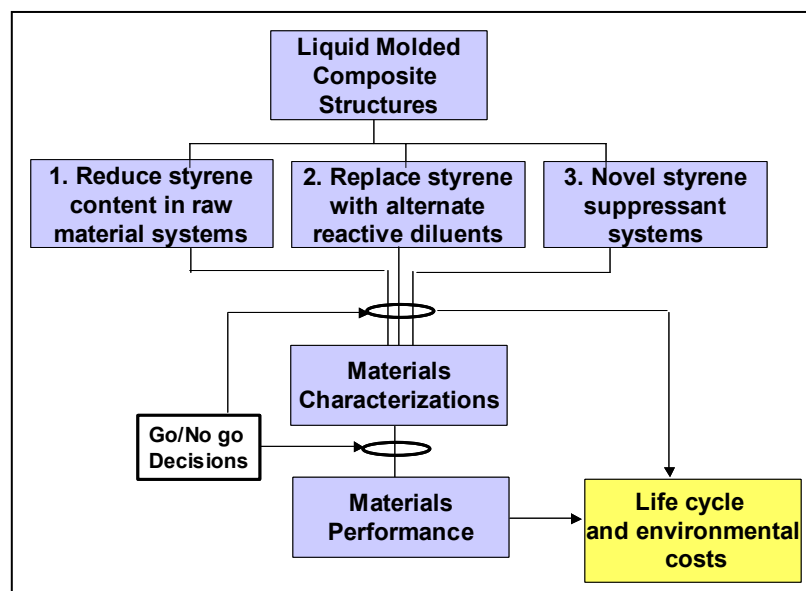


Figure 2. Technical approach for reducing VOC emissions in VE resins.

In the first method, the styrene content of VE resins is reduced using high molecular weight VE monomers to improve toughness and low molecular weight VE monomers to reduce the resin viscosity to acceptable levels. The key to this work is to be able to prepare VE monomers with narrow molecular weight distributions. In the second method, methacrylate-based reactive diluents with low vapor pressures are studied as replacements for styrene. Various monomers, including difunctional, aliphatic, cyclic, and aromatic monomers will be tested to not only determine possible styrene replacements, but to more successfully understand the effect of monomer structure on resin rheology, cure kinetics, and polymer properties. In addition, fatty acid (FA)-based monomers are prepared and assessed as replacements for styrene. FAs have very low volatilities and are derived from renewable resources, further improving the potential environmental impact of this project. In the third method, small amounts of multifunctional dendritic polymers are added to VE resins to suppress VOC emissions. In this work, we first understand and determine methods for inducing surface-segregation of these dendrimers. Then, means for incorporating these dendrimers into polymer networks are derived to ensure the formation of good interfaces for adhesive applications and so these dendrimers do not plasticize the polymer. Lastly, we must understand the effects of dendrimer molecular weight, architecture, functionality, etc., on the thermodynamics and kinetics of surface segregation to provide an effective barrier to styrene evaporation.

This report is subdivided into three subsections covering (1) measuring styrene emissions and baseline assessment for commercial VE resins; (2) synthesis, characterization, and development of VE with low VOC emissions; and (3) environmental impact and cost savings analysis. Overall, the emphasis should reflect successful identification of critical Department of Defense (DOD) environmental needs, fundamental understanding of VE resin systems, and developed practical solutions that reduce styrene emissions. The technologies developed in this work will

move forward to downselection processes to produce inexpensive, low-VOC VE resins composites for the U.S. Army (composite replacement parts, Future Combat System [FCS] platforms, sheet metal substitutes) and U.S. Navy (DDX surface vessels, Advanced Enclosed Mast Sensor System [AEM/S], high contour rudders, high corrosion replacements). We present results acquired during 1 year of investigation into these technologies.

2. Technology Development

2.1 Baseline Measurements

To determine whether alternative VE formulations have low VOC emissions and comparable material properties to commercial resins, baseline studies on current VE resins are necessary. The results and discussion of most of this work are discussed by Ulven et al. (2).

In order to gauge the effectiveness of a strategy to reduce VOC emissions, an accepted method of measuring VOC emissions was established. Traditional methods of volatiles analysis involve thermal gravimetric analysis (TGA) and desorption gas chromatography-mass spectrometry (DGC-MS). TGA includes a furnace to regulate temperature and a sensitive balance to measure weight changes. Temperature control is very good, but the sample size is quite small (~10–0.1 mg). Self-assembling vapor barriers that suppress styrene emissions are to be used in very small quantities (~1 weight-percent of resin mass). DGC-MS also uses small masses, but differs from TGA in that it measures the chemical composition of the volatiles emitted from the liquid sample. Preliminary work showed that the reproducibility of TGA and DGC-MS were very poor because of nonhomogeneous samples due to the very small masses involved.

As an extension of TGA methodology, we have combined a standard laboratory balance and a temperature-controlled oven to permit analysis of weight-loss behavior on a larger scale. The details of the setup and initial calibration of the macro-TGA setup were detailed by Ulven et al. (2) in the appendix of their report. Unlike micro-TGA, macro-TGA uses sample masses on the order of 10 g. The macro-TGA results were found to be mass dependent. Therefore, a standard mass of 10 g was chosen for this work.

We have performed a number of isothermal experiments at 40 °C, to provide a baseline reference for our future work. The precision of the macro-TGA was tested by examining a commercial sample (Derakane* 470-300) in triplicate. Figure 3 shows the change in mass (normalized to sample size) from three experiments plotted using the square root of time as the independent variable. All of the samples exhibited almost identical behavior, indicating the stability of the macro-TGA arrangement.

*Derakane is a registered trademark of The Dow Chemical Co.

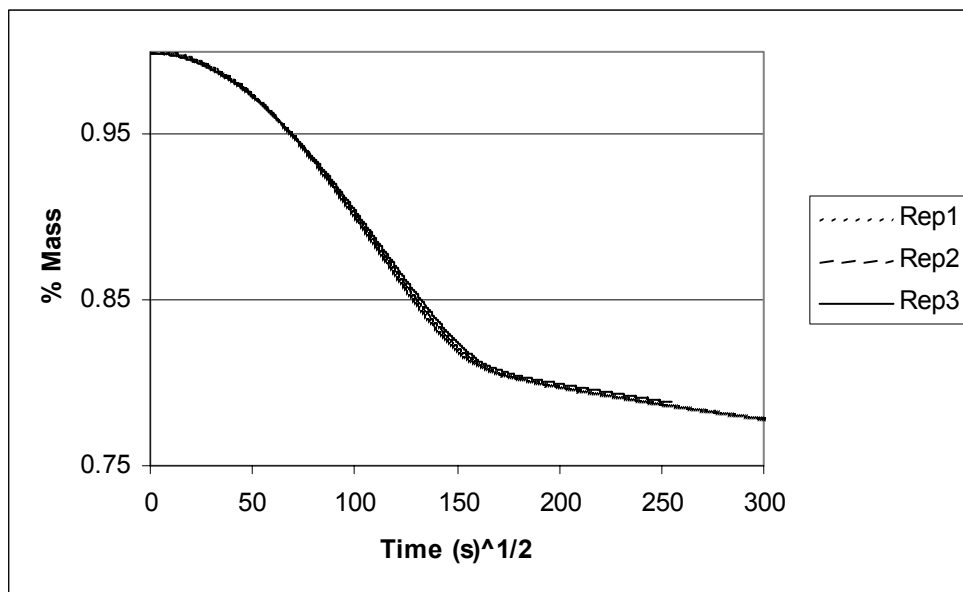


Figure 3. Reproducibility of macro-TGA analysis, 40 °C, Derakane 470-300 resin.

2.2 Reduce Styrene Content in Raw Materials Systems by Use of a Bimodal Molecular Weight Distribution of VE Monomer

In this section, we report on the synthetic procedure used to prepare VE monomers, their rheology, cure, and polymer properties. We first examine the properties of monodisperse VE/styrene blends. We have hypothesized that the styrene content in VE systems can be reduced while maintaining low viscosity and high toughness by using a bimodal distribution of VE molecular weights. Low molecular weight VE is used to maintain low resin viscosity, while high molecular weight VE imparts toughness to the system.

2.3 Preparation of VE Monomers

In previous work, 1% of a catalyst mixture containing 1 part triphenyl phosphine and 3 parts triphenyl antimony was used to catalyze the methacrylation of VE while preventing epoxy homopolymerization (3). Although this catalyst worked well, the reaction required ~5 hr to run. Previous work with triglyceride-based systems has shown that the acrylation of epoxidized triglycerides can be selectively catalyzed using a catalyst known as AMC-2* (4). This catalyst is a mixture of 50% trivalent organic chromium complexes and 50% phthalate esters according to the Material Safety Data Sheet. Studies with the AMC-2 catalyst show that the resulting VE is the same in all aspects to VE produced using the older catalyst system, except that the AMC-2 reduces the reaction duration from 5 to 1.5 hr. For this reason, the AMC-2 catalyst was used exclusively throughout the rest of this work to prepare VE monomers of various molecular weights.

* Aerojet Fine Chemicals, Rancho Cordova, CA.

To this end, VE and blends of low and high molecular weight VE have been prepared via methacrylation of diglycidyl ether of bisphenol (Figure 4). Table 1 lists the Epon resins that have been used and will be used in this work, their molecular weight, number of repeat units (n), and molecular weight of their resulting VE monomers. Currently, VE 828, 834, and 836 have been prepared. Pure VE 1001F and high molecular weight VE resins cannot be prepared without blending because these resins require very high temperatures (>100 °C) to completely melt them. These temperatures would cause high amounts of epoxy homopolymerization, resulting in a high polydispersity and poor model properties. Therefore, high molecular weight Epon resins were blended with low molecular weight Epon resins and the blend was methacrylated to form VE. VE blends containing up to 40-weight-percent VE 1001F in VE 828 have been prepared. Higher molecular weight blends have not been prepared for a few reasons. First, it was just recently hypothesized that higher molecular weight VE monomers may be necessary to effectively reduce the styrene content in VE resins. In addition, VE resins polymerize with time, and thus it is better to prepare the VE as they are needed.

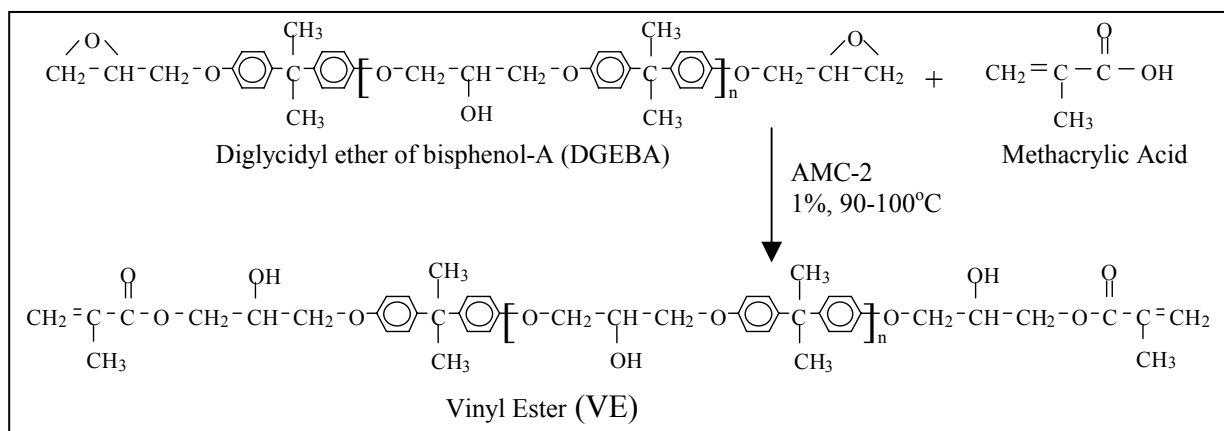


Figure 4. The reaction of methacrylic acid with Epon to form VE monomer.

Table 1. The type, molecular weight, and number of repeat units, n, for the starting Epon resins and the resulting VE monomers.

Epoxy Name	M _w of Epoxy (g/mol)	Repeat Units per Molecule, n	M _w of VE (g/mol)
Epon 828	368.2	0.098	540.2
Epon 834	469.5	0.454	641.5
Epon 836	614.1	0.962	786.1
Epon 1001F	982.5	2.26	1154.5
Epon 1004F	1750	5.0	1.9 × 10 ³
Epon 1007F	4000	13	4.2 × 10 ³
Epon 1009F	6100	20	6.3 × 10 ³
Epon 862	343.0	0.12	515.0

The Epon resins systems used were derived from bisphenol A, except for the VE 862, which is derived from bisphenol F. The only difference between these types of bisphenol is that type A has two methyl groups attached to the carbon linking the phenol groups, while type F has two hydrogen atoms instead. This should both reduce the rigidity and viscosity of type F systems. VE 862 was prepared for the purpose of having a VE with a low viscosity to more dramatically reduce the viscosity of bimodal VE systems.

2.4 VE Characterization

2.4.1 Acid Number

Acid number titration was used to measure the amount of free (unreacted) acid in the VE system. The acid number tests were performed in accordance with American Society for Testing and Materials (ASTM) Standard D 1980-87 (5). Approximately 1 g of the VE reaction mixture was dissolved in 5.0-g acetone. Three drops of 0.5-weight-percent phenolphthalein in 50% ethanol were added to the mixture to determine the neutralization point. The solution was then titrated with 0.5-N sodium hydroxide until the solution remained slightly pink in color for 30 s. The acid number of the VE mixture was then calculated as

$$AcidNumber = \frac{mg \cdot NaOH}{g \cdot VE} = \frac{V \cdot N \cdot MW_{NaOH}}{m}, \quad (1)$$

where V is the volume in milliliters of NaOH solution used, N is the normality of the NaOH solution, and m is the VE mass in grams. An acid number of 15—corresponding to ~3% free acid—was the maximum allowable acid number. If the acid number was too high, the methacrylation reaction was allowed to continue until future acid numbers were <15.

2.4.2 Fourier-Transform Infrared (FTIR) Spectroscopy

FTIR was used to measure the concentration of unreacted epoxides and attached methacrylate groups. A Thermo Nicolet Nexus 670 FTIR was used in absorbance mode, taking 16 scans with a resolution of 4 cm⁻¹. The peak at 917 cm⁻¹ represents the unreacted epoxide groups, whereas the peak at 940 cm⁻¹ represents methacrylate functionality (Figure 5). The FTIR spectra of these resins indicated that all of the epoxide groups reacted and methacrylate groups are present in the resin.

2.4.3 High-Performance Liquid Chromatography (HPLC)

HPLC was run on the VE samples to determine if extensive methacrylation and/or epoxy homopolymerization occurred. 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) as the elution solvent at a flow rate of 1 mL/min. 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 and 254 nm (absorbed by phenyl rings). Samples were prepared by dissolving a 2-mg sample in 1-mL THF. Because high molecular

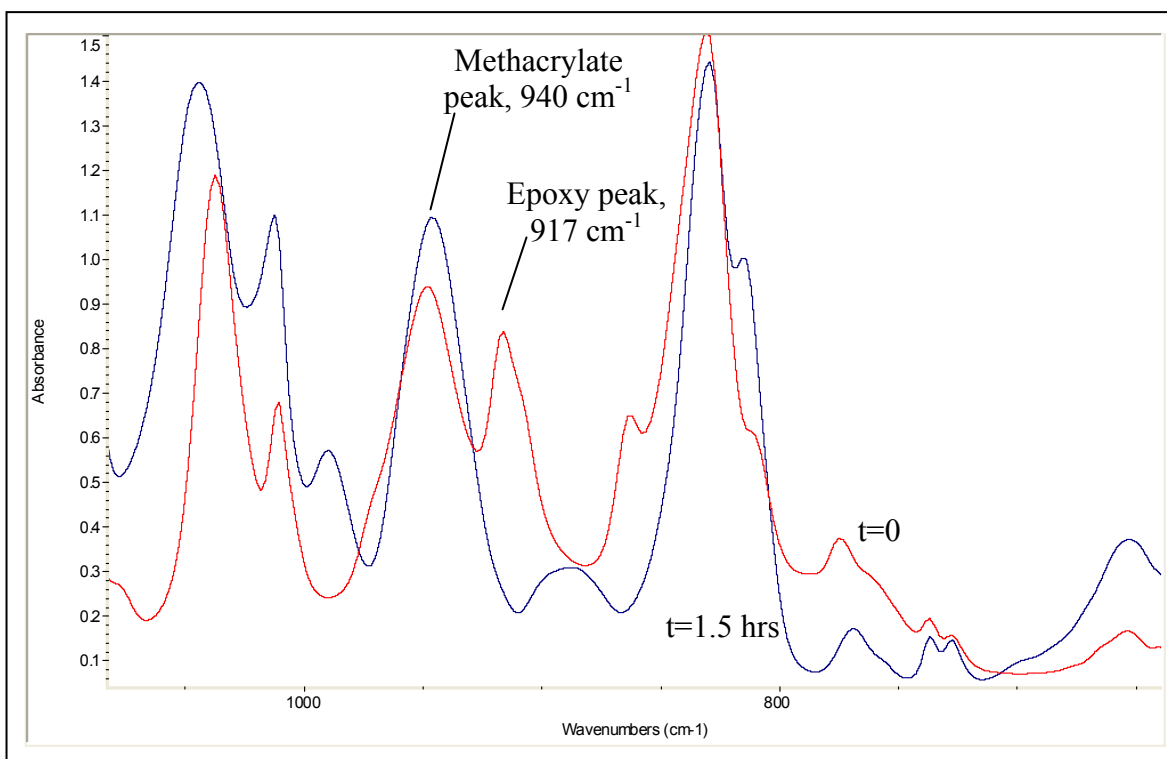


Figure 5. The FTIR spectra of Epon/methacrylic acid and the resulting VE formed after complete reaction.

weight species cannot diffuse into the packing, they elute first from the column, while lower molecular weight species elute later (6, 7).

Figure 6 shows the HPLC chromatograph for a representative Epon (834) and the VE formed after complete reaction with methacrylic acid. There are four peaks—15.66, 13.90, 13.20, and 11.40 min—representing Epon with 0, 1, 2, and 3 repeat units, respectively. Most of the individual peaks still appear in the VE, but they are shifted to shorter elution times (14.48, 13.55, and 11.18 min) because the VE molecular weight is ~ 172 g/mol greater than the Epon. The peak representing the $n = 2$ monomer is coincident with the peak representing the $n = 1$ monomer and the individual peaks cannot be resolved. Previous work has shown that if a significant amount of epoxy homopolymerization occurred, a broad peak appearing at 10 min and lower elution times would appear (3, 8). Because no such peak appeared in our prepared VE, we conclude that no epoxy homopolymerization occurred. In addition, these results conclusively show that Epon reacted with the methacrylic acid to form higher molecular weight VE monomers.

2.4.4 Rheological Characterization

The viscosities of the resins were measured using a Brookfield digital viscometer in Couette geometry. 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.

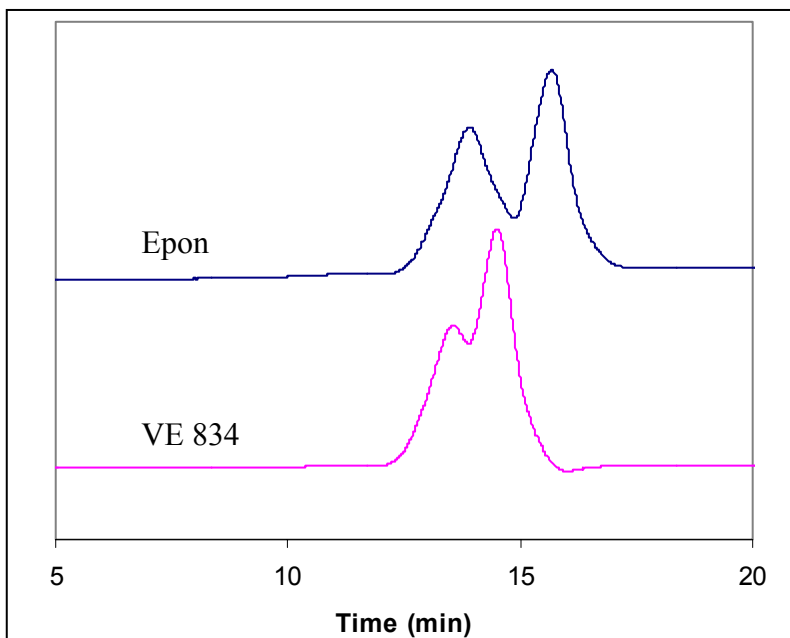


Figure 6. The HPLC chromatographs for Epon 834 and VE 834.

2.4.5 Cure of VE Resins

VE monomer and styrene were mixed in various ratios. Trigonox,^{*} containing 45-weight-percent cumene hydroperoxide, was used to initiate free radical polymerization of the resin. Cobalt naphthenate (CoNap) was used to catalyze the polymerization at room temperature (RT). The moles of cumene hydroperoxide used was one-hundredth the number of moles of vinyl functionality. A 4:1 weight ratio of Trigonox to CoNap was used. The resins were then poured into a mold and allowed to cure. Polymer samples were postcured in situ for dynamic mechanical analysis (DMA), but were postcured for 1 hr at 130 °C before tensile and fracture tests.

2.4.6 Thermal and Mechanical Characterization

The thermomechanical properties of VE were measured using DMA. Rectangular samples with approximate dimensions of 25 × 9 × 3 mm were tested using a TA Instruments DMA 2980 DMA in single cantilever geometry. The samples were tested at 1 Hz with a deflection of 15 μm while ramping the temperature from 30 to 200 °C at a rate of 5 °C/min. Three temperature ramp experiments were run for each sample. The first ramp usually completely postcured the polymer, but another ramp was performed to ensure this. The temperature at which the peak in the loss modulus occurred in the fully postcured polymer was considered the glass transition temperature (T_g) of the material (9).

Flexural tests, in accordance with ASTM D 790-96A (10), were performed to determine the modulus of elasticity and flexural strength. The samples had dimensions of 10 × 80 × 64 mm³

^{*}Trigonox is a registered trademark of Akzo Nobel Chemicals.

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 tester at a crosshead speed of 1.7 mm/min. A strain gage was applied to each sample to measure the strain of the sample as a function of applied load.

Three-point single-edge notch bend (SENB) specimens were used for fracture toughness measurements. ASTM 5045-93 (11) specifies the sample dimensions of $50.8 \times 12.8 \times 6.35 \text{ mm}^3$ to ensure 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 tester in flexural mode at a crosshead speed of 1.27 mm/min. All tests were performed at ambient conditions. When tests were completed, the fracture specimens were examined for signs of plastic deformation. If plastic deformation was apparent, the sample was not used in the reported results.

2.4.7 Material Properties

The rheological, mechanical, and thermal properties of VE resins are dependent on the molecular weight of the VE monomers and the styrene content. VE molecular weight and styrene content had opposite effects on the resin viscosity. Figure 7 shows that the viscosity of VE resins with constant styrene content increased with the VE molecular weight. On the other hand, the resin viscosity decreased exponentially as the styrene content increased (Figure 8). This occurred because styrene acts as a solvent and reduces the interactions (hydrogen bonding and entanglements) among VE, allowing these large molecules to more easily slide past one another (12).

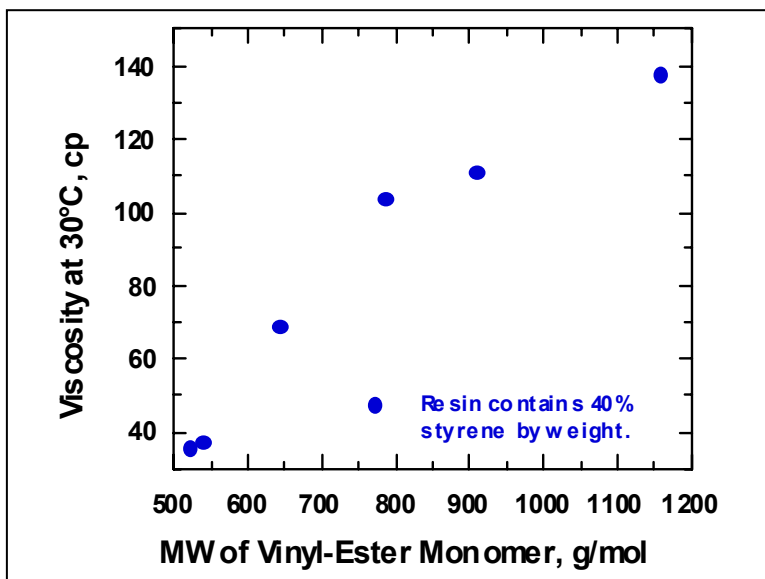


Figure 7. The viscosity of VE resins as a function of the molecular weight of the VE monomer.

The fracture toughness increased with the VE molecular weight (Figure 9) and with increasing styrene content (Figure 10). This occurred because both of these factors increase the molecular

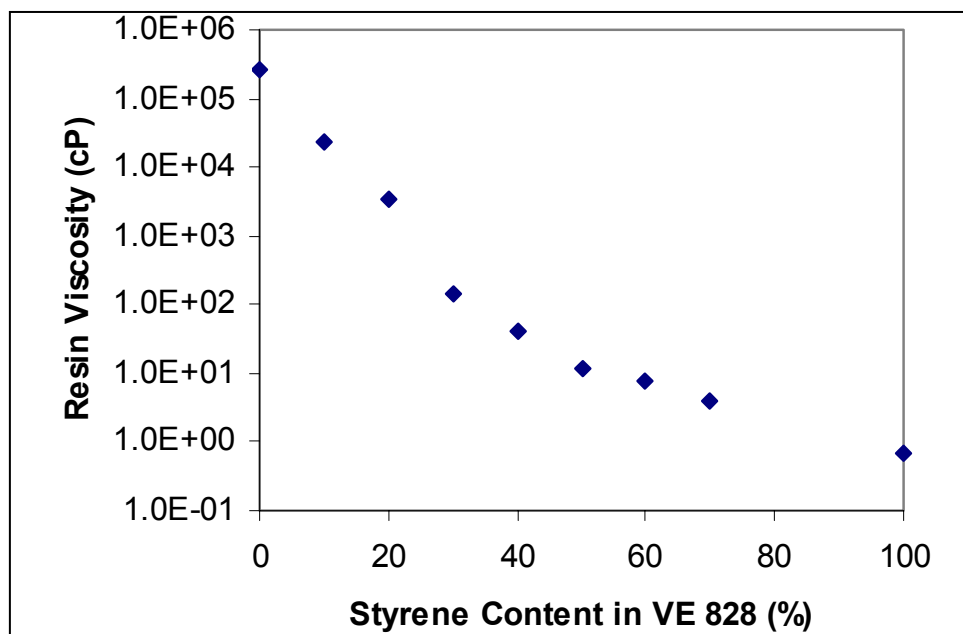


Figure 8. The viscosity of VE 828 resin as a function of styrene content.

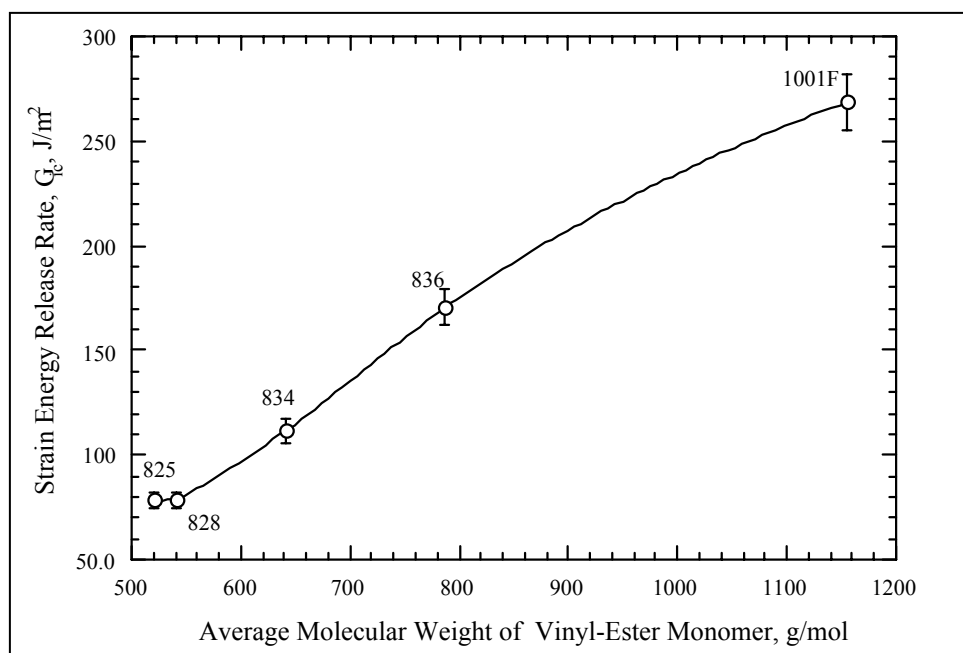


Figure 9. The fracture toughness as a function of VE molecular weight for VE with 40-weight-percent styrene.

weight between cross-links (i.e., decrease the cross-link density) (13). The modulus and T_g are affected in the opposite manner as the fracture toughness with increasing VE molecular weight and styrene content because of decreasing cross-link density (13). Figure 11 shows that T_g decreased as the VE molecular weight increased. It is important to note that the fracture toughness is a much larger function of styrene content and VE molecular weight than

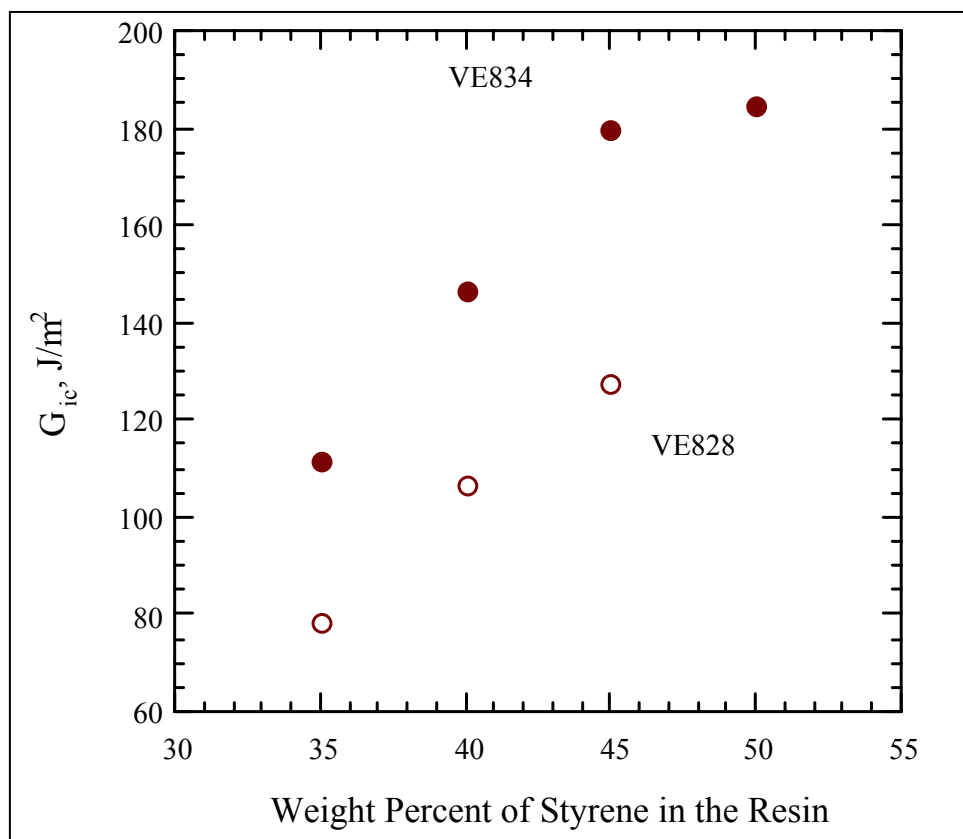


Figure 10. The fracture toughness as a function of styrene content for VE 834 and VE 828.

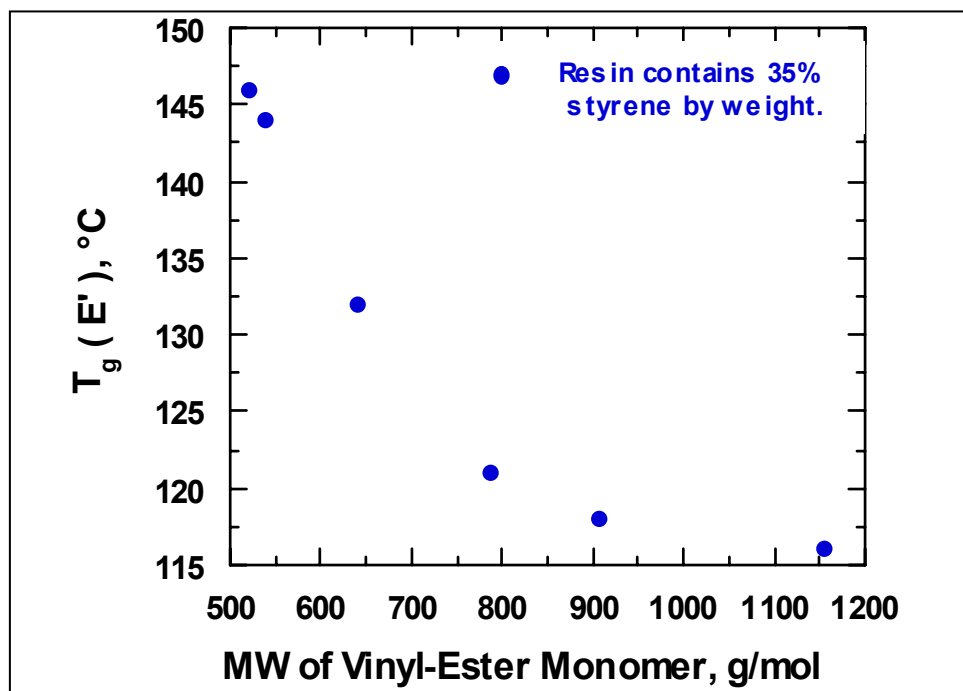


Figure 11. T_g as a function of VE molecular weight for samples with 35% styrene.

the modulus and T_g . In addition, the polymer matrix has only a small effect on the modulus of a composite part, whereas the fracture toughness is highly dependent on the toughness of the polymer (14).

This work shows that a strict reduction in the styrene content of VE resins not only decreases the processability of the resins, but also unacceptably decreases their toughness. Increasing the VE molecular weight can be used to increase the toughness, but requires a greater styrene content to have processable resins. We hypothesize that bimodal blends containing both low and high molecular weight VE monomers would yield resins with low viscosities and high fracture toughness. Therefore, these resins would require less styrene to maintain good fracture properties and acceptable viscosities. This hypothesis will be tested in the near future now that VE monomers of various molecular weights have been prepared.

2.4.8 Styrene Emissions

The styrene emissions from VE 828 resins were measured using macro-TGA. Approximately 10 g of resin and an isothermal temperature of 40 °C were used for these studies. The styrene concentration was varied from 20 to 50 weight-percent. The mass loss of pure styrene was also measured as a function of time.

The normalized mass fraction of resin remaining as a function of time displayed the elbow-type graph (Figure 12) as seen for the commercial resins. The normalized mass remaining is

$$NormalizedMass = \frac{m(t)}{m_{initial}}, \quad (2)$$

where $m(t)$ is the resin mass as a function of time and $m_{initial}$ is the initial resin mass. The transition from short-time to long-time mass loss* occurred at greater percent mass loss and time for samples with larger styrene contents, as expected. Pure styrene did not display an elbow. Thus, the elbow is a manifestation of the interactions between VE monomer and styrene. Although the Derakane 470-300 sample contains 33-weight-percent styrene, it did not act intermediate of 30% and 40% styrene in VE 828. The Derakane had a much sharper elbow and a larger emission rate reduction at the elbow than VE 828 resins. The reason for this difference is that Derakane 470-300 has a higher molecular weight than VE 828.

The resin mass as a function of time was also normalized by the content of volatiles (styrene) using equation 3:

* The terms short-time and long-time mass loss are somewhat misleading in that the short-time mass loss indicates mass loss through times of at least 7 hr.

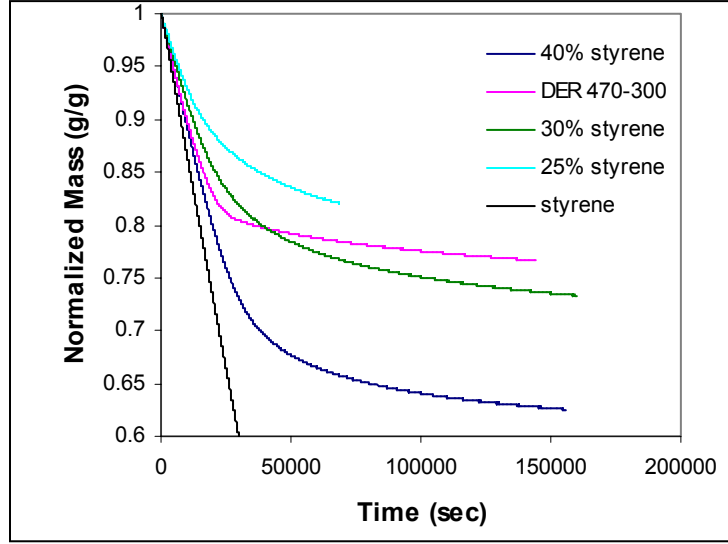


Figure 12. The normalized mass loss as a function of time at 40 °C for styrene, Derakane 470-300 (33% styrene), and VE 828 resins with various styrene contents.

$$NormalizedVolatileMass = \frac{m(t) - (\phi_{VE} m_{initial})}{\phi_{styrene} m_{initial}}, \quad (3)$$

where ϕ_{VE} and $\phi_{styrene}$ are the initial mass fractions of VE monomer and styrene, respectively.

Figure 13 shows how the percent volatile content decreased with time. In fact, most unbound styrene was lost to the atmosphere for VE 828 resins over time. It is evident that the short-time volatile-normalized mass loss rate was not a function of the styrene content (similar initial slopes). However, the time and volatile-normalized mass loss at which the elbow occurred increased with the styrene content. The Derakane sample had a slightly higher emission rate than the VE 828 resins. The reasons for this are unknown. Interestingly, the pure styrene sample had the lowest volatile-normalized mass loss rate of all the samples. Because of the high surface-to-volume ratio of these samples, this result can be explained by assuming a preferential segregation of styrene to the air-resin interface. Low polarity species, such as styrene, tend to have lower surface energies than higher polarity species, like VE monomer (15). Because of the preferential segregation of styrene, the volatile-normalized mass (equation 3) should be normalized by the styrene content near the interface, $\phi_{styrene,interface}$:

$$InterfaceVolatileNormalizedMass = \frac{m(t) - (\phi_{VE} m_{initial})}{\phi_{styrene,interface} m_{initial}}, \quad (4)$$

rather than the bulk styrene concentration (equation 3). Without this correction, the volatile-normalization is underestimated, causing the styrene evaporation rate in VE to be higher than for pure styrene samples. The bulk mass loss rate, r_{bulk} , is simply related to the interface mass loss rate, $r_{interface}$:

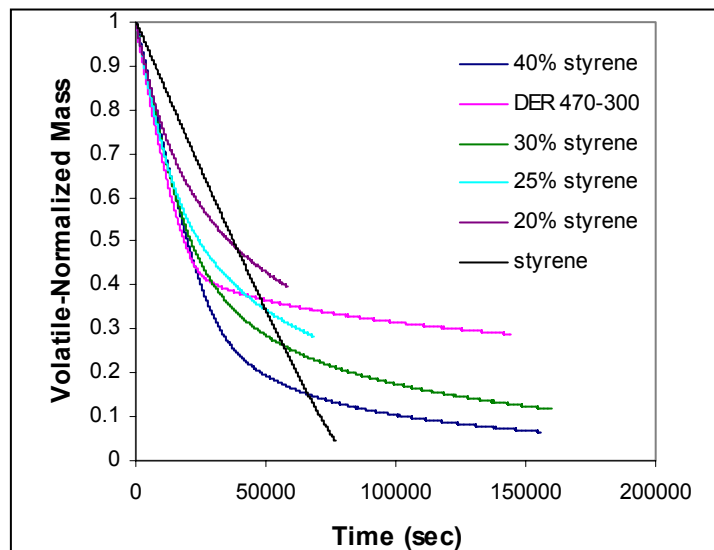


Figure 13. The volatile-normalized mass loss as a function of time at 40 °C for styrene, Derakane 470-300 (33% styrene), and VE 828 resins with various styrene contents.

$$r_{bulk} = \frac{\phi_{styrene,interface}}{\phi_{styrene}} r_{interface} \quad (5)$$

where $\phi_{styrene,interface}$ was calculated by finding the value where the initial volatile-normalized mass loss rates for the VE resins equated to that of pure styrene. The theoretical styrene mass fraction at the interface was a parabolic function of the bulk styrene content, as shown in Figure 14. The results show that the interfacial concentration of styrene was a large function of the bulk concentration at low styrene contents and a small function of styrene content at high styrene contents. Therefore, potential styrene emissions should be reduced most severely by reducing the styrene content in VE 828 resins to lower than 20%. ATR-FTIR can be used to measure the styrene content at the interface to determine if styrene preferentially segregates to the surface of VE resins. If this is the case, it is a very important point because it must be accounted for when modeling the diffusion of these systems and it offers evidence that surface segregation of dendritic polymers can be used to reduce styrene emissions.

2.5 Replacing Styrene With Other Reactive Diluents

One possible way to reduce the VOC emissions from VE systems is to replace some or all of the styrene with a low viscosity, low volatility monomer. Ideally, replacement monomers should not be much more expensive than styrene (~\$0.40/lb); however, the replacement monomer is acceptable as long as the VE resin is still less expensive than epoxy resins (\$6–\$10/lb).

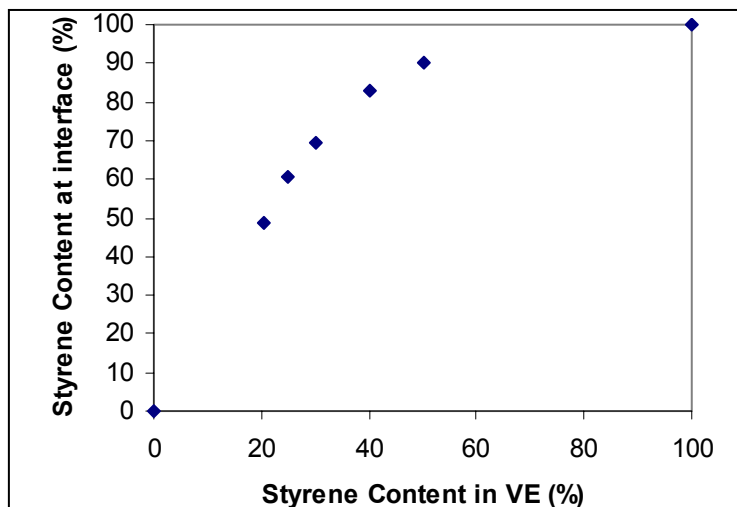


Figure 14. The theoretical styrene mass fraction at the air interface as a function of the bulk styrene content for VE 828 resins.

Two types of diluents were tested: petroleum-based diluents and FA-based diluents. Petroleum-based diluents are advantageous in that they are already being manufactured on large-scales and cost estimates are well known. FA-based monomers are simply derived from plant oils, which are composed of triglyceride molecules. Although FA-based monomers are not currently being manufactured, their cost estimates show that they are inexpensive, and they are advantageous to improved global sustainability because they are derived from renewable resources.

2.5.1 Theoretical Work

Monofunctional comonomers and difunctional comonomers as replacements for styrene have been proposed. Previous work has shown that a large percentage of styrene remains unreacted in a RT cure of VE resins (1). Therefore, difunctional comonomers can be advantageous because they are likely to have a lower vapor pressure and therefore would have lower levels of hazardous emissions. In addition, the conversion necessary to bind all of the monomers into the matrix is reduced. A simple analysis was done to determine the necessary conversion of monomer in difunctional resins that would result in lower free-monomer content in the cured VE polymer. This analysis does not factor in the effect of reduced vapor pressures, and therefore represents a worst-case scenario for difunctional monomers.

If a binomial distribution of unsaturation sites is assumed, the probability of having m reacted groups on an N -functional monomer is

$$P(N, m, x) = C \binom{N}{m} x^m (1-x)^{N-m}, \quad (6)$$

where x is the conversion and $C\binom{N}{m}$ is the combinatorial function (i.e., the number of ways of arranging the m reacted groups on an N -functional monomer [16]). The conversion at which the percentage of unreacted multifunctional monomer, $P'_0(x'_c)$, equals the percentage of unreacted styrene, $P_0(x)$, is the critical conversion, x'_c :

$$P'_0(x'_c) = P_0(x). \quad (7)$$

Substituting in equation 6, we have

$$(1 - x'_c)^N = 1 - x. \quad (8)$$

There is an analytical solution for the critical conversion for all multifunctional comonomers:

$$x'_c = 1 - (1 - x)^{1/N}. \quad (9)$$

For example, when the styrene conversion is 95% (5% unreacted styrene), which is typical of postcured VE (1), the conversion at which 5% unreacted difunctional monomer remains is $x'_c = 0.77$. This shows that amount of unbound monomer is lower for difunctional monomers relative to styrene at the same conversion. However, difunctional monomers will increase diffusion limitations during cure and will increase the cross-link density. These factors tend to decrease the ultimate conversion of multifunctional monomers. Regardless, this analysis shows that there is a large potential for reducing emissions using multifunctional monomers, although we do not offer experimental proof. FTIR experiments will be run to determine the achievable conversion using difunctional comonomers. The resin and polymer properties of VE using monofunctional and difunctional comonomers in the following subsections.

2.5.2 Petroleum-Based Comonomers

A number of petroleum comonomers were tested in place of styrene in VE resins (Figure 15). Cyclohexyl methacrylate (CHMA), isobornyl methacrylate (IBMA), and lauryl methacrylate (LM) were the monofunctional diluents tested. LM was not soluble in VE and thus was not tested further. The difunctional styrene replacements tested were 1,6-hexanediol diacrylate (HDDA) and 1,6-hexanediol dimethacrylate (HDDMA). These monomers were tested because of their low vapor pressures and viscosities (Table 2). The vapor pressure of these comonomers were determined as a function of temperature using the Antoine equation. These results show that these replacement comonomers have considerably lower vapor pressures than styrene at all temperatures (Figure 16). Although the cost of these monomers is substantial (Table 2), VE resins using these comonomers would still be considerably less expensive than epoxies.

2.5.2.1 Resin Viscosity and Gelation. The viscosities of VE resins using petroleum-derived styrene replacements were measured using a Brookfield digital viscometer. The resins contained 35-weight-percent comonomer in VE 828. One mole of cumene hydroperoxide (in Trigonox)

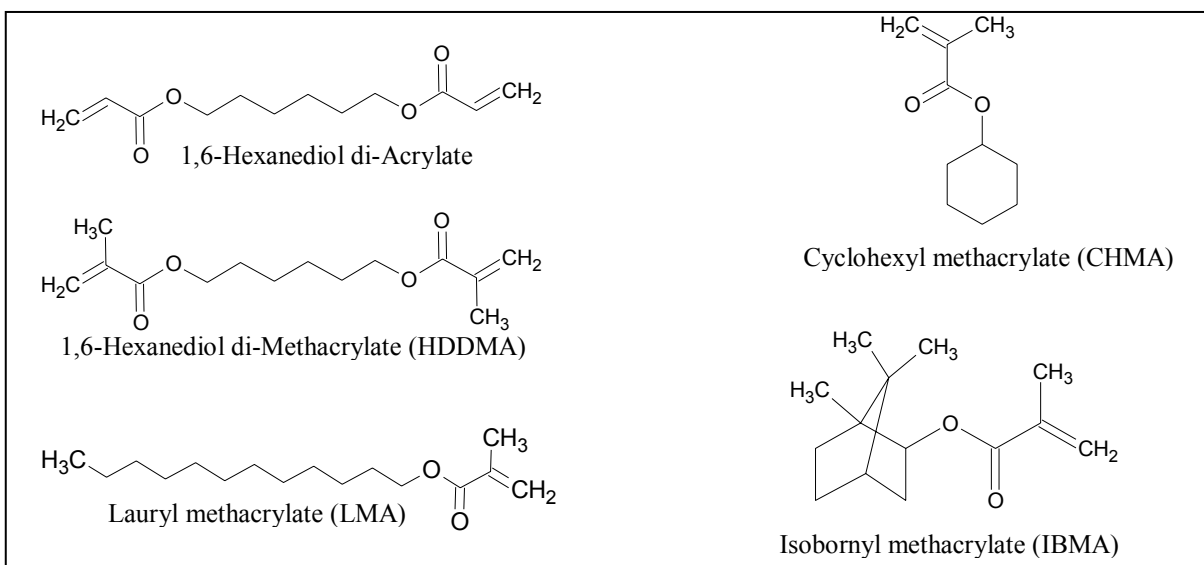


Figure 15. The molecular structure of tested petroleum-derived styrene replacements for VE resins.

Table 2. The vapor pressure, viscosity, and cost of potential styrene replacements for VE resins.

Comonomer	Vapor Pressure (mmHg)	Viscosity (cP)	Cost (\$/lb)
Styrene	6.594 at 25 °C	0.7 at 30 °C	~0.40
CHMA	0.994 at 25 °C	1.9 at 20 °C	3.55
IBMA	0.020 at 25 °C 28.6 at 142 °C	8.5 at 20 °C	3.90
HDDA	<0.01 at 25 °C	8 at 20 °C	2.58
HDDMA	0.02 at 100 °C	10 at 20 °C	2.97

was used per 100 moles of vinyl groups, and the CoNap mass used was one-fourth the mass of Trigonox. The viscosity was measured at 30 °C. The viscosity as a function of gel time is shown in Figure 17. The VE/styrene system had the lowest initial viscosity (Table 3) and gelation occurred suddenly, as marked by the rapid increase in viscosity after the induction period. The IBMA had a high initial viscosity and it gelled fairly rapidly. The CHMA resin had a fairly low initial viscosity and it took longer to gel than styrene-based VE. This was expected because styrene-methacrylate polymerization occurs faster than methacrylate-methacrylate polymerization (17). However, the polymerization kinetics of CHMA-VE polymerization have not been measured, as of yet. In addition, the diffusion rate of CHMA to growing radicals should be lower than that of styrene because CHMA is a larger molecule. The HDDMA and HDDA resins gelled very gradually over time, and the induction period was short. This was expected because both the VE and the comonomer are cross-linking agents.

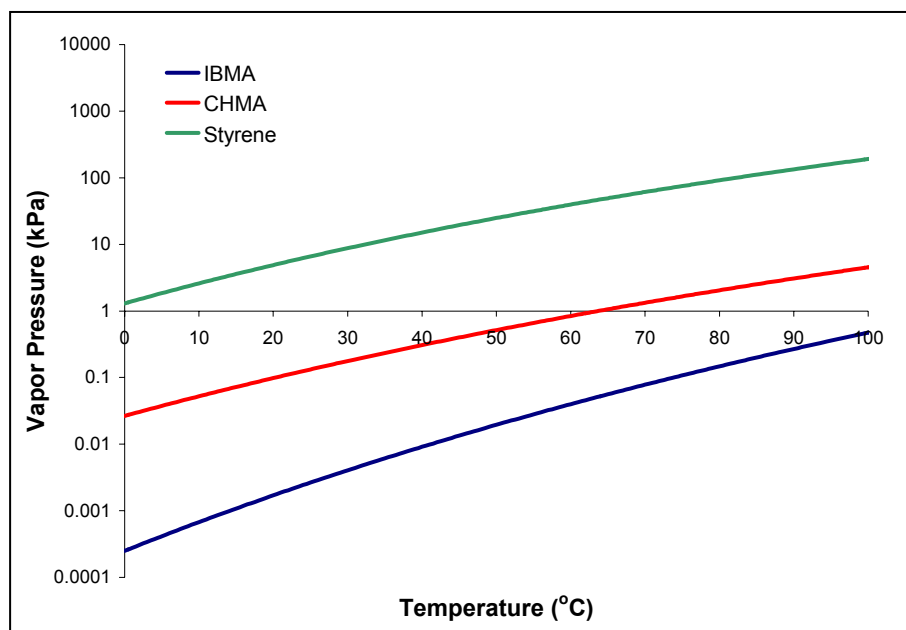


Figure 16. The vapor pressure of styrene, CHMA, and IBMA as a function of temperature as calculated with the Antoine equation.

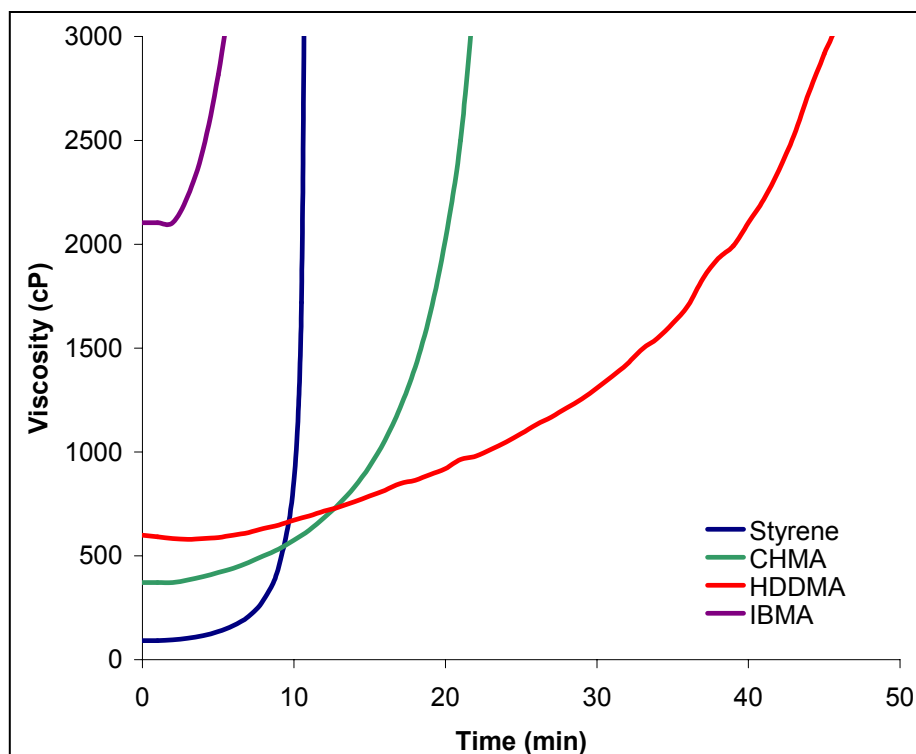


Figure 17. The viscosity of VE resins as a function of gel time and comonomer. VE/HDDMA results are very similar to VE/HDDMA results and are omitted for clarity.

Table 3. Initial viscosity of VE 828 resins at 30 °C using various comonomers.

Comonomer	Viscosity at 30 °C (cP)
Styrene	56
CHMA	364
IBMA	2104
HDDA	368
HDDMA	564

Figure 18 shows that the viscosity of VE/HDDMA resins decreased with HDDMA content similarly to VE/styrene resins. However, at all comonomer contents, the VE/HDDMA had a higher viscosity. These results also show that HDDMA contents of $\geq 40\%$ results in acceptable viscosities for liquid molding (<500 cP).

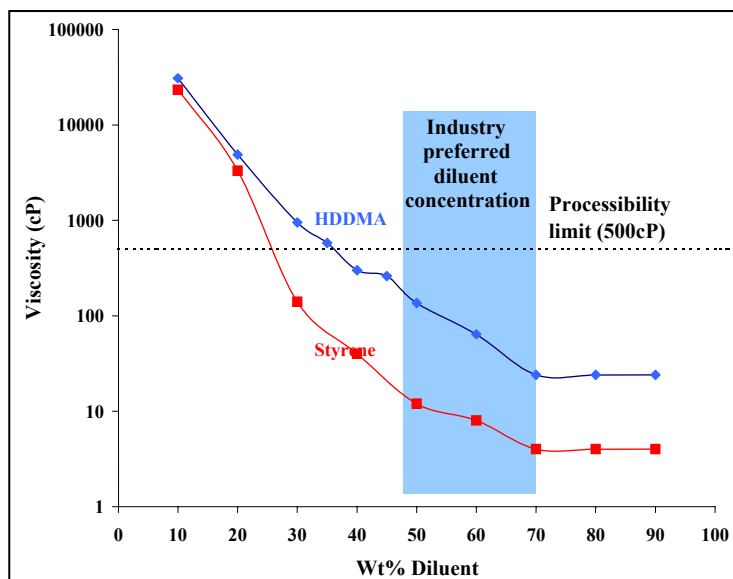


Figure 18. The viscosity of VE 828 resins as a function of styrene and HDDMA content at 30 °C.

Figure 19 shows the viscosity of blends of VE, HDDMA, and styrene as a function of gel time. The initial viscosity increased as the HDDMA content increased. In addition, the viscosity increased without an induction period, but more gradually as the HDDMA content increased. This is expected because HDDMA is a cross-linking agent, not a reactive diluent. These polymers continuously branch during the course of polymerization causing the step-wise increase in the viscosity.

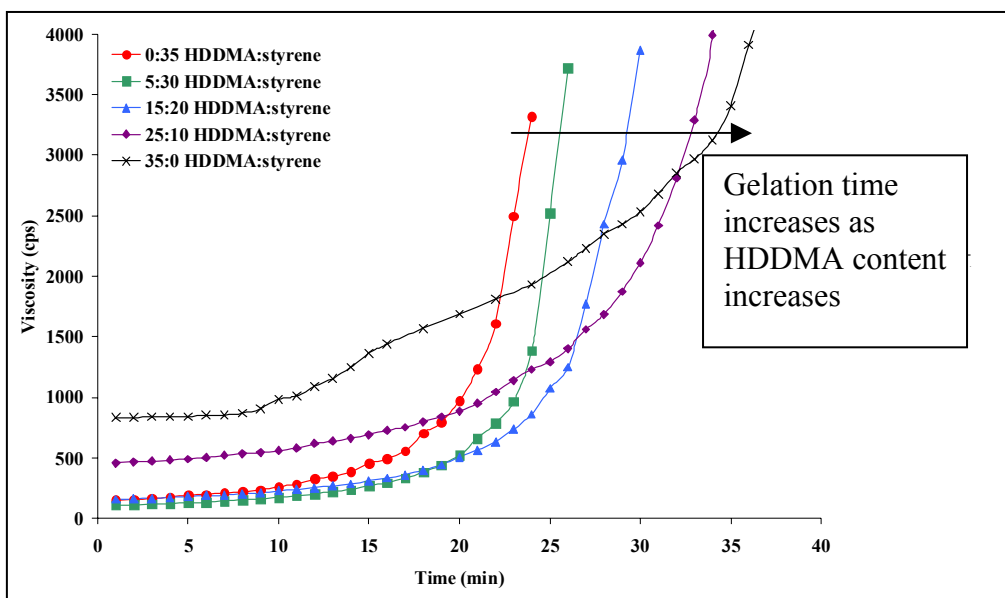


Figure 19. The viscosity as a function of gel time for VE/HDDMA/styrene blends at 30 °C.

2.5.2.2 Polymer Properties. The DMA results for HDDMA show that the storage modulus decreased as HDDMA content increased for the VE/HDDMA/styrene blends (Figure 20). In addition, the transition from glassy to rubbery behavior became less distinguished. Furthermore, the VE/HDDMA sample did not retain its modulus as a function of temperature as well as the VE/styrene samples. The rubbery modulus increased as the HDDMA content increased because HDDMA is a cross-linker and it thus increased the cross-link density of the resulting polymer. The polymer transitions, shown by the loss modulus, became much less prominent as the HDDMA content increased (Figure 21). Furthermore, there were two peaks for VE/HDDMA/styrene blends, showing the resin mixture was inhomogeneous. It is hypothesized that the properties of VE/HDDMA polymers are lower than VE/styrene polymers because of low monomer conversion as a result of low conversions at gelation. Polymerization kinetics studies with FTIR need to be done to prove this hypothesis. Although the VE/HDDMA samples do not have ideal thermomechanical properties, resin mixtures with 10%–20% have good polymer properties and acceptable resin viscosities. Therefore, resins with lower styrene contents can be synthesized by replacing some styrene monomer with HDDMA. HDDA behaved similarly to HDDMA, but had inferior properties. For example, Figure 22 shows that the loss modulus peak of VE/HDDA was hardly visible.

The DMA properties of CHMA were similar to VE/styrene blends. The storage modulus was only slightly lower than VE/styrene in the glassy regime, and the glass transition was well pronounced. Figure 23 also shows that T_g of VE/CHMA was very similar to styrene-based resins. However, the glass transition was broader for CHMA-based resins probably due to a lower final monomer conversion in these resins. Polymerization kinetics work must be done to confirm this hypothesis. Regardless, these results show that CHMA is an excellent candidate for replacing styrene in VE resins.

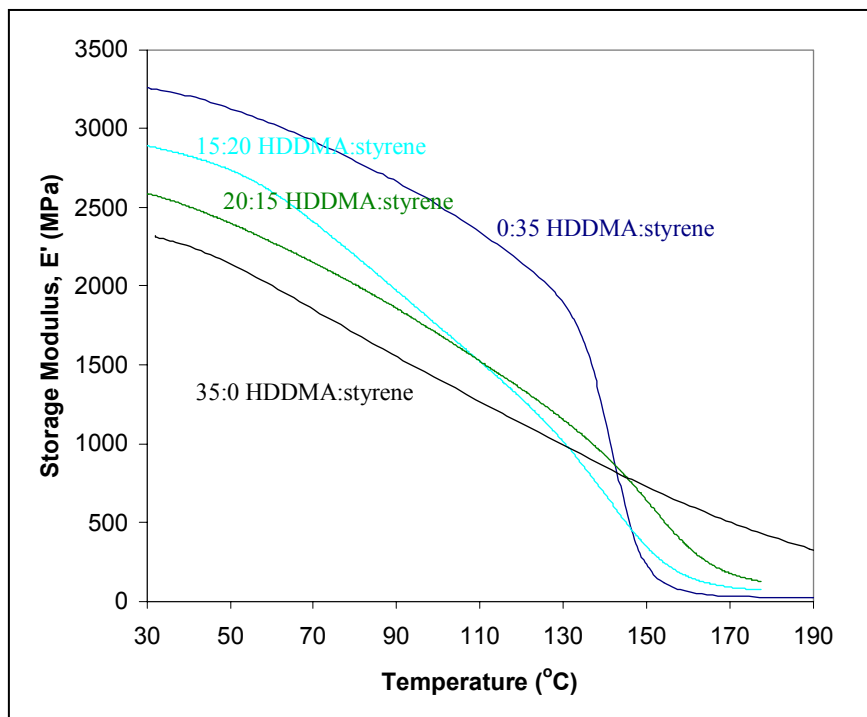


Figure 20. The storage modulus as a function of temperature for VE/HDDMA/styrene blends.

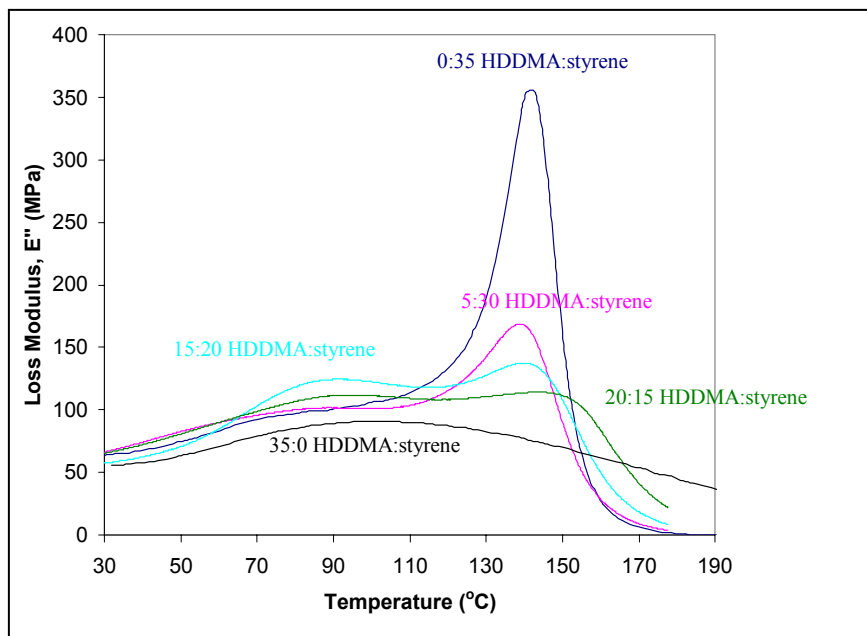


Figure 21. The loss modulus as a function of temperature for VE/HDDMA/styrene blends.

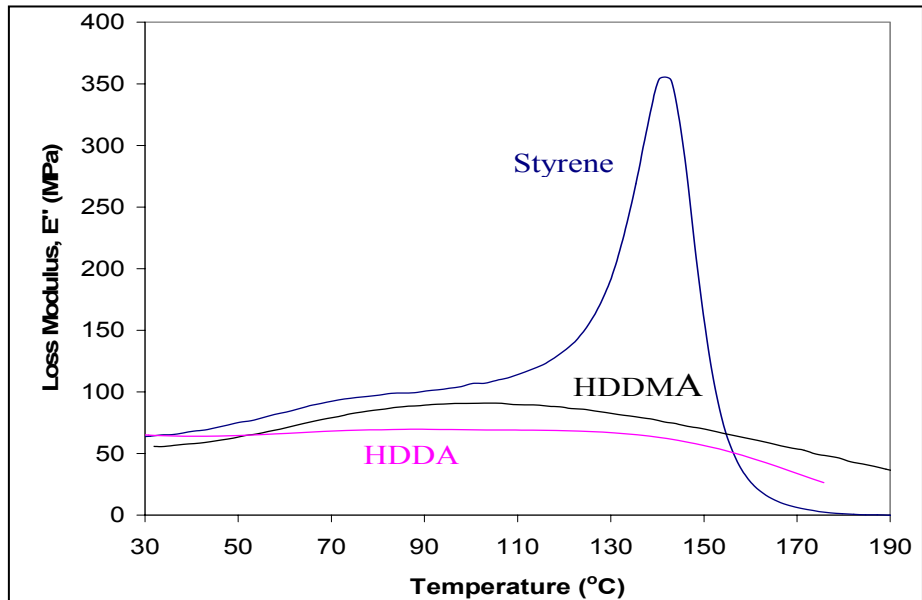


Figure 22. The loss modulus as a function of temperature for VE/HDDA relative to VE/HDDMA and VE/styrene.

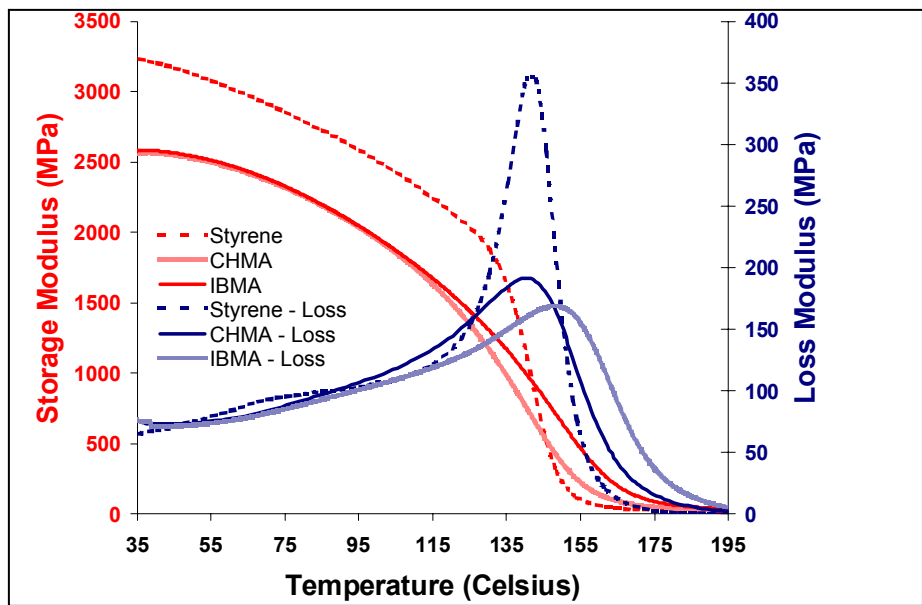


Figure 23. The DMA behavior of VE/CHMA and VE/IBMA resins relative to VE/styrene.

IBMA has DMA properties that are very similar to VE/CHMA (Figure 23). Although T_g of IBMA resins are higher than that of CHMA resins, the viscosities of IBMA resins are 1 order of magnitude higher (Figure 17). IBMA would have to be blended with styrene to yield VE resins with acceptable viscosities for liquid molding. Therefore, IBMA can be used as a styrene replacement, but the slight improvements in polymer properties over CHMA resins are not worth the much lower processability of these resins relative to CHMA resins.

2.5.2.3 Petroleum-Based Comonomer Conclusions. Currently, CHMA appears to be the best styrene replacement for VE resins. This comonomer does not have to be blended with styrene to produce VE with good properties and acceptable resin viscosities. Other comonomers, such as HDDMA and IBMA, can be used to reduce the styrene content in VE resins but cannot be used to completely replace styrene because of poor polymer properties or unacceptable resin viscosities. Overall, petroleum-based monomers show good potential for replacing styrene in VE resins, but the cost of these comonomers are ~5–7 times that of styrene, making economics a strong deciding factor. For this reason, the use of FA-based monomers as styrene replacements is attractive because of their low potential cost.

2.5.3 FA-Based Comonomers

2.5.3.1 Synthetic Routes. A number of synthetic procedures have been established for using FA-based monomers as the reactive diluent in VE resins. Figure 24 lists the synthetic routes that have been established. In all of the synthetic routes, the starting materials are either triglycerides (structure 0), FA (structure 1), fatty acid methyl esters (FAME) (structure 2), or cyclic FAs (structure 5). Refined plant oils contain ~99% triglyceride molecules (18). Industrially, FAs are produced from triglycerides by reaction with a strong acid, such as hydrochloride (HCl) (19–21). FAME are produced from a methanolysis reaction. In this reaction, methanol replaces the glycerol ester linkages under basic conditions (19–21). Cyclized acids are produced by reacting polyunsaturated FAs of triglycerides at high temperatures under basic conditions (19–21).

In route 1, FAs are reacted with an epoxy-methacrylate species, such as glycidyl methacrylate (GM). The carboxylic acid group of the FAs adds to the epoxide group on GM. The resulting species is a fairly long hydrocarbon (20–26 atoms in length depending on the FA used) with a terminal unsaturation site that is capable of free radically polymerizing. The length of the FA chain may affect the polymer properties. Therefore, the particular FA used is of importance, and its effect on polymer properties has been studied and will be studied in more detail.

In route 2, unsaturation sites on FAME are first epoxidized, and then acrylated (22, 23). The resulting monomer has an acrylate group, which is capable of free radically polymerizing, in the middle of the long hydrocarbon chain (20 atoms long). Ideally, this monomer will have no more and no less than a single acrylate group. For this to be the case, monounsaturated FAs need to be used. Pure monounsaturated acids are fairly expensive.

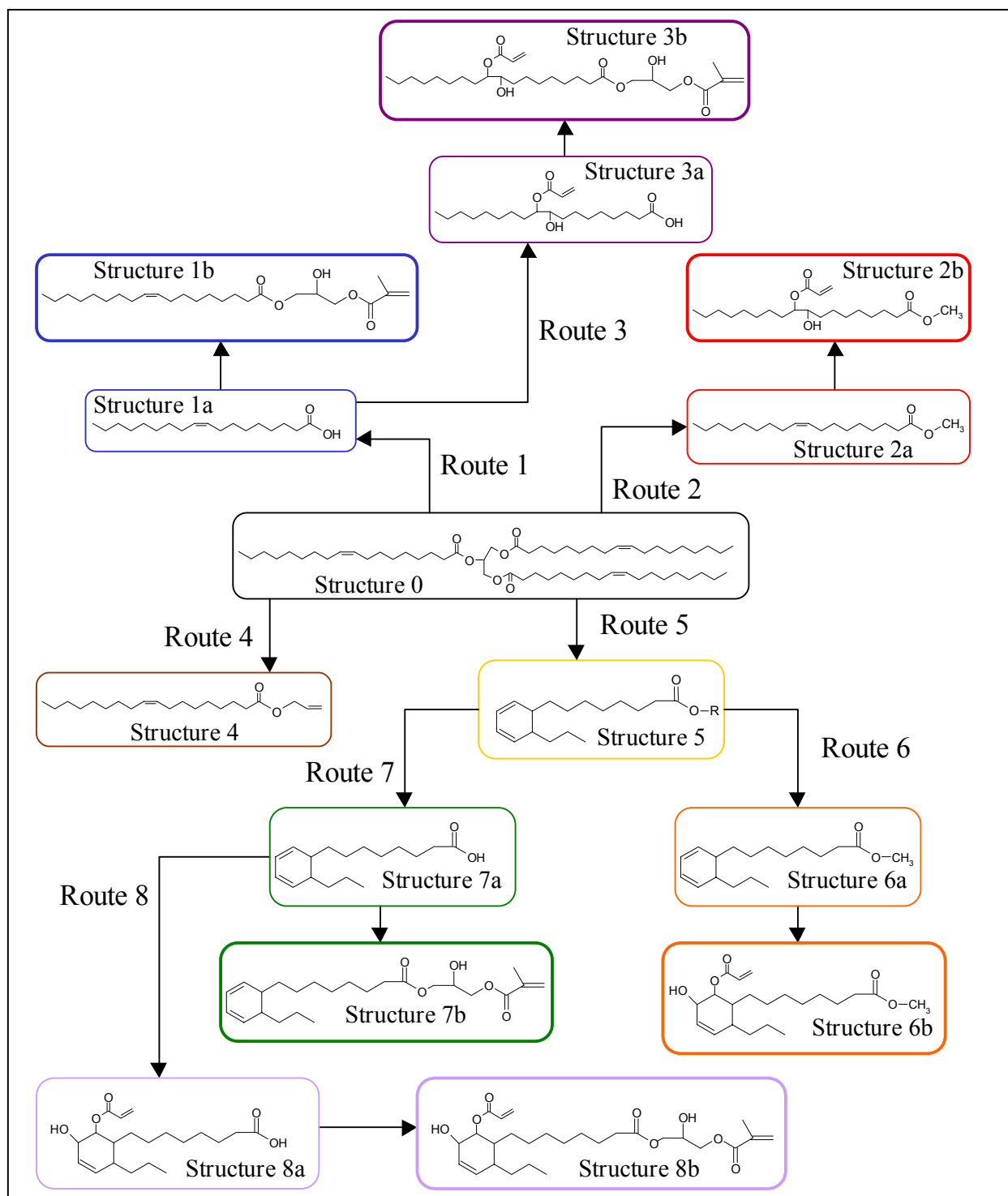


Figure 24. The proposed synthetic routes to produce FA-based monomers.

Canola oil and olive oil are relatively inexpensive sources of monounsaturated acids, but they do have significant contents of saturated and polyunsaturated acids (18).

As discussed previously, difunctional monomers can be used to improve the properties of VE resins. Route 3 shows a way to produce difunctional monomers (structure 3b) by combining the synthetic procedures of routes 1 and 2.

Allyl alcohol is used to break up the triglycerides into allyl FA monomers (route 4, structure 4) in a procedure that is very similar to the methanolysis reaction. These monomers have a primary unsaturation site that could potentially be used for free radical polymerization.

Routes 6–8 make use of the cyclized derivatives of triglycerides. In route 6, a methyl ester (ME) of the cyclized species is formed via methanolysis (structure 6a). The remaining unsaturation sites on the FA are then epoxidized and acrylated to add free radical functionality to the FA (structure 6b). In route 7, cyclized FAs are produced by acidolysis of cyclized triglycerides (structure 7a). This species is then reacted with GM, in the same manner as route 1, to attach vinyl functionality to the end of the cyclized FA. Route 8 is just a combination of routes 6 and 7, resulting in divinyl, cyclized FA monomers (structure 8b).

2.5.3.2 Synthesis of Glycidyl Methacrylate Modified Fatty Acid Monomers (GM-FA), FAME, Acrylated Methyl Esters (AME), and Allyl Alcohol Modified Soybean Oil (AOH-SBO). Synthesis procedures for preparing the GM-FA in route 1 (Figure 24) were first established. Epoxides and FAs react at fairly low temperatures ($<100\text{ }^{\circ}\text{C}$) with short reaction times if properly catalyzed. The AMC-2 (1–2 weight-percent) catalyst was used to catalyze this reaction. Near infrared (IR) or mid-IR (FTIR) can be used to determine the extent of reaction. The epoxide peaks at 4530 and 917 cm^{-1} (24) were tracked during the reaction (Figure 25). Table 4 lists the reaction conditions tested and the corresponding extent of reaction and reaction time.

The reaction between a stoichiometric amount of oleic acid (OA) (18 carbon atoms, 1 unsaturation site) and GM was catalyzed with 2-weight-percent AMC-2 catalyst and run at RT. The reaction went to ~90% completion after 3 days of reaction.

The reaction between a stoichiometric amount of OA and GM was catalyzed with 0.5-, 1-, and 2-weight-percent AMC-2 catalyst and run at $70\text{ }^{\circ}\text{C}$. The reaction went to completion in 1.5 hr when 2-weight-percent catalyst was used. The reaction went to completion after 2.5 hr when 1-weight-percent catalyst was used. When 0.5-weight-percent catalyst was used, the reaction took longer than 4 hr. In order to simultaneously minimize the catalyst concentration and reaction time, 1-weight-percent AMC-2 was found to be optimum for this reaction.

Work with acrylating epoxidized triglycerides showed that adding the acid in aliquots decreased the extent of etherification (8). One-third the stoichiometric amount of OA was added to GM. The reaction was run at $70\text{ }^{\circ}\text{C}$ and catalyzed with 2-weight-percent AMC-2. Gelation occurred after 1.5 hr of reaction, as a result of the etherification reaction. Therefore, adding OA in aliquots to the GM was found to be a poor method for producing the GM-OA monomer.

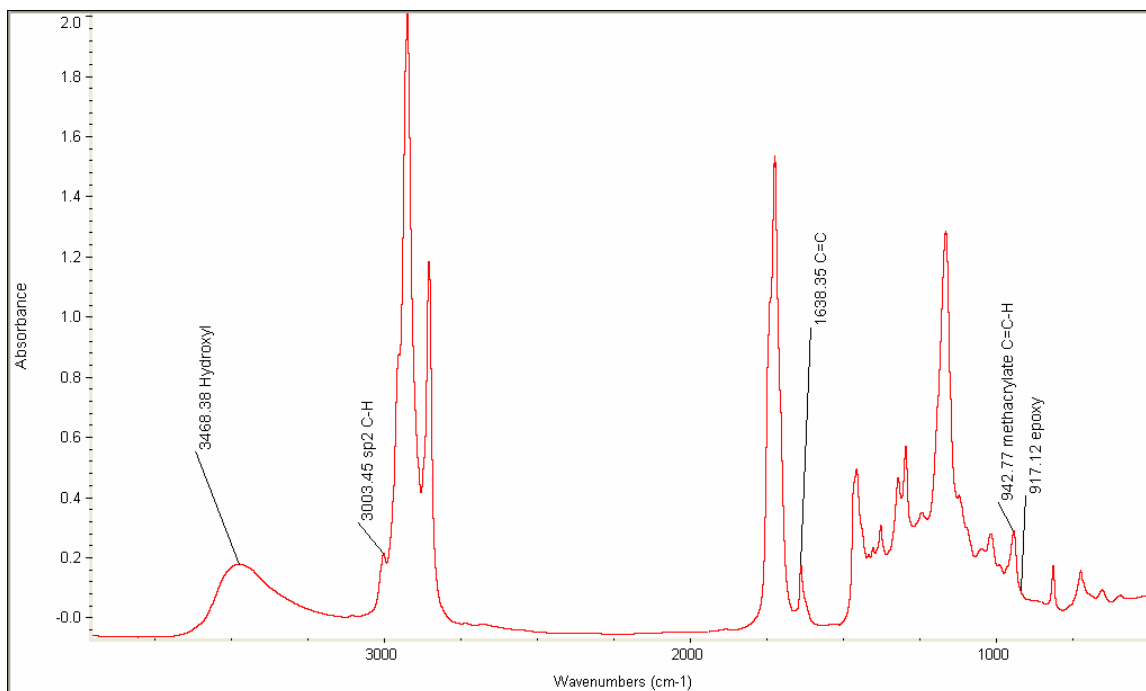


Figure 25. The mid-IR spectra of GM-OA after reaction.

Table 4. The reaction conditions tested to produce GM-OA and the resulting reaction times and extents of reaction.

GM:OA	AMC-2 (weight-percent)	Reaction Temperature	Reaction Time
1:1	0.5	70 °C	>4 hr
1:1	1	70 °C	2.5 hr
1:1	2	RT	>3 days
1:1	2	70 °C	1.5 hr
1:0.33	2	70 °C	gelled in 1.5 hr

Three FAs were used to determine the effect of FA structure on resin and polymer properties: (1) lauric acid, (2) OA, and (3) linoleic acid. The molecular structure differences of these FAs are summarized in Table 5.

Table 5. The molecular structure differences of the FAs used to prepare GM-FA monomers.

FA	Chain Length in Carbon Atoms	Unsaturation Sites
Lau	12	0
OA	18	1
Lin	18	2

Note: Lau = lauric acid; Lin = linoleic acid.

FAME (Figure 24, structure 2a) are formed by the methanolysis of triglycerides. A genetically engineered high oleic soybean oil* (HOSO) and canola oil were used to make ME. For both oils, 100 g of oil, 17.9 g of methanol, and 20.6 g of 0.5 N KOH in methanol were mixed together. The reaction was run at 60 °C for 1 day. The products were recovered using ether extraction (22). The reaction mixture was dissolved in ~150-mL diethyl ether and poured into a separatory funnel. Distilled water was added to remove the acid from the ether phase. The layers were allowed to separate, and the water layer was discarded. This step was repeated four times. The ether solution was washed with saturated aqueous sodium chloride to remove water from the ether phase and dried over anhydrous sodium sulfate. The ether was evaporated away at RT. Nuclear magnetic resonance (¹H-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† AC250 Spectrometer was used to determine if methanolysis was complete (20, 22). In all cases, the methanolysis reaction was complete.

In the next experiments, epoxidized samples of AME were made by reacting the unsaturation sites of FAME with a mixture of formic acid and hydrogen peroxide (25). The amount of formic acid used was one-third the oil mass. The amount of hydrogen peroxide used was twice the molar ratio needed to produce the completely epoxidized sample. This amount of hydrogen peroxide was used to drive the epoxidation to completion. The unsaturated ME were added to an Erlenmeyer flask, which contained a magnetic stir bar. The appropriate mass of hydrogen peroxide was added, followed by the formic acid. The flask was stoppered and stirred vigorously. The reaction was run at RT, using a water bath for cooling. At the end of 16-hr reaction time, the samples were ether extracted to recover purified epoxidized oils. In the ether extraction, the samples were dissolved in diethyl ether and washed with aqueous sodium bicarbonate until the pH of the solution was slightly alkaline. The contents were allowed to phase separate, and the aqueous layer was discarded. Finally, the solution was washed with aqueous sodium chloride and dried over anhydrous sodium sulfate. The ether was evaporated at RT. The extent of epoxidation was measured using ¹H-NMR (25). The level of epoxidation of epoxidized HOSO and epoxidized canola ME were 0.8 and 1.1 epoxides/FAME, respectively. Thus, the extent of epoxidation of HOSO ME is low, considering we would like to have one functional group per FAME. This occurred because the level of unsaturation of HOSO is only 0.9/FAME and epoxidation was not complete. ME of canola oil have 1.17 unsaturation sites on average. Therefore, the epoxidation of canola oil ME was successful.

Acrylated samples (Figure 24, structure 2b) were made by reacting the epoxide groups of epoxidized FAME with acrylic acid (26). The AMC-2 catalyst was used to reduce the extent of epoxy homopolymerization (4). The AMC-2 was used in every sample at a concentration of 0.02 g/mL. A concentration of 0.0033-g/mL hydroquinone (HQ) was used to inhibit free-radical

*E. I. du Pont de Nemours and Company (DuPont), Wilmington, DE.

†Bruker Corp., Billerica, MA.

polymerization. The reaction mixture was equilibrated at 70 °C before adding acrylic acid to the mixture. The reaction was run at 70 °C in a silicon oil bath on a hot plate while stirring vigorously.

The oils were acrylated by adding 1.1 moles of acrylic acid per epoxide group. The acrylic acid was added in aliquots during the course of the reaction to reduce the amount of epoxy homopolymerization (4). The 1/3-mole acrylic acid/mole of FAME was added until the last aliquot, where the remaining acrylic acid was added to the mixture. Upon addition of the acrylic acid, the solution became a bright green color. This was due to the interaction of the acid with the chromium-based catalyst (4). When the acid was consumed, as measured by pH paper, the reaction mixture became brown in color, and the next aliquot of acrylic acid was added. An aliquot of acrylic acid was added after 2 hr even if the reaction mixture was not brown. The reaction mixtures were removed from the heat 2 hr after the last acrylic acid aliquot was added. The acrylated oils were purified via ether extraction as described for the epoxidized oils. The level of acrylation in the product was measured using ¹H-NMR (25). The level of acrylation of HOSO ME was 0.7 acrylates/FAME. This number is low because of the low level of epoxidation achieved. Therefore, some ME molecules have no functional groups and will act as plasticizers when polymerized with VE. The level of acrylation of acrylated canola oil ME has not been established.

In the next experiment, allyl alcohol was used to break apart the glycerol linkage of triglycerides to produce AOH-SBO (structure 4, Figure 24). The reaction mixture contained 70 g of oil (SBO), 22 mL of allyl alcohol, and 25.5 mL of a 0.5 N KOH/allyl alcohol solution. The contents were mixed and reacted at 60 °C for 3 days. Afterward, the reaction products were recovered using an ether extraction, as for the methanolysis reaction. The level of functionalization with allyl alcohol was measured using ¹H-NMR. The peaks at 5.9, 5.2, and 4.6 parts per million (ppm) represent the vinyl C-H, the vinyl C-H₂, and the allylic methylene protons of the allyl group (26). The areas of these peaks relative to the areas of the peaks representing the two protons alpha to the carbonyl and the three FA methyl protons should be 1:2:2:3 at complete functionalization. Results have shown that the allyl alcohololysis reaction only proceeds to ~80% completion.

2.5.3.3 Monomer Viscosity. The viscosity of the FA monomers and the reactants used to produce these monomers were measured using a Brookfield digital viscometer at 30 °C or found through the literature (27, 28). FAME and AOH-SBO had the lowest viscosity (Table 6) because they do not have functional groups that induce hydrogen bonding. The GM-FA and AME have hydroxy-ester groups, which cause these monomers to have considerably higher viscosities. The viscosities of these monomers are higher than their starting materials (reactants) for this same reason. On the other hand, AOH-SBO and FAME have an even lower viscosity than triglycerides because of their considerably lower molecular weight. In addition, AOH-SBO and FAME have lower viscosities than FAs (Table 7) because FAs have highly polar carboxylic acid

Table 6. The viscosity of FA-based monomers and precursors.

Type	Chemical	Viscosity (cP)
Precursor	Canola-ME	8
Precursor	HOSO-ME	8
Monomer	AOH-SBO	10
Monomer	GM-Lau	48
Monomer	GM-Lau	56
Monomer	GM-OA	58
Monomer	AHOSO-ME	56
Monomer	Styrene	0.7

Note: AHOSO = acrylated high oleic soybean oil.

Table 7. The viscosity of the starting materials/reactants for FA monomers.

Chemical	Viscosity (cP)
Methanol	<1
GM	~1
Allyl Alcohol	~1
OA	24
Lin	24
Lau	NA (Crystalline Solid)
HOSO	52
Canola Oil	51
SBO	45

Note: NA = not applicable.

groups. The viscosities of GM-FA and AME are higher than their starting materials because of increasing molecular weight and polarity.

2.5.3.4 Phase Separation and Cure of Mixtures of FA Monomers and VE. A number of FA and triglyceride-based monomers were polymerized with VE. It was found that a number of such monomers phase separated with VE upon cure. Even more surprising was that phase separation and cure would occur upon the addition of only CoNap (i.e., no initiator) to the resin mixtures. The following describes the experiments that have been done and some conclusions that have been made.

AOH-SBO-VE Resins. The AOH-SBO is shown in Figure 24, structure 4. The chemical is a FA with an allyl group attached to the ester linkage. The molecule is aliphatic and nonpolar in nature, with only a single ester group, no hydroxyl, epoxies or other such polar groups.

VE 828 and AOH-SBO formed miscible solutions in the mass ratios of 1:1 and 2:1, respectively. Other mass ratios were not tested. The solution was stable with time with no phase separation. However, upon addition of CoNap, the sample cured at RT and microphase separated. We use the term microphase separation to mean that the resulting polymer was opaque, but no distinct layers of the immiscible components formed. The polymer, although fairly hard, was very

brittle. When curing with Trigonox, the polymer became harder and tougher, but it was still very brittle. The resin mixture was cured with Trigonox at elevated temperature without using CoNap as an accelerator. The mixture again microphase separated, and formed a polymer that was very similar to the one formed at RT with the CoNap and Trigonox.

Resins were formed using 2 parts VE, 1 part AOH-SBO, and 1 part styrene. The resulting resins phase separated and cured in the same manner as the resins without styrene did.

To ensure that the AMC-2 catalyst used in synthesizing the VE from Epon and methacrylic acid was not causing this effect, VE 828 synthesized using the triphenylantimony/triphenylphosphine ($\text{SbPh}_3/\text{PPh}_3$) catalysts were used (3). This VE was mixed with the AOH-SBO monomer, and the same results were found as for the VE synthesized using the AMC-2 catalyst. However, it should be noted that cure occurred faster for VE that was prepared with the AMC-2 catalyst. This fact was also seen for the cure of VE with styrene, CoNap, and Trigonox; the VE prepared using AMC-2 cured 10 min faster than with the VE prepared using $\text{PPh}_3/\text{SbPh}_3$. Therefore, the AMC-2 catalyst is not the cause for the phase separation and premature curing, but it may accelerate the cure process.

A mixture of AOH-SBO and VE 828 was cured in the presence of CoNap at RT while monitoring with FTIR. The VE peak dropped relative to the internal reference as a function of reaction time, indicating VE cure (Figure 26). The allyl group appears at 929.6 cm^{-1} and 989.2 cm^{-1} (26) (Figure 26). The 929.6 cm^{-1} peak is coincident with the vinyl group on VE. However, the 989.2 cm^{-1} peak is clearly resolved over the course of reaction. The 989.2 cm^{-1} peak height did not change relative to the internal reference, indicating that AOH-SBO did not cure with the VE.

Differential scanning calorimeter (DSC) results showed that the T_g of the material was $135\text{ }^\circ\text{C}$. However, when the sample was heated to $130\text{ }^\circ\text{C}$, a layer of low viscosity liquid diffused to the surface. Upon returning the sample to RT, the liquid layer redissolved into the solid layer. We conclude that the T_g of $135\text{ }^\circ\text{C}$ is that of the plasticized cured VE, while the liquid is the nonreacted AOH-SBO.

Acrylated Soybean Oil (SBO)–VE Mixture. Acrylated SBO (Ebecryl 860*), as seen in Figure 27, was mixed with AOH-SBO. The resin only cured at elevated temperatures ($130\text{ }^\circ\text{C}$) in the presence of Trigonox alone or with the mixture of CoNap and Trigonox (Table 3). The components were miscible at all stages of cure. Unfortunately, the resulting polymers were very fragile rubbers. FTIR results show that the AOH-SBO monomers are not polymerizing. Even though the AOH-SBO did not cure, we believe that the polymer did not phase separate upon cure because of the chemical similarity of AOH-SBO to acrylated SBO.

*Ebecryl is a registered trademark of Societe Anonyme Corp., Belgium.

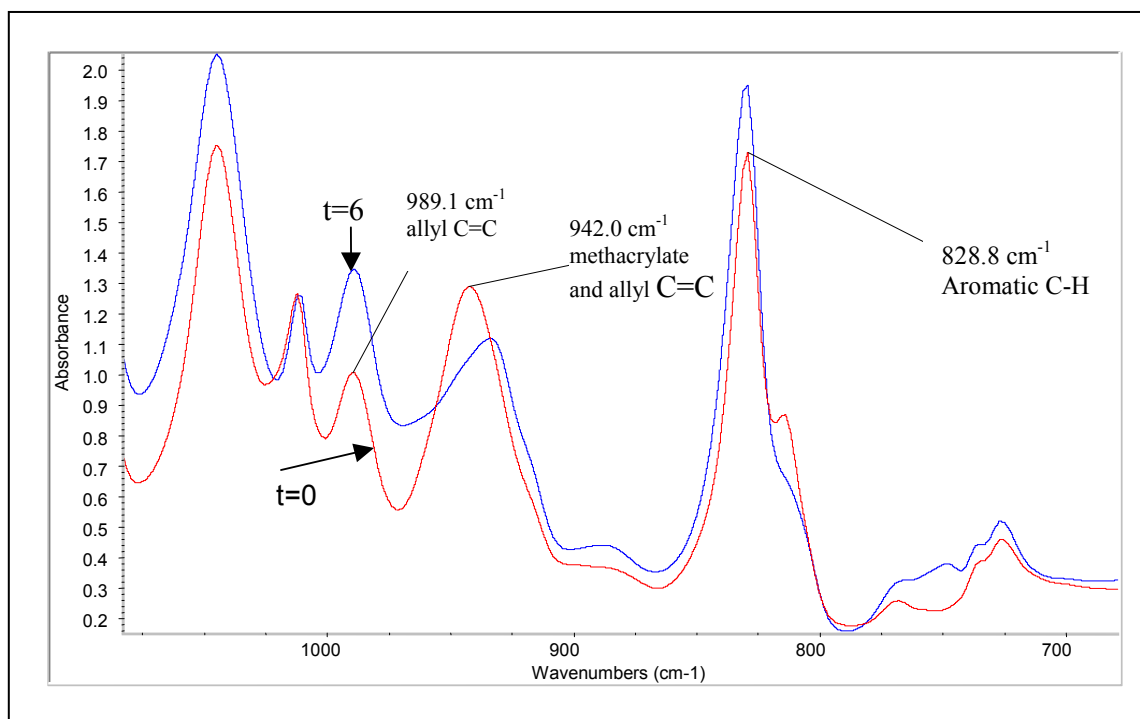


Figure 26. The FTIR spectra of VE/AOH-SBO with CoNap at $t = 0$ and $t = 6$ days.

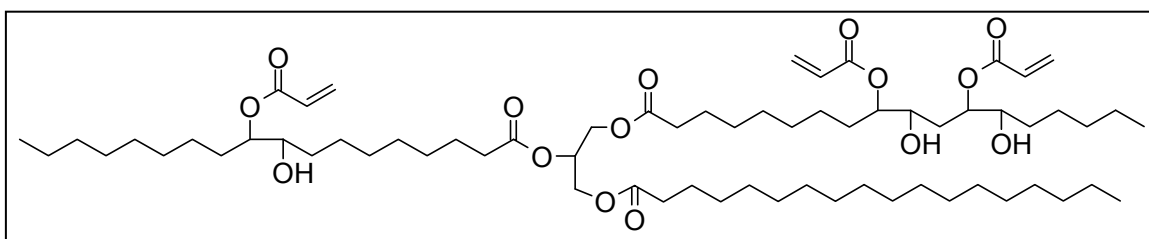


Figure 27. The molecular structure of acrylated SBO.

Control Samples. Just to rule out any simple explanations, a number of control samples were made. As was expected, VE did not cure in the presence of CoNap alone, but did cure in the presence of Trigonox alone at elevated temperatures and cured at RT in the presence of both chemicals. AOH-SBO and allyl alcohol did not cure in the presence of CoNap and Trigonox, even at elevated temperatures. Therefore, our conclusion that AOH-SBO does not polymerize in the presence of acrylated SBO or VE seems justified.

FAME/SBO-VE Resins. FAME (Figure 24, structure 2a) were synthesized via a methanolysis reaction of HOSO. FAME were mixed with VE and were fully miscible. These resins cured at RT in the presence of CoNap alone. As in the case for the AOH-SBO/VE resins, the resulting polymers microphase separated. Furthermore, the apparent physical properties of these polymers were very similar to the AOH-SBO/VE polymers. The phase-separation behavior of these polymers was the same when the resin was cured at elevated temperature using Trigonox or

cured at RT using CoNap and Trigonox. However, the samples cured with Trigonox were harder and less brittle.

A mixture of VE and FAME of HOSO was made. CoNap, in the amount of 0.5 weight-percent, was added to the resin mixture. The sample was monitored in mid-IR as a function of time for 12 days at RT. Figure 28 shows that the methacrylic acid group of the VE decreased (945 cm^{-1}) as a function of reaction time relative to the internal reference (830 cm^{-1}), which represents the bending of the aromatic C-H. Therefore, VE cured in the presence of FAME. The extent of cure of VE as a function of time is shown in Figure 29. The behavior does not seem to be autocatalytic; however, curing occurs so quickly that the initial cure kinetics was not observed with FTIR. In addition, the cure continues at least through 12 days, even though it appeared that the extent of cure was leveling off with reaction time after 300 min. The extent of cure even after 12 days was 75%, which is very high, especially considering the cure of VE with styrene at RT results in only 60% cure of VE. The unsaturation sites on the FAME (724 cm^{-1}) did not react, as this peak height relative to the reference did not change over the course of the reaction.

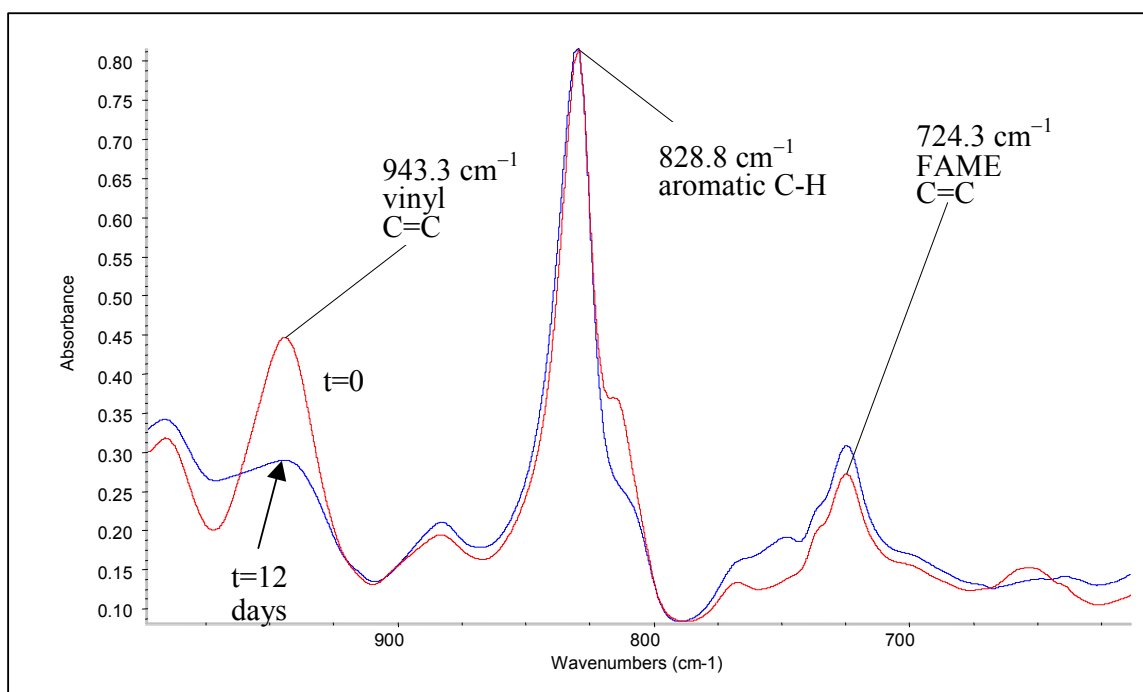


Figure 28. The FTIR spectra at $t = 0$ and $t = 12$ days for the induced cure of VE in the presence of FAME and CoNap.

SBO was mixed with VE monomer. Unfortunately, SBO and VE are not miscible. Therefore, the molecular weight difference of FAME and the SBO had a large impact on the solubility with VE. However, good mixing can produce a partially mixed resin. The addition of CoNap resulted in a cured, but phase-separated polymer. The bottom layer was a hard solid, presumably VE, while the top layer was soft and grainy (probably a mixture of SBO and other nonpolymerized components).

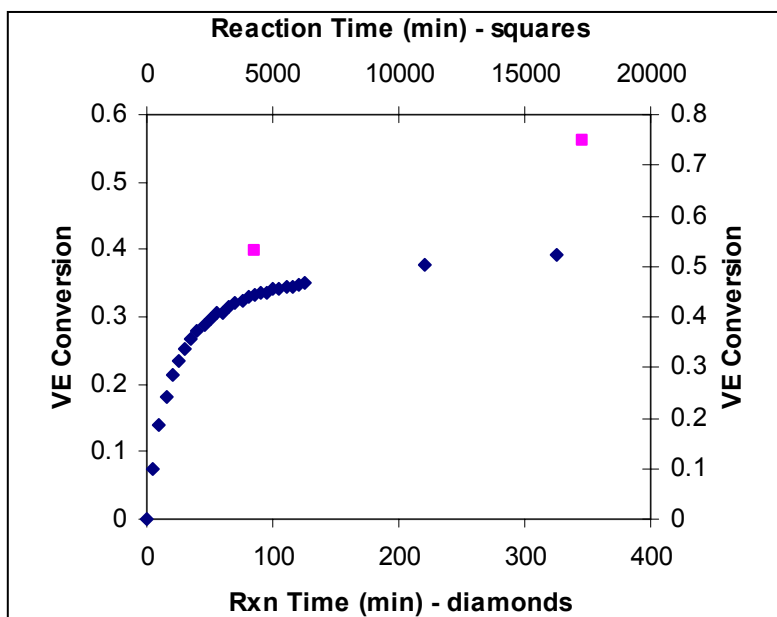


Figure 29. The extent of cure of VE as a function of time in the mixture of VE, FAME, and CoNap. There are two x-axes in order to show both the short-term VE cure and the long-term VE cure.

Epoxidized Oils–VE Resins. The FAME were epoxidized, as shown in Figure 30. These epoxidized oils (EHOSO-FAME) were mixed with VE. The components were fully miscible before cure. Upon addition of CoNap, the VE cured. However, the polymer was phase separated, where the top layer was a viscous liquid and the bottom layer was a hard solid (cured VE). The use of both Trigonox and CoNap resulted in a single-phase polymer that was clear. When heated to temperatures of $\sim 150\text{ }^{\circ}\text{C}$, a layer of liquid formed at the top of the polymer.

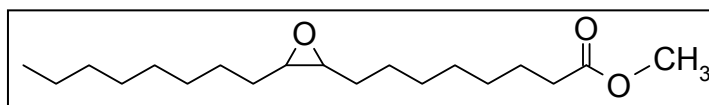


Figure 30. The molecular structure of epoxidized FAME.

This liquid was probably the EHOSO-FAME, indicating that it did not react into the polymer network. FTIR of this layer shows that the layer is epoxidized oil contaminated with other chemicals (VE, catalysts, etc.).

ESO also induced cure of VE upon addition of CoNap. Two phases were formed where the bottom layer was a hard polymer and the top was a soft and viscous liquid. However, when Trigonox and CoNap were used, the resulting polymer was microphase separated. The higher molecular weight of the ESO probably caused a larger driving force for phase separation during cure relative to the epoxidized FAME.

FTIR experiments were performed to monitor the cure of VE/epoxidized FAME resins. The results show that the VE molecules cured, while the epoxidized FAME did not polymerize (epoxy peak was constant with time).

The VE prepared using the triphenylantimony/triphenylphosphine catalyst was used instead of the VE prepared using the AMC-2 catalyst. No differences in the cure of epoxidized FAME with VE was observed with the different catalyst systems. However, CoNap did not induce the cure of the VE-ESO when $\text{PPh}_3/\text{SbPh}_3$ was present, as it did when the AMC-2 catalyst was present. The cause for this is unknown, except that it seems that the AMC-2 does accelerate the cure process, and could thus increase the likelihood of cure as well.

AME-VE Resins. CoNap was added to VE/AHOSO-ME resin in the amount of 1 weight-percent. The resulting resin did not cure. The resin also did not cure at elevated temperatures with or without the CoNap. Although both AHOSO-ME and FAME are FA derivatives, somehow the chemical makeup of AHOSO-ME does not induce cure of VE, whereas cure is induced using FAME, epoxidized FAME, and AOH-SBO. A possible reason for this is that 2000-ppm HQ inhibitor is added during the acrylation of EHOSO-ME (although some was removed during the ether extraction), which was not present in the other FA derivatives. However, the fact that the resin cured in a fairly short time (<30 min) in the presence of CoNap and Trigonox indicates that the inhibitor content in this resin was low.

AME and VE cure in any proportion to form single-phase hard polymers upon addition of Trigonox and CoNap (or Trigonox alone if cured at elevated temperatures). On the other hand, AME does not cure in the presence of CoNap and Trigonox, even at high temperatures.

GM-FA-VE Resins. A resin mixture containing GM-OA and VE was made containing 1-weight-percent CoNap. This mixture also did not cure at RT or 62 °C even after 5 hr of reaction. Somehow the chemical makeup of GM-OA does not induce cure of VE. A possible reason for this is again the presence of inhibitor in the GM (100-ppm hydroquinone monomethyl ether [MEHQ]), which is not present in the other FA derivatives, but this does not seem likely.

GM-OA monomer alone cured in the presence of CoNap and Trigonox at RT. The sample did not melt at temperatures as high as 130 °C, indicating the sample was cross-linked. The unsaturation site on the backbone of GM-OA can result in chain transfer, which can cross-link the polymer. The sample was rubbery, and as expected, no T_g was visible in the DSC sweep from RT to 200 °C. The extent of cure and cure kinetics has not been measured. In addition, GM-OA did not cure using 2-weight-percent Irgacure* with exposure to an ultraviolet (UV) lamp for 2 hr. GM-OA cured with 1-weight-percent Trigonox at 130 °C. However, samples of GM-OA with CoNap did not cure.

GM-FA and VE cure in any proportion to form a single-phase polymer in the presence of CoNap and Trigonox (or just Trigonox if curing at elevated temperatures). VE/GM-FA did not cure when only CoNap was added. VE/GM-FA cured using 2-weight-percent Irgacure with exposure to a UV lamp for 10 min. The material was nearly as stiff and tough as VE/styrene polymers. The extent of cure and reaction kinetics has not been measured.

*Irgacure is a registered trademark of Ciba-Geigy.

Effect of CoNap. VE cured in the presence of FAME, AOH-SBO, or epoxidized FAME and CoNap. However, VE did not cure in the presence of CoNap at RT or 62 °C even after 1 day of reaction. Furthermore, VE itself did not cure at 62 °C even after 3 days of cure. FAME, epoxidized FAME, and AOH-SBO did not cure in the presence of CoNap after 1 day of reaction at RT. Although VE and FAME, epoxidized FAME, or AOH-SBO (no CoNap) did not cure at RT, these samples did cure at 62 °C. This shows that a free-radical reaction is occurring and the CoNap only accelerates the breakdown of the free-radical initiator.

Free Radical Inhibitors. HQ was added to mixtures of VE/AOH-SBO resins to try to prevent the premature curing of these resins. The resins contained 1 part AOH-SBO and 1.5 parts VE, and 0.5-weight-percent CoNap was added to the resin to decrease the cure time. HQ in the amounts of 259, 1275, and 17,000 ppm was added to the resin. Only the sample with 17,000-ppm HQ did not cure, while the others cured within 10 min of the addition of CoNap. Because a free-radical inhibitor can inhibit the gelation of VE/FA resins, it appears that the curing process is free-radical based. Unfortunately, a very large amount of free-radical inhibitor needs to be added to successfully prevent unwanted gelation (~10,000 ppm), which is ~100 times the amount that is typically added to monomeric resins.

Phase Behavior Conclusions. The phase behavior studies of VE/FA resins has led to a number of conclusions:

- Even if the resin is miscible before cure, phase separation can occur because of one of two scenarios:
 - (1) No polar character (epoxies, hydroxyl groups) in the resin.
 - (2) Monomer molecular weight is too high (tendency for phase separation increases with molecular weight).
- Phase separation does not occur if the monomers are similar in character (e.g., Ebecryl resin with the FA-based monomers), but this has no effect on the cure.
- The AMC-2 catalyst accelerates the cure of VE resins.
- The AMC-2 catalyst has little effect on the phase separation behavior and tendency to cure of the VE-FA/triglyceride resins.
- VE cures in the presence of FAME with or without CoNap. CoNap acts only as a promoter for the reaction.
- The unsaturation sites on FAME and allyl groups on AOH-SBO do not participate in the premature cure of VE/AOH-SBO resins.
- AHOSO-ME and GM-OA do not induce cure and phase separation of VE.

- Free-radical inhibitors used in very large quantities can inhibit the gelation process of VE/FA resins. Therefore, the premature gelation process can be regarded as a free-radical process.
- Because a very high amount of inhibitor must be used to prevent gelation, we conclude that there is a large quantity of the species that yields the free radicals.

Unfortunately, we have yet to determine why VE cures in the presence of these non-vinyl FA and CoNap. Work will be done in the near future to elucidate this mechanism.

2.5.3.5 Resin Viscosity and Gelation. The viscosities of FA-based VE resins were measured at 30 °C. CoNap and Trigonox (45% cumene hydroperoxide) were used to cure the resins. One mole of cumene hydroperoxide was used per 100 moles of vinyl groups. The mass of CoNap was one-fourth the mass of Trigonox. The viscosities of the resins before cure are shown in Table 8. The viscosity of the GM-FA resins increased with chain length and decreased as level of unsaturation along the FA backbone decreased. The level of unsaturation affected the viscosity because these sites put kinks along the FA chain and increase the intermolecular spacing (12). AHOSO-ME had a lower viscosity than GM-OA because it was not completely functionalized (some FA did not have acrylate/hydroxyl groups on them) and it has a lower molecular weight. Figure 31 shows the gelation behavior of these resins. There was a significant induction period before gelation occurred, where the viscosity increased very rapidly, just as for VE/styrene resins.

Table 8. The initial viscosity of FA-based VE resins at 30 °C.

Comonomer	Viscosity (cP)	
	35% Comonomer	45% Comonomer
GM-Lau	1720 ± 4	792 ± 4
GM-Lin	2500 ± 4	1900 ± 4
GM-OA	2720 ± 4	2000 ± 4
AHOSO-ME	2000 ± 4	1300 ± 4

2.5.3.6 Polymer Properties. The polymer properties were measured using DMA. Table 9 lists the properties of the VE/GM-OA and VE/GM-Lau polymers cured at RT and then postcured with a 5 °C temperature ramp from RT to 200 °C. The moduli were >1 GPa.

DMA shows that T_g was <100 °C for these polymers. Both T_g and the modulus increase as the FA chain length decreased. This was expected because longer FA chains increase the free volume of the polymer. The rubber moduli of the polymers were ~45 MPa, indicating the molecular weight between cross-links, M_c , was ~250 g/mol. M_c can be calculated theoretically assuming complete reaction using rubber elasticity:

$$E = 3RT\rho/M_c, \quad (10)$$

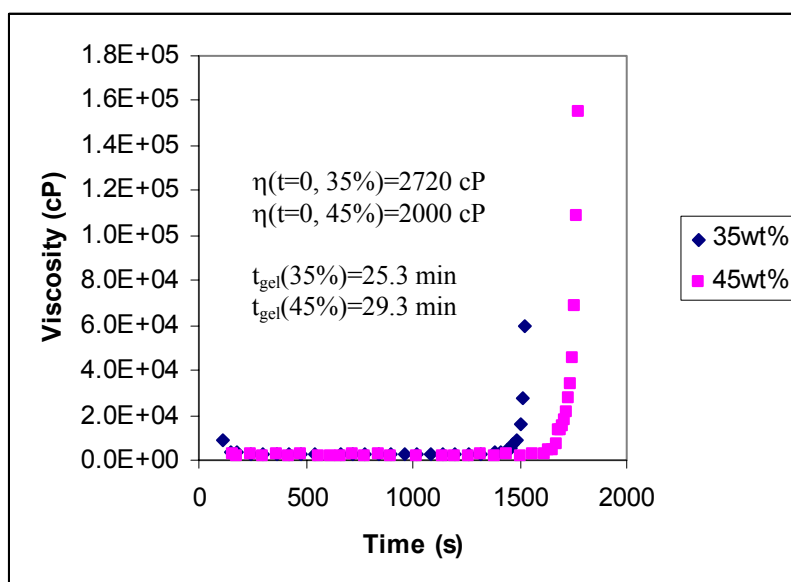


Figure 31. The viscosity of VE/GM-OA resins as a function of cure time.

Table 9. The properties of FA-based VE.

Comonomer/Content	T _g (°C)	E' at 35 °C (MPa)
GM-OA/35%	74	1.6
GM-OA/45%	75	1.1
GM-Lau/35%	85	1.7
GM-Lau/45%	71	1.3
AHOSO-ME/35%	70	1.1

where E is the modulus, R is the ideal gas constant, T is the absolute temperature, and ρ is the sample density (9, 29). M_c should be 280 g/mol and 300 g/mol for 35% and 45% GM-FA, respectively, which is in good agreement with our results. Table 9 also lists the DMA properties for AME. The moduli and T_g are lower because of the fairly low level of acrylation of the AME (~ 0.7 AA/FAME).

Curing the resins at elevated temperature increases the polymer properties. The resins were cured in the same manner as the resins cured at RT, except that no CoNap was used and the samples were cured at 90 °C in an oven. Comparing Tables 9 and 10, it is obvious that both T_g and the modulus increase as the cure temperature increases. These results were expected because elevated temperatures typically increase the extent of polymerization (1).

2.5.3.7 VE/GM-OA/Styrene Blends. The properties of VE resins using GM-FA were fairly low and the viscosities were fairly high. To improve these properties, blends of GM-FA and styrene were used as the reactive diluent in VE 828.

Table 10. The properties of GM-OA cured at 90 °C and then postcured with a temperature ramp at 5 °C/min from RT to 200 °C.

GM-OA Content (%)	T _g (°C)	E' (35 °C) (GPa)
35	108	1.7
45	82	1.3

Viscosity. The viscosity of VE/GM-OA/styrene was measured at 30 °C and was found to decrease exponentially with styrene content for resins containing 55-weight-percent and 65-weight-percent VE 828 resin (Figure 32). Styrene contents of $\geq 10\%$ reduced the viscosity of VE resins to the acceptable range (< 500 cP). Therefore, only low styrene contents are necessary, from a viscosity viewpoint.

Polymer Properties. The DMA character of these resins improved as the styrene content increased (Figure 33). Figures 34 and 35 show that both the modulus and T_g improved with increasing styrene content. These results show that 15% styrene is sufficient to obtain an acceptable modulus and T_g. Furthermore, at this styrene content, the resin viscosity is well within the acceptable window. Another interesting aspect of these polymers, which will be pursued more in the near future, is that VE/GM-FA/styrene blends cured in open molds with a perfectly hard finish. There was no uncured layer that typically forms due to oxygen inhibition.

A possible reason for this is that the high hydrocarbon content of the resin formed a waxy layer at the surface. However, unlike waxes, these hydrocarbons were functionalized enabling them to react into the polymer network. This indicates that hydrocarbon monomers may segregate to the surface and could potentially reduce styrene emissions. Further work must be done to validate this hypothesis. Regardless, these materials do not need to be polished to form a good and useable surface. The financial, production, and environmental implications of this result are enormous and warrant further investigation.

2.5.3.8 Cyclized FA. No work is reported here with regard to making cyclized FA-based (Figure 24, structures 5–8) monomers.

2.5.3.9 Difunctional FA Monomers. Divinyl monomers have not been prepared from FA. Figure 24 shows that the synthetic routes are similar to the chemical routes already explored. Therefore, we should be able to prepare difunctional monomers shortly.

2.5.3.10 Cost. Because the GM-OA monomer has the potential to be used as a styrene replacement, the cost of the final product is of prime importance. Table 11 lists the costs of the reactants and the estimated cost of GM-OA. GM makes up 33% of the GM-OA by mass. The cost of this monomer is more than that of styrene, but it is still fairly inexpensive for an alternative comonomer.

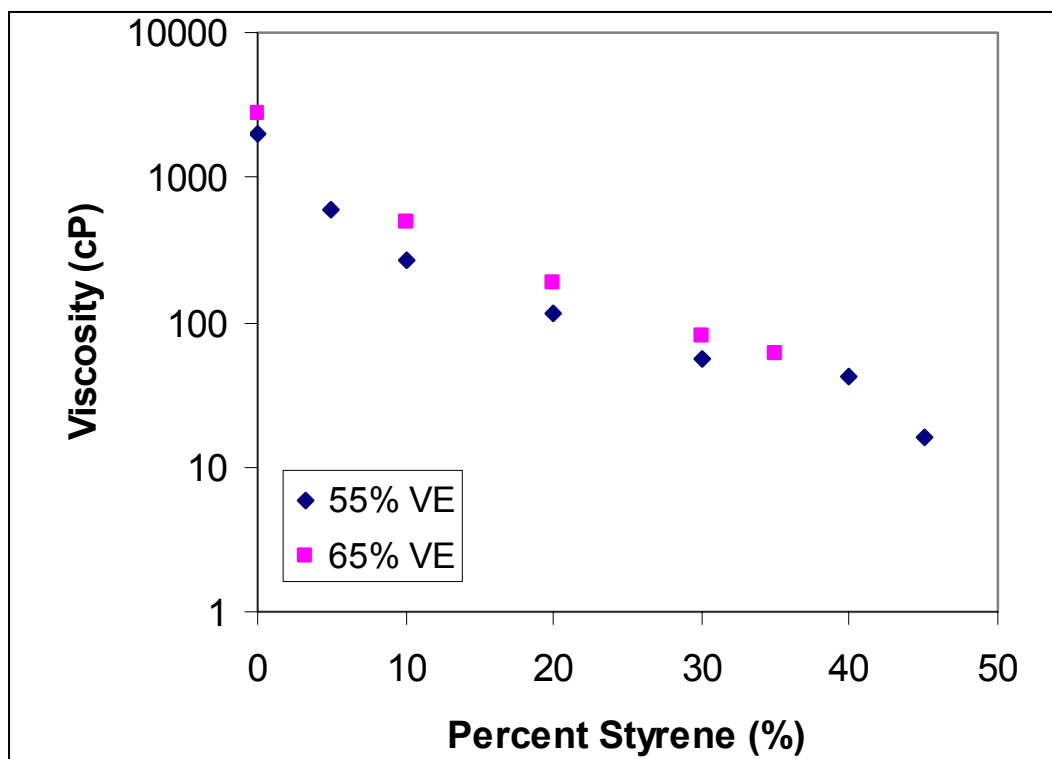


Figure 32. The viscosity of VE/GM-OA/styrene as a function of styrene content in the resin for resins containing 55-weight-percent and 65-weight-percent VE 828.

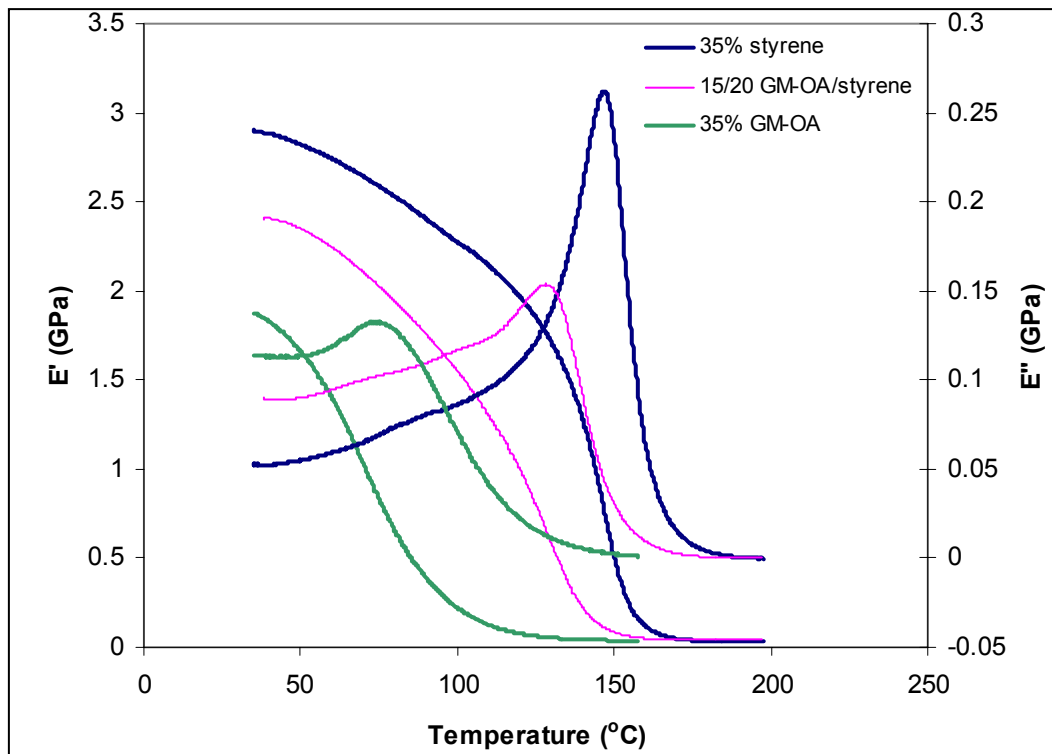


Figure 33. DMA behavior of VE/GM-FA/styrene with 65-weight-percent VE 828.

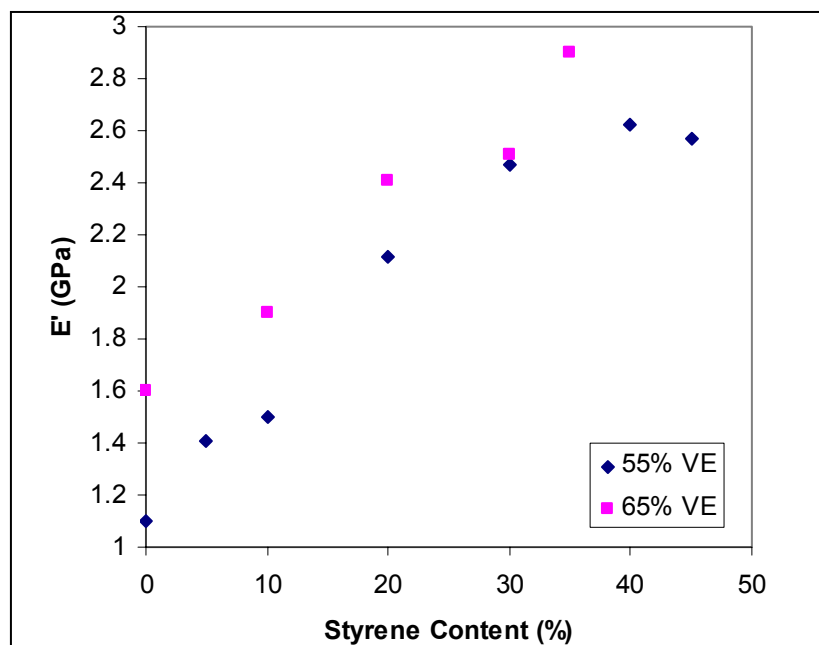


Figure 34. The storage modulus as a function of styrene content for VE/GM-OA/styrene blends.

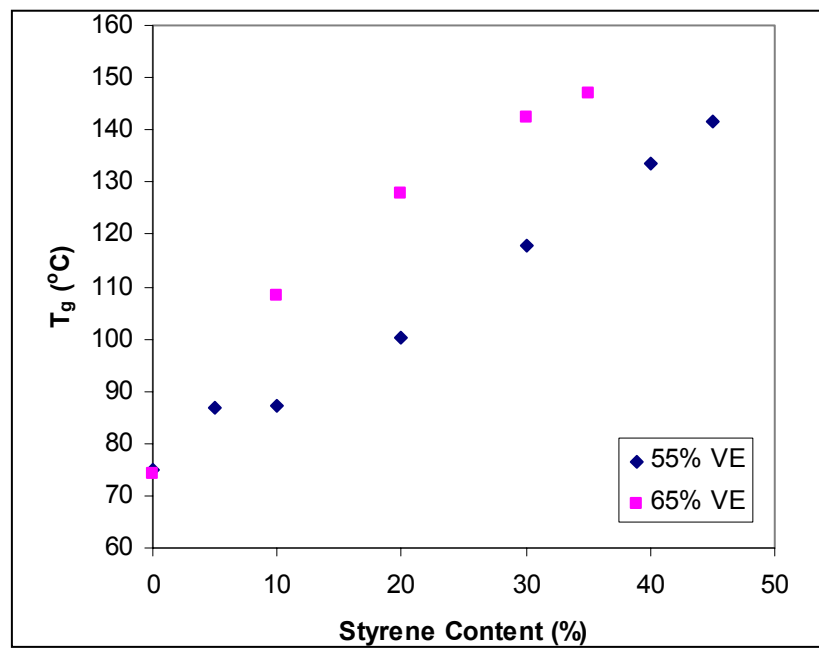


Figure 35. T_g as a function of styrene content for VE/GM-OA/styrene blends.

Table 11. The cost of the reactants and products for the GM-FA reaction.

Chemical	Cost (\$/lb)	Comments
GM	2.29	Sartomer—by the truck load
FA	0.10	Archer Daniels Midland Co.; Cargill
GM-FA	0.83	Estimate, not accounting for reaction costs
Styrene	~0.40	—

2.6 Novel Styrene Suppressant Systems

Rather than actually reducing the styrene content in current VE, we propose to add small amounts of surface-active dendritic polymers that can react into the polymer matrix. The surface-active nature should allow these molecules to self-assemble into a vapor barrier to reduce styrene emissions. Commercial petroleum-based dendritic polymers and triglyceride-based dendrimers will be used to achieve these goals. The benefits of highly branched systems, such as dendrimers and hyperbranched polymers, include low viscosity, high solubility, and a large number of end-groups per chain. The resulting properties of the polymers are dominated by the end-groups, which provide the most accessible route to developing novel styrene suppressant systems. Commercial dendritic systems are already established and are fairly inexpensive. However, these systems have to be modified to enable them to react into a polymer network and preferentially migrate to the surface. Triglycerides are first generation dendrimers. Yet, methods for making higher generation dendrimers from triglycerides have not been established. On the other hand, there already exist commercial methods and products enabling them to react into a polymer network. Functionality that induces preferential migration to the surface will be added in a similar manner as for the commercial petroleum-based dendritic polymers.

Recent work has also revealed the potential of highly branched polymers to function as switchable surfaces. As detailed by Bratcher et al. (30), blends of linear polyesters and partially fluorinated polyethyleneimines (PEIs) were shown to present hydrophobic groups at the surface prior to contact with water. After exposure to water the end-groups flipped, presenting the more hydrophilic backbone of the polymer. In this way, we envision using partial end-group fluorination to transport branched polymers to the surface of a styrene/VE system. Once there, the polymers may act as a barrier against styrene emission. Once exposed to a different material (e.g., a protective coating or adhesive layer), the polymer may undergo a surface switching, exposing a more compatible interface. In this fashion, macromolecular styrene suppressants may outperform the current technology (e.g., paraffin-based, STYRID^{*}-type suppressants). Dendrimer structure, molecular weight, and functionality should all affect the ability of surface-active dendrimers to reduce the styrene emissions from VE resins. Simple experiments to lay the groundwork have been performed.

^{*} STYRID is a trademark of Specialty Products Co.

2.6.1 Commercial Petroleum-Based Dendritic Systems

To begin our investigation of branched polymer modifiers, we identified potential commercial sources. It was found that BASF produces a highly branched PEI, trademarked Lupasol, and Perstorp Specialty Chemicals produces the Boltorn series of hyperbranched polyesters. Both of the polymers possess reactive end-groups. Lupasol polymer chains are amine terminated, while Boltorn chain ends are functionalized with hydroxyl groups. Potential routes for the preparation of modified polymers are shown in Figure 36.

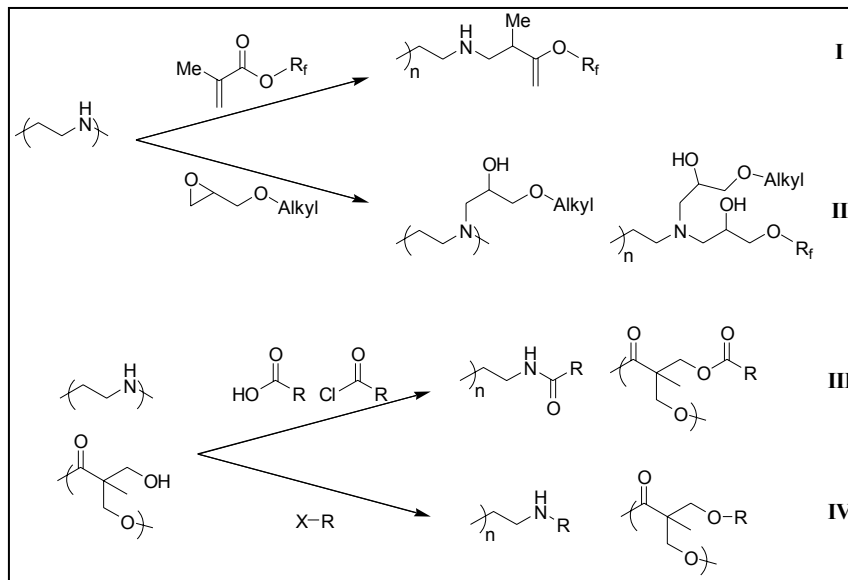


Figure 36. Potential methods of end-group modification. Routes I (Michael addition) and II (epoxide opening) are more suited to the PEI end-groups, while routes III (acyl condensation) and IV (halide displacement) should be applicable to either system.

The routes shown in Figure 36 (I and II) represent very facile reactions. The double bond of a methacrylate or acrylate is very susceptible to nucleophilic attack by primary amines, dubbed a Michael addition. The reaction occurs rapidly, works in the absence of solvent, and quantifies the extent of reaction using IR spectroscopic techniques. While the Michael addition has been observed to proceed with secondary amines, the rate of the reaction decreases by more than 1 order of magnitude. The Michael addition may therefore be used to functionalize a branched polymer almost exclusively at the end-groups.

In contrast, the ring opening of an epoxide is very rapid for both primary and secondary amines. As a result, a greater degree of substitution may be predicted using epoxies to install end-group functionality. In addition, they make a nice complement to the Michael addition chemistry and permit the preparation of polymers with mixed end-group composition.

The reactions shown in Figure 36 (III and IV) should provide additional routes to functionalize the Lupasol PEIs, and should also provide means to make modified Boltorn polyesters. The

attachment of an acid chloride to an amine or alcohol is one of the classic methods of amide or ester formation, respectively. The tertiary amines (branch points) of the Lupasol PEIs may preclude the use of this chemistry for their modification, as they will likely condense HCl salts in the backbone of the polymer. The Boltorns should form esters very easily, and similar modifications have been reported in the literature.

If the acid chlorides prove difficult to handle or salt condensation becomes a paralyzing issue, alternate modes of carboxylic acid activation may be employed to achieve the same functional group preparation. The use of coupling agents such as 4-dimethylaminopyridine (DMAP) and N,N'-dicyclohexylcarbodiimide (DCC) will allow the amide formation with dicyclohexyl urea condensation instead of HCl salts. The main question to be answered about ester/amide formation is which route will yield easier polymer isolation.

The substitution of end-groups by nucleophilic displacement of an alkyl halide will also be attempted, as shown in Figure 36 (IV). The chemistry involved is not as facile as the other routes, but the successful development of the approach should allow for a very wide selection of functionalities for the polymer end-groups.

There exists a large assortment of candidate groups to attach to the periphery of the branched polymers. Chief among them is the inclusion of fluorinated end-groups that should provide the enthalpic driving force to bring the suppressant system to the surface of the resin. We are also investigating long aliphatic chains, as they should reduce styrene emissions by reducing the permeability of the resin surface. Since this type of sealing approach has been demonstrated with suppressants like STYRID, it has the greatest chance of success. Other potential sealing groups include functionalized silanes, which would provide an alternative to the aliphatic end-groups.

We have already made great strides to functionalize the periphery of the branched polymers, Lupasol and Boltorn. Both the Michael addition and ring opening of epoxide have been successfully carried out. The Zonyl TM* fluorosurfactant provides an inexpensive Michael acceptor for the nucleophilic amine to attack. We have functionalized Lupasols with fluorinated chains up to 50% by weight.

The Heloxy line of epoxy modifiers from Resolution Performance Products proved to undergo rapid quantitative reaction with Lupasol PEIs. They have been incorporated up to ~80% by weight, which is very near the theoretical limit for loading of the polymer.

The other routes to modified polymers are also currently being explored. The search for effective reaction conditions is being facilitated through the use of a heated reaction block and oscillatory shaker table. The reaction block consists of 63 wells sized to accommodate 40-mL disposable vials. The block is arranged such that it has three layers. The bottom layer is the

* Zonyl and Zonyl TM are registered trademarks of E.I. du Pont de Nemours and Co.

heated portion. An external controller regulates heating, and feedback is provided through the use of a thermocouple. The top layer of the block is a cooling zone and is equipped with cutouts to allow for coolant fluid circulation. Bridging the heating and cooling zones is a thin insulating layer, which provides good thermal separation between the two layers.

Because of the 3-zone design of the reaction block, we can investigate a wide range of reaction conditions. The cooling zone allows us to reflux low boiling solvents without danger of over-pressurization of the reaction vials. The use of vials to scout reactions also saves greatly in terms of time and material requirements. Instead of using several oil baths and several condensers to search out reaction conditions (e.g., solvent, base, catalyst, nucleophile, etc.), many parameters can be varied at the same time, allowing us to use a semi-combinatorial approach to method development. In some cases, the capacity of the vials is also sufficient for significant material generation.

In the preparation of fluorinated Lupasols via Michael's addition with Zonyl fluorosurfactants, several multigram batches were prepared in parallel. The spontaneous nature of the reactions and the lack of solvent permitted ~6 g of material to be reacted in a single vial. If necessary, the reaction block could likely be used to prepare samples of twice that size. The reaction block has therefore proven its value in both method development and sample preparation.

The ability of dendrimers to mitigate the VOC emissions from VE resins has not been studied. The most commonly used commercial styrene suppressant is STYRID. This chemical is a paraffin wax that segregates to the surface to form a waxy barrier. Unfortunately, STYRID cannot polymerize into the polymer matrix. As a result, STYRID plasticizes the resulting polymers. The remnants of the skin upon the formed piece are also of concern, as they make for poor interfacial properties and must typically be removed by mechanical means from the structure's surface. The interfacial properties in fabric-reinforced composites are also diminished because of the wax/fabric interactions. These interlaminar properties cannot be repaired using mechanical methods to remove the STYRID barrier layer. Regardless, it is important to quantify the ability of STYRID to reduce VOC emissions from VE resins to assess the ability of our multifunctional dendritic polymers to reduce emissions.

VE resins containing 50-weight-percent styrene and 50-weight-percent VE 828 were prepared. To one part of this sample, 2% STYRID by mass was added. This amount of STYRID is supposed to allow for rapid skin formation. The normalized weight loss as a function of time for resins with and without STYRID is shown in Figure 37. The addition of STYRID decreased the percent mass loss and time at which the elbow occurred and decreased the evaporation rate in the long-time mass loss region. However, the period of time required for skin formation is crucial, as it is during this initial period that styrene emission is greatest in systems undergoing cure. Unfortunately, STYRID did not affect the initial mass loss rate. Furthermore, the time scale for cure is typically <1 hr. Yet the time scale for the formation of the elbow is ~7 hr for the sample with STYRID. This indicates that STYRID does not reduce the evaporation rate of styrene

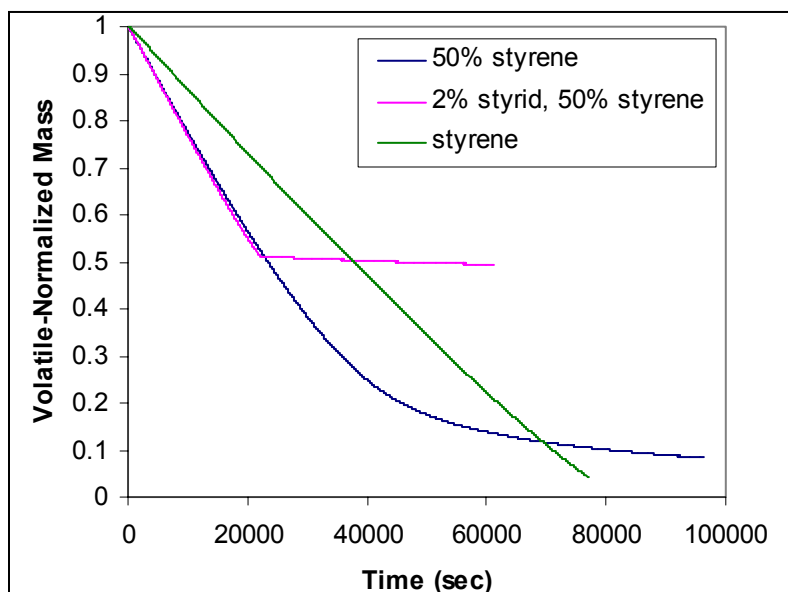


Figure 37. The volatile-normalized mass loss as a function of time at 40 °C for VE resins with and without STYRID, a commercial styrene suppressant.

during the cure of VE resins. Our dendritic systems need to reduce the initial mass loss rate to effectively decrease styrene emissions from VE resins.

2.6.2 Triglyceride-Based Dendritic Systems

2.6.2.1 Preparation of Fluorinated, Acrylated Triglycerides. Triglycerides are first generation dendrimers. Although we hypothesize that increases in the molecular weight of the dendritic polymer should reduce the styrene emissions, first generation dendrimers should also be tested because they are inexpensive and simple to prepare, especially in the case of triglyceride-based dendrimers. Epoxized SBO was chosen as the starting material for this study because it is the least expensive commercially produced epoxidized oil. In addition, it has sufficient epoxide functionality (4 epoxides/triglyceride) for adding both acrylate functionality and surface-active functionality. Epoxidized linseed oil (~6 epoxides/triglyceride) can be used in the future. However, this oil has a greater tendency for epoxy homopolymerization, which will produce undesired structures for this study. There are a number of ways of attaching vinyl functionality to triglycerides (31). We have initially chosen to add acrylic acid to the triglycerides to enable triglyceride-based dendrimers to polymerize with the VE resin. The addition of acrylate functionality has been studied extensively, the synthesis procedures are well known, and the starting material (epoxidized oils) is inexpensive and commercially produced. In addition, the methods we foresee to producing higher generation dendrimers make use of epoxidized oils. As for the commercial dendrimers, the addition of fluorinated chains should make the triglycerides surface-active. The simplest method for adding fluorine functionality is to add a fluorinated acid to the epoxide groups of the triglycerides.

Epoxidized SBO with 4 epoxides/triglyceride, as measured with NMR (32), was reacted with both perfluorooctanoic acid (completely fluorinated, 8-carbon atom acid) and acrylic acid. AMC-2 in the amount of 1 weight-percent was added to the epoxidized oil to catalyze the acid-epoxy reaction and prevent epoxy homopolymerization (4). HQ in the amount of 0.0033 g/mL was added to the oil to inhibit free-radical polymerization of the acrylic acid (33).

Perfluorooctanoic acid in the amount of 1 group/triglyceride was first added to the epoxidized oil and reacted at 75 °C for 1 hr. Then, 3.1 moles of acrylic acid/mole of epoxidized oil was added to the reaction mixture. The reaction was allowed to run for an additional 5 hr. To remove inhibitor and any unreacted acid, the reaction mixture was ether extracted (25). The mixture was dissolved in diethyl ether and poured into a separatory funnel. Distilled water was added to remove some of the acid from the ether phase. The layers were allowed to separate, and the water layer was discarded. This step was repeated three times. An aqueous solution of saturated sodium bicarbonate was added, which was then shaken to ensure good mixing. The contents were allowed to separate into oil and water layers. The aqueous layer was discarded. Sodium bicarbonate washes were repeated, if necessary, until the pH of the water layer was neutral or alkaline, as determined by pH paper. The ether solution was washed with saturated aqueous sodium chloride to remove water from the ether phase and dried over anhydrous sodium sulfate. The ether was evaporated away at RT. NMR confirms the presence of three acrylate groups and one fluorinated chain on average per triglyceride. Thus, a triglyceride with both anchor and buoy functionality was prepared. Other monomers will be prepared, and further studies to determine the ability of this monomer to reduce styrene emissions will be performed in the near future.

2.6.2.2 Triglyceride-Based Dendritic Polymers. There are a number of methods for producing dendrimers. Many of these are time-consuming and require very careful chemistry. The cheapest and easiest way to synthesize triglyceride-based dendrimers is through AB₂ monomers. These monomers have one A group, two B groups, and A and B add to each other when they react. So far, two possible synthetic routes have been hypothesized (Figure 38).

In route 1, a triepoxy triglyceride is reacted with a primary monoamine. The two remaining epoxide groups can react with secondary amines attached to other triglycerides to form a dendritic structure. In order to form a perfect dendrimer, we must start with a triepoxy triglyceride and only one primary amine should react with a given triglyceride. Olive oil, canola oil, and genetically engineered HOSO are excellent candidates as starting materials because of their high likelihood of having one unsaturation site (and thus one epoxide) per FA. In this work so far, epoxidized SBO is being used because it is inexpensive and readily available. Cyclohexylamine is an excellent candidate as the monoamine because its primary amines are much more reactive than its secondary amines (34). Therefore, stable AB₂ monomers can be prepared, which can later be polymerized into dendrimers.

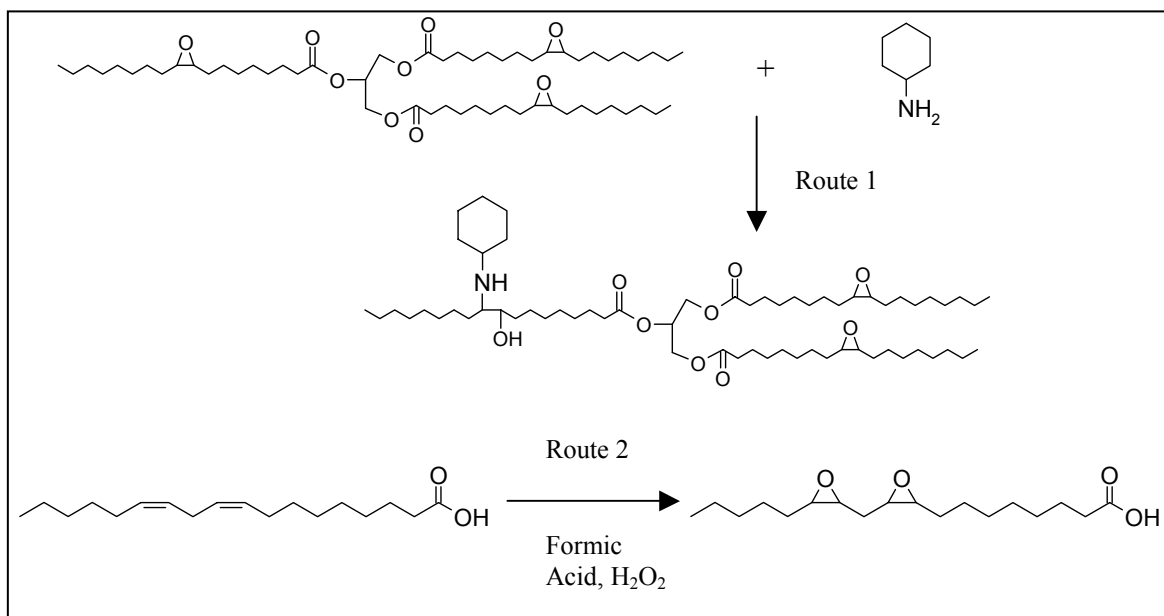


Figure 38. Potential methods of producing AB₂ monomers from triglycerides and FA. In route 1, epoxidized triglycerides are modified with cyclohexyl amine. In route 2, linoleic acid is reacted to form epoxidized linoleic acid.

Epoxidized SBO was reacted with cyclohexylamine in the stoichiometric amount. The reaction was performed at 60 °C initially, but because the sample viscosity remained very low, the temperature was increased to 90 °C. After 1 week of reaction, the reaction mixture became fairly viscous, but did not gel. If complete reaction were to occur, this reaction mixture should gel because of the excess epoxides and the high likelihood of having at least two or more epoxides on the same triglyceride reacting with primary epoxides. HPLC was performed on the sample after results determine if the molecular weight of the triglycerides increased. Unfortunately, no change in the HPLC chromatograph was observed. Therefore, epoxidized SBO was then reacted with cyclohexylamine at 90 °C for 1 week in the presence of 1-weight-percent phenol, which catalyzes this reaction (34). The viscosity of the sample increased much more rapidly than for the case without phenol. In addition, small gel-like particles were observed in this reaction mixture. However, the samples have not been analyzed with HPLC to determine their molecular weight. More work will be done to characterize and improve the synthesis of these dendrimers.

In route 2, linoleic acid, a FA rather than a triglyceride, is used as the starting material and is epoxidized. The monomer has one acid group and two epoxide groups, and is thus an AB₂ monomer. The AMC-2 catalyst can be used to inhibit epoxy homopolymerization, while catalyzing the acid-epoxy reaction. Current results only prove that epoxidized linoleic acid was successfully produced. Unfortunately, our source of linoleic acid was poor, so that the epoxide functionality is <2 (~1.4 epoxides/FA), as determined by NMR (32). Pure linoleic acid can be used, but this acid is fairly expensive. Alternatively, safflower oil, which has a very high linoleic acid content, can be broken down into its FA and used as an inexpensive source of linoleic acid.

However, imperfections in the resulting dendrimer will be produced due to the presence of saturated, monounsaturated, and triunsaturated acids.

3. Environmental Impact and Cost Savings Analysis

An initial analysis of military platforms has been completed in order to determine potential use applications of new VE resin technologies. Among the factors influencing resin selection are performance requirements including thermal limits and resin durability in harsh environments. Because of the complex nature of end-use for military composites, it is difficult to narrow applications to focus on only select resin systems. In our effort, however, we can conclude that cost is a substantial driver to resin selection for both the naval surface warfare structures and for the U.S. Army FCS suite of platforms.

Additionally, an even greater cost restriction is observed in Army composite replacement platforms, where composite structures are being implemented as corrosion resistant replacement parts in legacy platforms. Among the platforms scheduled to see composite replacement parts in the near term are Army transport vehicles, such as high-mobility, multipurpose, wheeled vehicle (HMMWV) hoods and doors, M939 5-ton truck hoods and cargo floors, and M35A2 and M35A3 truck hoods, doors and fenders. The total volume of replacement components in these military platforms approaches \$20 million annually, which if replaced with low-cost VE resins, as is currently proposed in designed technologies, could result in substantial increases in pollution from military fielded structures.

So, for the remainder of the present program year, a cost model will investigate pollution contributions resulting from replacement of metallic structures with composite substitutes and evaluate impact of VE emission from AEM/S and naval high contour rudder structures. The frequent replacement requirements for these applications implies that such applications will represent an substantial recurring cost and pollution contribution to the DOD, an issue which should remain a high priority of DOD institutes, rather than fall to commercial manufacturing enterprises. The cost baselines will be completed with remaining funds from the current calendar year of funding.

4. Conclusions

Styrene emissions from VE resins occur during all phases of processing and fielding of the composite part. Reducing the styrene content in VE resins decreases the processability of and fracture toughness of these resins, and is therefore not an acceptable means of reducing styrene emissions. Styrene emissions can be reduced or eliminated from VE resins by using a bimodal

distribution of VE monomers, replacing styrene with methacrylate monomers or FA-based monomers, and using multifunctional dendritic polymers to suppress styrene emissions.

Synthetic procedures to produce VE monomers with a narrow molecular weight distribution have been developed. In addition, the use of techniques, including FTIR, HPLC, and NMR, to characterize the monomers has been established. The properties of model VE systems and commercial VE resins have been measured, and the effect of VE molecular weight and styrene content were assessed.

A macro-TGA was designed and developed to measure the styrene emissions from commercial and model VE resins. VE resin mass loss as a function of time displays a characteristic elbow, where the mass loss rate decreases significantly. In addition, initial styrene emission rates are not a function of styrene content. However, the total content of styrene evaporated is a function of styrene content, indicating that using a bimodal distribution of VE monomer can reduce styrene emissions. The styrene emissions of commercial resins have been assessed.

A number of methacrylate comonomers were used in place of styrene in VE resins. CHMA appears to be the best choice as a styrene replacement because its resins have low viscosities, and the polymer properties are similar to VE/styrene resins. Synthetic procedures for preparing FA-based comonomers have been developed because of the potential environmental and economic benefit. Current results show that FA-based comonomers need to be blended with styrene to give resins and polymers with acceptable properties. However, there are ways of modifying FA structure to improve the properties of the resulting polymers, but these have not been tested. In addition, FA-based monomers themselves could potentially be used as styrene suppressants.

Commercial styrene suppressants do not decrease styrene evaporation within the time-scale for cure. Therefore, the styrene suppressants developed in this work must segregate to the surface faster to effectively reduce styrene emissions. Multifunctional dendritic styrene suppressants have been prepared. Triglycerides, FAs, and commercial dendritic polymers were used. Fluorine functionality has been introduced into the dendritic polymer to induce surface segregation. Vinyl functionality has been added to these dendrimers to anchor the dendrimers into the polymer network upon cure.

Overall, this program has been successful at both identifying critical DOD environmental needs and developing practical solutions to reduce styrene emissions from VE resins for military applications. More work must still be done to further develop these methodologies to significantly reduce styrene emissions and produce composites with excellent properties.

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List of Abbreviations

AEM/S	advanced enclosed mast sensor
AHOSO	acrylated HOSO
AME	acrylated methyl esters
AOH-SBO	allyl alcohol modified soybean oil
ASTM	American Society for Testing and Materials
ATR	attenuated total reflectance
CHMA	cyclohexyl methacrylate
CoNap	cobalt naphthenate
DCC	N,N'-dicyclohexylcarbodiimide
DGC-MS	desorption gas chromatography-mass spectrometry
DMA	dynamic mechanical analysis
DMAP	4-dimethylaminopyridine
DSC	differential scanning calorimeter
DOD	Department of Defense
EHOSO	epoxidised HOSO
EPA	U.S. Environmental Protection Agency
ESO	epoxidized soybean oil
FA	fatty acid
FAME	fatty acid methyl esters
FCS	Future Combat System
FTIR	Fourier-transform infrared spectroscopy
GM	glycidyl methacrylate
GM-FA	glycidyl methacrylate modified fatty acid
HAP	hazardous air pollutants
HCl	hydrochloride
HDDA	1,6-hexanediol diacrylate
HDDMA	1,6-hexanediol dimethacrylate
HOSO	high oleic soybean oil
HMMWV	high-mobility, multipurpose, wheeled vehicle

HPLC	high-performance liquid chromatography
HQ	hydroquinone
IBMA	isobornyl methacrylate
IR	infrared
Lau	lauric acid
Lin	linoleic acid
LM	lauryl methacrylate
ME	methyl esters
MEHQ	hydroquinone monomethyl ether
NMR	nuclear magnetic resonance
OA	oleic acid
PEI	polyethyleneimine
ppm	parts per million
RT	room temperature
SBO	soybean oil
SENB	single-edge notch bend
T _g	glass transition temperature
TGA	thermal gravimetric analysis
THF	tetrahydrofuran
UV	ultraviolet
VE	vinyl ester
VOC	volatile organic compound

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