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## **Predicting the Viscosity of Low VOC Vinyl Ester and Fatty Acid-Based Resins**

**by John J. La Scala, Amutha Jeyarajasingam, Cherise Winston,  
James M. Sands, and Giuseppe R. Palmese**

**ARL-TR-3681**

**December 2005**

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## 1. Introduction

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Vinyl-ester resins are used to make polymer matrix composites in military and commercial applications because of their high modulus, high strength, high glass transition temperature, low weight, and low cost (1, 2). These resins have superior properties relative to unsaturated polyester systems and are less expensive and easier to process than epoxy systems (1). Vinyl-ester resins contain vinyl-ester monomers and a reactive diluent, such as styrene. The vinyl-ester monomers have two terminal free-radically polymerizable unsaturation sites, enabling the resin to cross-link. Reactive diluents, such as styrene, have a single vinyl group and act as linear chain extenders. The reactive diluent is used because it severely reduces the resin viscosity and improves overall polymer performance by allowing for a higher degree of reaction of the monomers by delaying the onset of gelation and reducing diffusion limitations (3). These properties provided by the reactive diluent also allow for the use of low cost composite fabrication processing methods, such as vacuum-assisted resin transfer molding. On the other hand, styrene and other commonly used reactive diluents are volatile organic compounds (VOC) and hazardous air pollutants (HAP) that are damaging to health and the environment.

VOCs are liberated during all of the phases of composite fabrication (2, 4). VOC emissions occur during the mixing of diluents, catalysts, and initiators into the system. In open mold fabrication, composite parts typically have very large surface to volume ratios, which allow substantial styrene contents to be lost during the molding stage. During cure, elevated temperatures increase the vapor pressure of styrene and thus increase the rate of VOC emission. Unfortunately, even after cure during the lifetime of the part, VOC emissions can be substantial. Past work has shown that up to 40% of the styrene in vinyl-ester resins is unreacted after cure (5). Because styrene is an HAP and a VOC, the Federal Environmental Protection Agency of the United States of America introduced legislation to limit styrene emissions from composite manufacturing (4). Therefore, liberation of VOCs must be mitigated not only during composite processing, but also during curing and fielding of the composite part. Thus, a means of reducing the styrene emissions from vinyl-ester resins is desired. Current low VOC vinyl-ester systems do exist, such as Dow Derakane 441-400 (6). However, the use of these resins is limited because of their low fracture toughness ( $\sim 100 \text{ J/m}^2$ ), higher viscosity (400 cP), and higher cost relative to standard vinyl-ester systems, such as Derakane 411-350, which have viscosities below 200 cP and fracture toughness values above  $200 \text{ J/m}^2$  (5–8).

Unfortunately, decreasing the styrene content in vinyl-ester resins does not offer an acceptable solution to this problem. As the styrene content is reduced, the resin viscosity increases, making it difficult to use inexpensive molding techniques (1, 9). In addition, Dow Derakane 441-400 uses 27% less styrene than Derakane 411-350 (6) but has less than half the fracture toughness (5, 8).

Various monomers with volatilities lower than that of styrene have been used as styrene replacements, such as vinyl toluene (10). These styrene replacements still produce significant VOC emissions and are therefore still regulated by the EPA (4). In addition, few monomers yield resins with properties comparable to styrene-based resins and even fewer can match the low cost of styrene.

Fatty-acid monomers are derived from plant oils, such as soybean oil, which are composed of over 99% triglyceride molecules (11). Triglycerides are composed of three fatty acids connected by a glycerol center. The triglycerides in plant oils typically contain 10 or more different fatty acids, which range in length, level of unsaturation, and functionality (e.g., epoxide and hydroxyl functionality as found in vernonia and castor oils, respectively) (11).

Fatty acids and triglycerides have been used in a number of polymeric applications. Epoxidized and acrylated triglycerides have been used as plasticizers and toughening agents (12). In fact, the largest non-food use of triglycerides is the use of epoxidized soybean and linseed oils as plasticizers in poly(vinyl chloride) (12). Pressure sensitive adhesives have been made from fatty-acid methyl esters (13). In addition, thermosetting liquid molding resins, similar to vinyl-ester resins have been made using plant oils as the cross-linkers (14–17). However, until recently, fatty-acids have not been used as reactive diluents in thermosetting liquid molding resins. In fact, fatty acid-based vinyl-ester resins use less than 20 weight-percent styrene monomer, while maintaining low resin viscosities and high polymer performance (18).

Simply altering the molecular weight of vinyl-ester monomers does not provide a means for both reducing styrene emissions and maintaining resin and polymer properties. Low molecular weight vinyl-ester monomers have poor fracture properties because of their high cross-link densities (9, 19). High molecular weight vinyl-ester monomers yield resins with high fracture properties via matrix toughening. However, low styrene contents cannot be used because the resin viscosity increases severely and processing becomes unacceptably difficult (20). On the other hand, using a mixture of low and high molecular weight vinyl-ester monomers (i.e., bimodal blend) produces high performance polymers with low viscosities along with VOC/HAP reduction of up to 38% (21).

The resins examined in this work have sufficient properties for at least low-tech nondemanding composite applications where polyester or vinyl-ester quality performances are sought. Some of these resins are appropriate for high-tech Department of Defense applications. The resin viscosity governs the manufacturing method, regardless of the end-use application. When the resin viscosity is too high, the pressure driving force in liquid molding operations is not enough to push the viscous resin into the gaps between the fibers (glass, carbon, flax, etc.) before the resin cures. Consequently, viscous resins produce composite parts with high void contents. To reduce the void contents, long production times are necessary. As a result, a viscosity of 500 cP is considered about the maximum for most inexpensive liquid molding techniques (1, 22). The use of bimodal blends of vinyl-esters and fatty-acid monomers to reduce styrene content in

vinyl-ester resins are acceptable solutions. However, the operating window for processing these resins has not been established. This report examines the effect of possible solutions (fatty-acid monomers and bimodal blends of vinyl-ester monomers) on resin viscosity. Specifically, this report will present models that allow predictive determination of resin viscosity as functions of reactive diluent content, diluent type, vinyl-ester molecular weight, and temperature for DGEBA-based vinyl esters.

## 2. Experimental Procedure

### 2.1 Preparation of Vinyl-Ester Monomers

Vinyl-ester monomers were prepared via methacrylation of diglycidyl ether of bisphenol A (DGEBA) (figure 1) (1). Epon 828, 834, 836, 1001F, 1004F, 1007F, and 1009F (Miller-Stephenson, Danbury, CT) were used as the source of DGEBA. To determine the epoxy equivalent weight of the Epon resins, epoxy titration was performed as per ASTM D1652-90, Procedure B (23). The epoxy resin was dissolved in 10–15 mL methylene chloride (Aldrich, Milwaukee, WI), and 10 mL tetraethylammonium bromide solution (Aldrich, 0.4 g/mL) was then added to the mixture. The sample was titrated with the perchloric acid/peracetic acid solution (Aldrich) until the indicator, 0.1% crystal violet in acetic acid (Aldrich), changed color from blue to green. The epoxy titration results agreed well with literature values for the epoxy equivalent weight (EEQ) (table 1) (20).

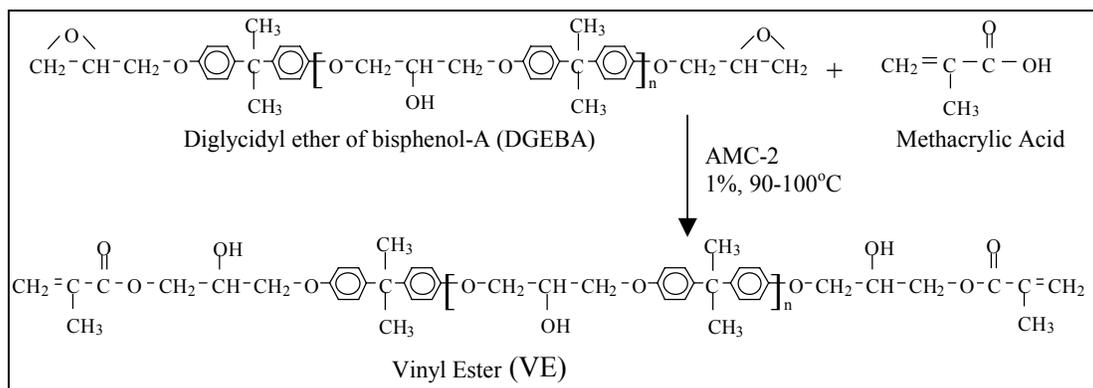


Figure 1. The reaction of methacrylic acid with Epon to form vinyl-ester monomer.

Pure vinyl ester was prepared via methacrylation of Epon 828, 834, or 836 (figure 1). Approximately 500-g Epon resin was reacted with  $1.01 \times$  the stoichiometric amount of methacrylaic acid (i.e., as determined through epoxy titration). AMC-2 (Aerojet Chemicals, Rancho Cordova, CA), which is a mixture of 50% trivalent organic chromium complexes and 50% phthalate esters, was used as a catalyst for the reaction and to prevent epoxy homopolymerization (24) in the amount of 1 weight-percent. The reaction was run at  $\sim 90$  °C,

Table 1. Epoxy equivalent weight as determined by epoxy titration and literature values (20).

<b>Epon Resin</b>	<b>Literature EEQ (g/mol)</b>	<b>Experimental EEQ (g/mol)</b>	<b>Calculated MW (g/mol)</b>
828	185–192	186 ± 3	372 ± 6
834	230–280	255 ± 4	510 ± 8
836	290–335	307 ± 3	614 ± 6
1001F	525–550	548 ± 3	1096 ± 6
1004F	800–950	900 ± 5	1800 ± 10
1007F	1700–2300	1990 ± 7	3980 ± 14
1009F	2300–3800	2770 ± 8	5550 ± 16

but because of the exothermicity of this reaction, water was periodically flowed through cooling coils within the reactor to keep the temperature below 95 °C. Acid number titration was used during the course of the reaction to measure the amount of free (unreacted) acid in the vinyl-ester system. The acid number tests were performed in accordance with ASTM D1980-87 (25). Approximately 1 g of the vinyl-ester reaction mixture was dissolved in 5-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. An acid number (mg NaOH/g VE) of 5, corresponding to ~2% 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 number measurements were below 5. Although the vinyl ester 828 has a small percentage of higher molecular weight monomer, it will be referred to as the “monodisperse” vinyl ester throughout because the distribution of molecular weights is far smaller than that of the bimodal resins prepared.

Bimodal blends of vinyl-ester monomers (BM-VE) were prepared by methacrylation of blends of Epon 828, used as the low molecular weight DGEBA, and Epon 100XF (1001F, 1004F, 1007F, or 1009F) used as the high molecular weight DGEBA. Epon 100XF are solids at room temperature. The viscosities of these resins are too high to effectively mix during the vinyl-ester reaction, even at 100 °C. Therefore, these resins were blended with Epon 828 to prepare bimodal vinyl-ester blends. Unfortunately, the solid contents were just too high for only Epon 828 and the required amount of methacrylic acid to dissolve, even at 100 °C. Therefore, low styrene (Aldrich, 99%) contents (< 20 weight-percent) were added to completely dissolve the high molecular weight Epon 100XF. Addition of styrene during the methacrylation reaction normally causes gelation. Therefore, hydroquinone (Aldrich, 99%) in the amount of 1000 ppm based on the entire reaction contents was added to inhibit polymerization.

Approximately 200-g Epon 828 was added to the reactor. Approximately 100-g styrene (20 weight-percent) was added to the reaction vessel. The reaction vessel was sealed and stirred vigorously with the mechanical mixer. While heating to 90 °C, the desired content of Epon 100XF was added to the reactor in aliquots over the course of 1 hr to prevent excessive clumping

of the solid Epon 100XF. In addition,  $1.01 \times$  the stoichiometric amount of methacrylic acid along with 1 weight-percent AMC-2 catalyst (based on Epon and methacrylic acid masses only) were added to the solution. The reaction temperature was kept in the range of 90–95 °C, while using the cooling coils for cooling as needed. Once the acid number was  $\sim 5$ , the reaction was ended.

Bimodal blends of vinyl ester were prepared with the specific mass ratios of 828/1001F 29/71, 828/1004F 42/58, 828/1007F 50/50, and 828/1009F 50/50. These mass ratios only compare the low and high vinyl-ester weight fractions and are independent of styrene content. The styrene content in vinyl-ester resins is listed as weight percentage of the entire resin. Bimodal blends with higher vinyl-ester 828 weight fractions were also desired for this study. These were prepared by mixing a specific amount of bimodal blend with the desired amount of pure vinyl ester 828 and styrene.

Derakane 411-350 and 441-400 resins were provided by the Dow Chemical Company (Channahon, IL) and used as received. Styrene content and viscosity were provided by the manufacturer and verified by measurement. Derakane 411-350 is a recent replacement for Derakane 411-C50, and the resin and polymer properties are comparable (6).

Fourier Transform Infrared Spectroscopy (FTIR) and near-IR were used to measure the concentration of unreacted epoxides and attached methacrylate groups (figure 2). A Thermo Nicolet Nexus 670 FTIR was used in absorbance mode, taking 16 scans per spectrum with a resolution of  $4 \text{ cm}^{-1}$ . The raw FTIR spectra of these resins showed that the peaks representing the epoxide groups ( $6066 \text{ cm}^{-1}$ ,  $4530 \text{ cm}^{-1}$ ,  $917 \text{ cm}^{-1}$ ) were no longer visible after reaction, and methacrylate groups ( $6160 \text{ cm}^{-1}$ ,  $942 \text{ cm}^{-1}$ ) were present in the resin (7, 26). Interference with other peaks prevented determining the extent of reaction over 95% conversion, but other characterization techniques were also used to quantify the extent of reaction. These results indicate that the epoxide groups reacted to near completion with methacrylic acid.

Size exclusion chromatography (SEC) was run on styrene and the vinyl-ester resins to determine vinyl-ester molecular weight and styrene content in the bimodal blends (figure 3). A Waters 515 GPC was used with two 30-cm long, 7.5-mm diameter, 5- $\mu\text{m}$  styrene-divinyl benzene columns in series. The columns were equilibrated and run at 45 °C using tetrahydrofuran (Aldrich) as the elution solvent at a flow rate of 1 mL/minute. The column effluent was monitored by two detectors operating at 25 °C: a Waters 2410 refractive index detector and a Waters 2487 dual absorbance detector operating at 270 and 254 nm (absorbed by phenyl rings). Samples were prepared by dissolving 2-mg sample in 1-mL THF. Because high molecular weight species cannot diffuse into the packing, they elute first from the column, while lower molecular weight species elute later (27). Figure 3 shows that these blends do indeed have bimodal molecular weight distributions. The peak at 14.5 min represents the vinyl-ester 828 fraction of the resin, while the peak at lower elution times represents the higher molecular weight vinyl-ester

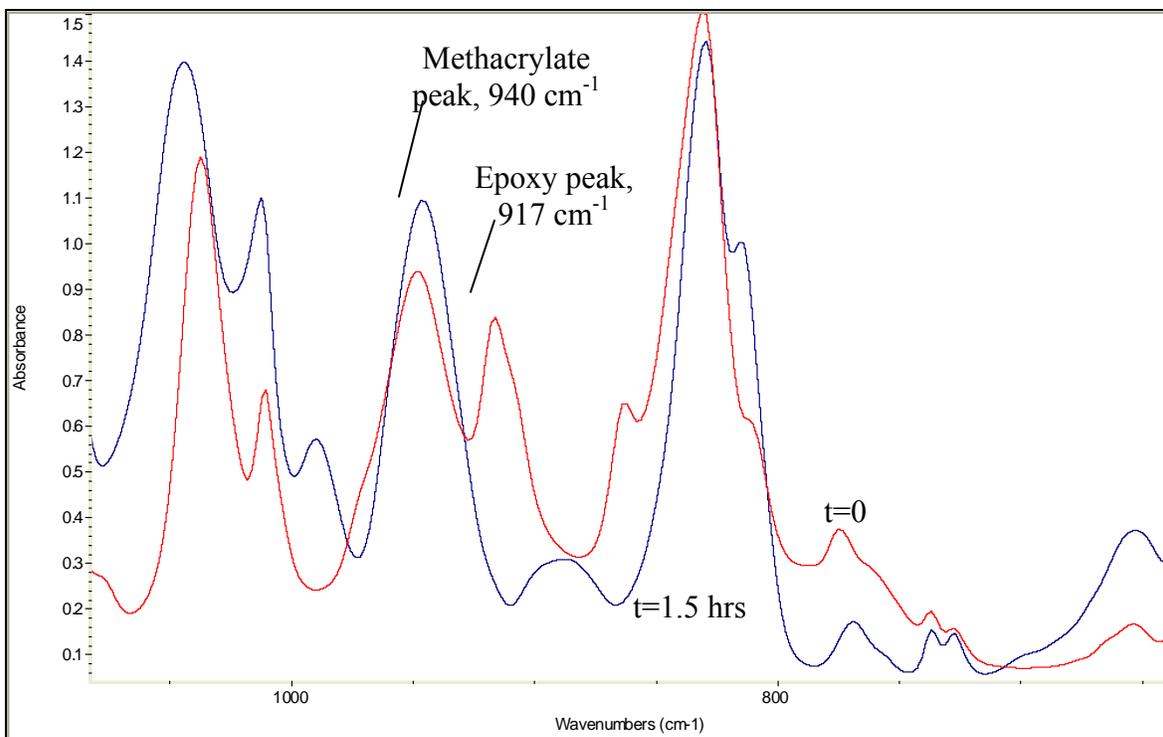


Figure 2. The FTIR spectra of Epon/methacrylic acid and the resulting vinyl ester formed after complete reaction.

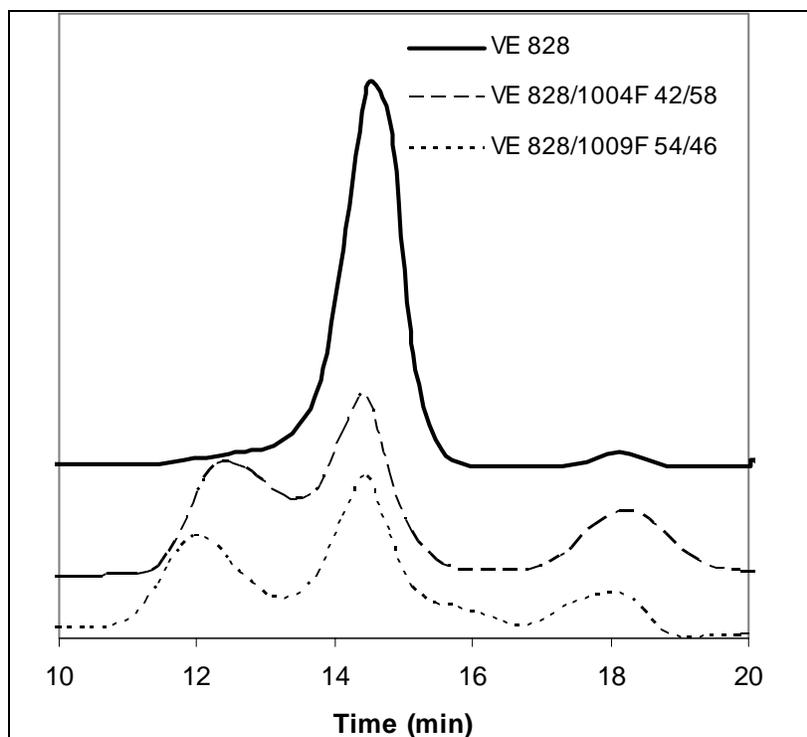


Figure 3. SEC chromatographs of vinyl ester 828 and representative vinyl-ester bimodal blends. The curves are vertically offset for clarity.

monomers. The peak representing Epon 828 appeared at 15.5 min. The lower retention time of the vinyl-ester peak (14.5 min) indicates that the epoxy reacted with methacrylic acid to form a higher molecular weight species (i.e., vinyl ester). The peak at 18 min represents low molecular weight species, such as styrene, methacrylic acid, and catalysts. 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 (27, 28). Because no such peak appeared in our prepared vinyl-esters, we conclude that no epoxy homopolymerization occurred. SEC analysis of the methacrylation of epoxies as a function of time showed that the peak at 18 min decreased with reaction time, while the vinyl-ester/epoxy peaks shifted to lower elution times. The peak at 18 min decreased to less than 95% of its original size when the methacrylation was run without styrene, as was done when preparing vinyl ester 828. These results conclusively show that Epon reacted with the methacrylic acid to form higher molecular weight vinyl-ester monomers.

To measure the molecular weights of vinyl-ester resins using SEC, the molecular weight as a function of retention time was calibrated using Epon resin samples (29). The number average molecular weight of the Epon 100XF resins is known through epoxy titration results. The calibration curve relating peak retention time to Epon molecular weight was constructed and used to calculate the number average molecular weights of the vinyl-ester peaks. For the bimodal blends, the relative areas of the peaks and the two different number average molecular weights were used to simply calculate the number average ( $M_n$ ) and weight average molecular weights ( $M_w$ ):

$$M_n = \frac{n_{high}M_{high} + n_{low}M_{low}}{n_{high} + n_{low}}, \quad (1)$$

and

$$M_w = \frac{n_{high}M_{high}^2 + n_{low}M_{low}^2}{n_{high}M_{high} + n_{low}M_{low}}, \quad (2)$$

where the subscripts *high* and *low* refer to the high and low vinyl-ester molecular weight species/peak, respectively,  $M$  is the molecular weight as determined by the Epon calibration, and  $n$  is the number of moles. Table 2 shows that there was good agreement between experimental and literature values (20). Chromatography gives the volume ratio of low and high molecular weight species, from which the molar ratios can be calculated. The Epon standards used had a narrow distribution of molecular weights. The effect of these distributions was ignored in calculating the vinyl-ester molecular weights. Because we are using the same Epon standards to prepare the vinyl-ester monomers, there will be little error in the calculation of  $M_n$ , but the distribution of molecular weights in the Epon standards should yield significant error in the weight average molecular weight. We expect this error to be no more than 10% in the calculation of  $M_w$ .

Table 2. The vinyl-ester molecular weights and styrene contents as determined using NMR and SEC along with literature/known values. The styrene contents listed for the bimodal blends of vinyl ester 828/100XF are the experimentally determined values and the initial weight fraction styrene (known) in the reaction mixture of the prepared vinyl ester.

Resin	Exp. VE $M_w$ (g/mol)	Exp. VE $M_n$ (g/mol)	Literature VE $M_n$ (g/mol)	Exp. Styrene Content (weight-percent)	Literature/Known Styrene Content (weight-percent)
Derakane 411-C50	1320 ± 60	880 ± 50	910 <sup>[5,6]</sup>	43 ± 3	45-50 <sup>[5,6]</sup>
Derakane 411-350	1540 ± 60	960 ± 50	NA	45 ± 3	45 <sup>[6]</sup>
Derakane 441-400	720 ± 50	700 ± 20	700 <sup>[6,7]</sup>	29 ± 3	28 <sup>[6,7]</sup>
828 + 30% styrene	550 ± 50	540 ± 10	540 <sup>a</sup>	29 ± 3	30 <sup>a</sup>
834	740 ± 50	680 ± 10	630-730 <sup>a</sup>	NA	NA
836	864 ± 50	790 ± 10	750-840 <sup>a</sup>	NA	NA
828/1001F 29/71	867 ± 60	802 ± 20	NA	16.5 ± 2	16.6 <sup>a</sup>
828/1004F 42/58	1370 ± 70	933 ± 20	NA	16.5 ± 2	16.6 <sup>a</sup>
828/1007F 53/47	2257 ± 90	920 ± 30	NA	19.5 ± 2	19.5 <sup>a</sup>
828/1009F 50/50	3130 ± 100	987 ± 20	NA	19.5 ± 2	19.6 <sup>a</sup>

<sup>a</sup>Values were taken from product specifications sheets.

Notes: VE = vinyl ester, and NA = not available.

SEC shows that pure styrene had a single peak at 18 min. This peak appeared at the same retention time regardless of the vinyl-ester resin used. The styrene content was calculated by measuring the area of the low molecular weight peak at 18 min relative to the area of the vinyl-ester peaks from 12–16 min (figure 3). However, pure vinyl ester 828 also had a small peak at 18 min as a result of catalyst and unreacted methacrylic acid. The effect of these components were small, but were removed anyway using a calibration procedure. Vinyl ester 828 standards with 30–50 weight-percent styrene were prepared and tested to calibrate SEC results. Using this calibration curve, the styrene content in commercial resins was measured. In all cases, the results agreed within 1% of the amount of styrene added to the bimodal resin system (table 2).

Nuclear magnetic resonance (NMR) spectroscopy was run on the Epon resins, the prepared vinyl esters, and commercial vinyl-ester resins to verify the extent of methacrylation, styrene content, and vinyl-ester molecular weight. A Bruker (Billerica, MA) 600-MHz spectrometer with spectral window of ±2000 Hz, 16 scans at 293 K, and 90° pulse width was used. The method used to analyze the vinyl ester is described in the literature (5, 7). The internal standards for vinyl ester are the 4 methylene protons and the 6 methyl protons of the methacrylate groups per vinyl ester (figure 4). The area per proton for these standards should be in agreement. The value of  $n$  for the vinyl ester (figure 1) is calculated based on the area of the  $5n+10$  isopropyl protons, the  $8n+8$  phenyl protons, or the  $6n+6$  DGEBA methyl protons. These values of  $n$  resulting from all three standards were always equal within 3% error. In addition, the calculated values of  $n$  were always within experimental error of the values calculated using epoxy titration. The styrene content was calculated by measuring the relative area of the styrene methylene protons (5.2 and 5.8 ppm) to the internal standards. The extent of methacrylation was determined by measuring the height of the three epoxide peaks at 3.33, 2.88, and 2.73 ppm (26, 30) relative to the heights of the phenyl protons and the DGEBA methyl protons before and after methacrylation. In all cases, the epoxide peaks were nearly gone, indicating epoxide

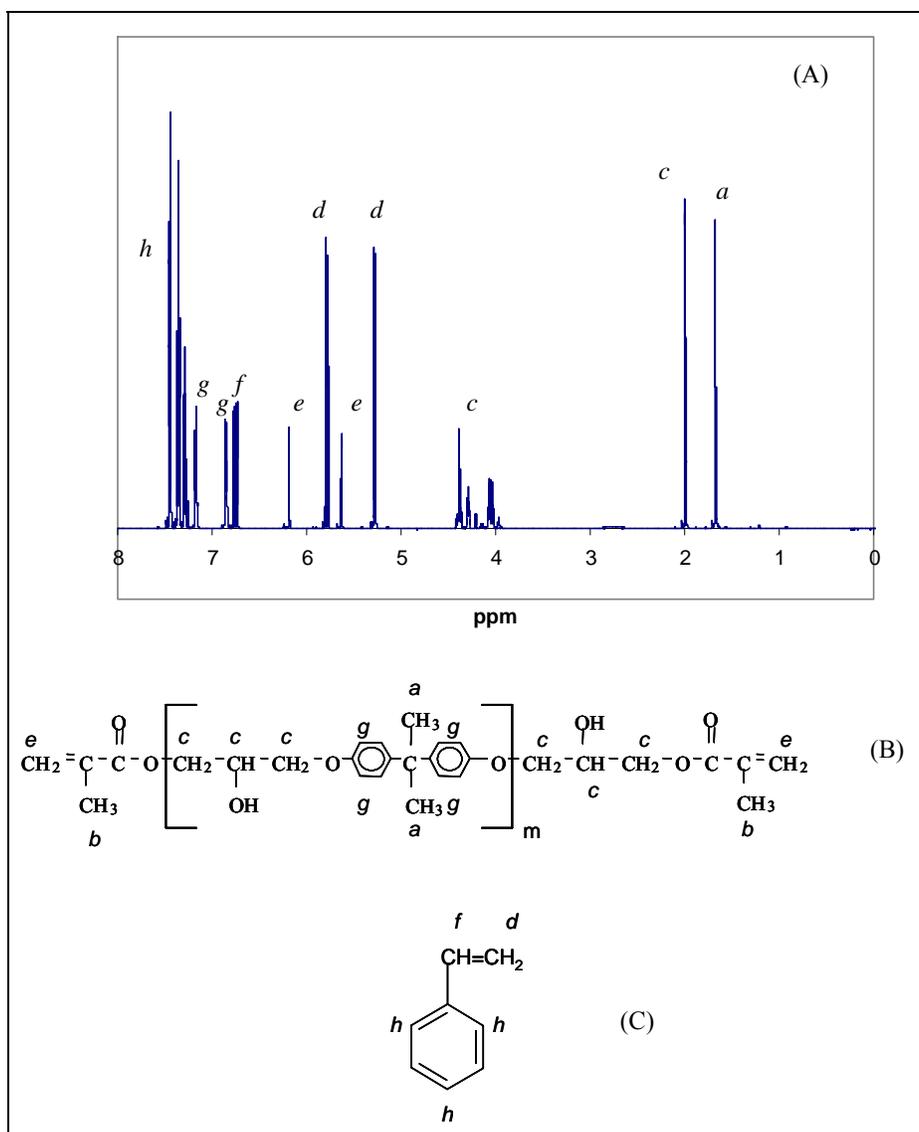


Figure 4. The NMR spectrum of (A) vinyl ester 828 with 50 weight-percent styrene, with the peaks labeled to correspond to chemical groups of (B) vinyl-ester monomer and (C) styrene (5). Note the definition of  $m$  ( $m = 1$  represents the lowest possible value of  $m$  for DGEBA-based resins).

conversions greater than 99%, verifying the FTIR results. Derakane 411-350 and 441-400 were analyzed in this manner along with the vinyl ester 828 and bimodal blends of vinyl-ester resins. The experimental results for Derakane resins and the vinyl ester 828 resin were similar to the literature results (table 2) (5–7). Table 2 shows that the agreement between literature and experiment was good. Furthermore, vinyl ester 828 with 30 weight-percent styrene was determined to have 29 weight-percent styrene using NMR, which proves the validity of this method.

## 2.2 Fatty-Acid Monomer Preparation

A number of synthetic procedures have been established for making fatty acid-based monomers to be used as the reactive diluent in vinyl-ester resins (31). Figure 5 depicts the synthetic route used to form methacrylated fatty acid (MFA). The carboxylic acid of fatty acids undergoes a simple addition reaction with the epoxide group of glycidyl methacrylate (GM) (Aldrich, Milwaukee, WI) to form a single product. Stoichiometric quantities of the reactants were mixed together and reacted at 70 °C for 2.5 hr using 1 weight-percent AMC-2 catalyst. FTIR and <sup>1</sup>H-NMR (250.13 MHz, spectral window of ±2000 Hz, 0.427 Hz/pt digital resolution, 16 scans at 293 K, 90° pulse width) with a Bruker AC250 spectrometer showed that methacrylation of the fatty acids went to completion. Each MFA contains one terminal polymerizable unsaturation site per molecule. In this way, the fatty-acid monomers act as chain extenders, analogous to styrene, in vinyl-ester resins. Various fatty-acids were used to prepare MFA monomers (table 3). Short fatty acid chains result in better polymer properties than any long fatty acids (18), but are more expensive. Therefore, moderate chain lengths, such as lauric acid, represent a good balance between properties and cost.

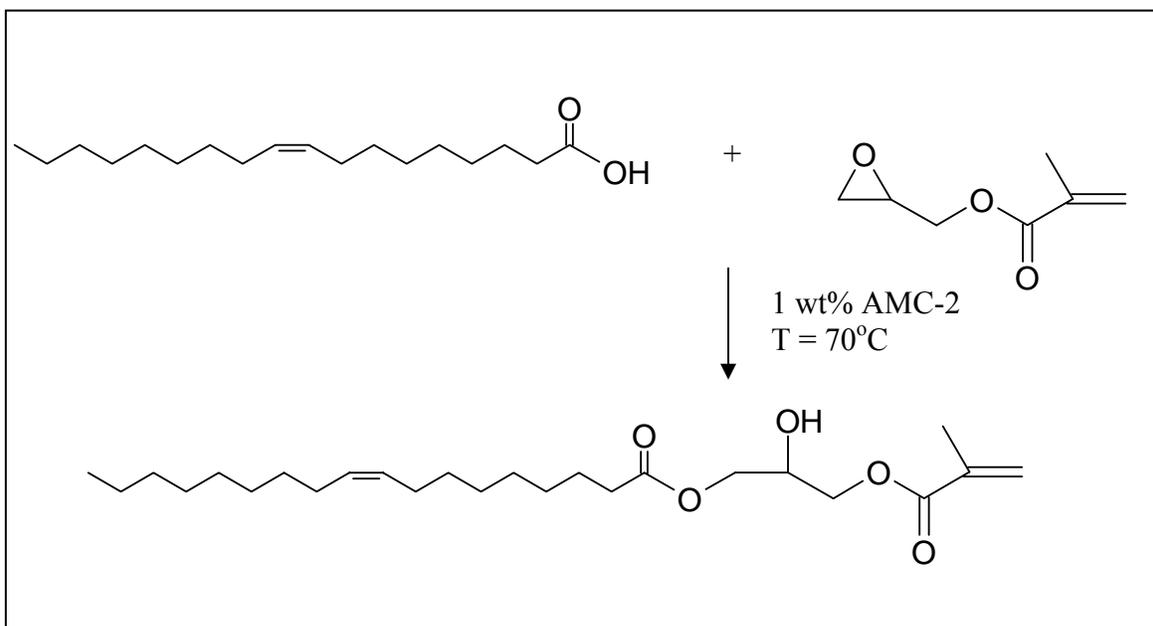


Figure 5. The reaction of glycidyl methacrylate and oleic acid to produce the MOA monomer.

## 2.3 Resin Formulation

Fatty acid-based vinyl ester resins (FA-VE) were formulated using 55 weight-percent and 65 weight-percent vinyl-ester 828 monomers, 0–45 weight-percent styrene (Aldrich 99%), and 0–45 weight-percent MFA. MFA monomers with fatty acid chain lengths ranging from 4 to 18 carbon atoms were used with 0–2 unsaturation sites along the fatty acid backbone.

Table 3. The fatty acids used to make MFA monomers.

Fatty Acid	Chain Length	Unsaturation Sites	MFA
Butyric acid	4	0	MBut
Hexanoic (Caproic) acid	6	0	MHex
Octanoic (Caprylic) acid	8	0	MOct
Decanoic acid	10	0	MDec
Lauric acid	12	0	MLau
Myristic acid	14	0	MMyr
Palmitic acid	16	0	MPalm
Stearic acid	18	0	MSA
Oleic acid	18	1	MOA
Linoleic acid	18	2	MLin

Resins using bimodal blends of vinyl ester 828/1001F 29/71, 828/1004F 42/58, 828/1007F 50/50, and 828/1009F 50/50 were formulated. In addition, the viscosities of resins with higher vinyl-ester 828 fractions were analyzed by adding pure vinyl ester 828 to these blends. Styrene contents ranging from 20–55 weight-percent were used for all blends. Vinyl ester 834 and 836 were blended with 20–55 weight-percent styrene as a baseline to determine the effect of bimodal blends on the viscosity.

The vinyl-ester resins were heated for 10 min at 70 °C for easy pouring. After heating the vinyl ester, ~10 g were carefully poured into a 20-mL scintillation vial. Based on this vinyl ester content, the amounts of other monomers were calculated according to their particular formulation. If MFA was used, it was added next. Lastly, the styrene was added to minimize VOC mass loss during mixing. After all of the monomers were added to the vial, it was heated at 70 °C for 5 min and then manually stirred with a glass stirring rod to dissolve the components. The clarity of the solution was noted.

## 2.4 Rheological Characterization

### 2.4.1 Steady Flow Experiments

The viscosities of the resins were measured using a Brookfield digital viscometer in Couette geometry (i.e., concentric cylinders). Approximately 8 ml of the sample were placed into the sample holder. Spindle 21 was used in all cases because of its large diameter of 1.5 cm, which allows the measurement of the low viscosity samples. Because this viscometer provides more reliable numbers when the torque applied is near the middle of the instrument’s range, the shear rate was varied, depending on the sample viscosity, to do this. As a result, the rotation rate was varied from 2.5 rpm to 100 rpm depending on the sample viscosity. All samples were run at 30 °C. The bimodal blends 828/1001F 29/71, 828/1004F 42/58, 828/1007F 52.5/47.5, and 828/1009F 50/50 were tested. Each bimodal blend system was also tested using two higher vinyl-ester 828 weight fractions to examine the effect of molecular weight and polydispersity on the resin viscosity. The vinyl-ester resins were prepared with styrene contents of 20, 30, 35, and 45 weight-percent. The viscosities of selected samples were also measured using a TA

Instruments (New Castle, DE) AR2000 Rheometer in steady shear flow experiments using parallel plate geometry (40-mm plates) to prove that the resins have Newtonian behavior. The shear rate was increased from  $1 \text{ s}^{-1}$  to  $3000 \text{ s}^{-1}$  and then decreased back to  $1 \text{ s}^{-1}$ , and 10 measurements were taken per decade. At a given shear rate, the shear stress was measured every 2 s. The shear rate and viscosity were recorded when the shear rate stabilized to within 5% tolerance for three consecutive intervals.

#### **2.4.2 Temperature Experiments**

Selected vinyl-ester resins with different molecular weights, reactive diluent, and diluent content were used to determine the effect of temperature on vinyl-ester resins. All resins were blended with diluent contents ranging from 20–55 weight-percent. The viscosity-temperature dependence of pure vinyl ester 828 was also measured.

The resin viscosity was measured using a TA Instruments AR2000 Rheometer in steady shear flow experiments using parallel plate geometry (40-mm plates). The temperature was equilibrated at  $30 \text{ }^{\circ}\text{C}$  for 5 min. The viscosity was measured at shear rates of  $30\text{--}100 \text{ s}^{-1}$  with 4 points per decade. The shear rate and viscosity were recorded when the shear rate stabilized to within 5% tolerance for three consecutive points. The temperature was incremented by  $2.5^{\circ}$ , and the system was allowed to equilibrate for 3 min. This procedure was repeated until the temperature reached  $60 \text{ }^{\circ}\text{C}$ . The temperature was then decreased by increments of  $10\text{--}30 \text{ }^{\circ}\text{C}$  with 5 min equilibration times, and the viscosity was measured. In most cases, there was no viscosity-temperature hysteresis. This indicates that the equilibration times were sufficient for thermal stabilization. However, in the few cases where hysteresis did occur, the viscosity was always higher when decreasing the temperature. This indicates that the resin polymerized slightly upon heating.

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### **3. Results**

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#### **3.1 Viscosity of Bimodal Blends of Vinyl-Ester Monomers**

##### **3.1.1 Effect of Vinyl-Ester Molecular Weight and Styrene Content**

Both the viscometer and rheometer results showed that the viscosity of the resins did not depend on the shear rate and no shear history was observed. Therefore, the vinyl-ester resins used in this work are Newtonian, nonpolymeric fluids (32).

The viscosity decreased as the molecular weight of the bimodal blend decreased (figure 6). This result was expected because the viscosity of epoxy resins increases with the molecular weight of the monomer (20). A decrease in the degrees of freedom of the vinyl-ester monomers caused this viscosity increase with molecular weight (33). The viscosity decreased exponentially with styrene content for all bimodal blends (figure 7). Styrene is a nonpolar small molecule that

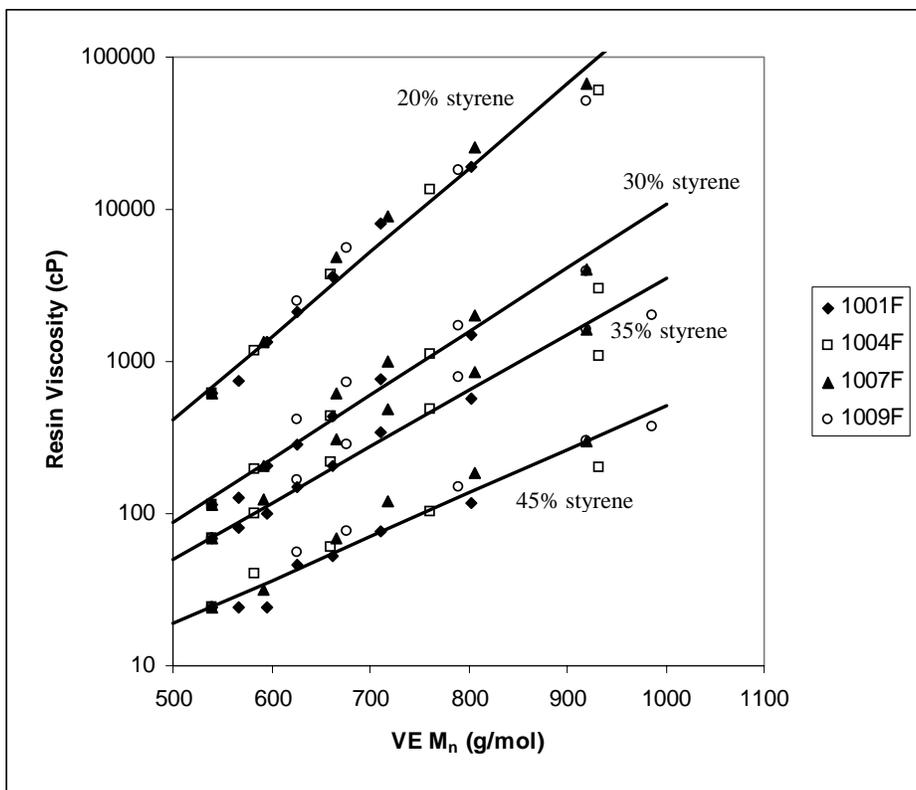


Figure 6. The resin viscosity as a function of VE  $M_n$  for different styrene contents, showing that resin viscosity is normalized by VE  $M_n$ .

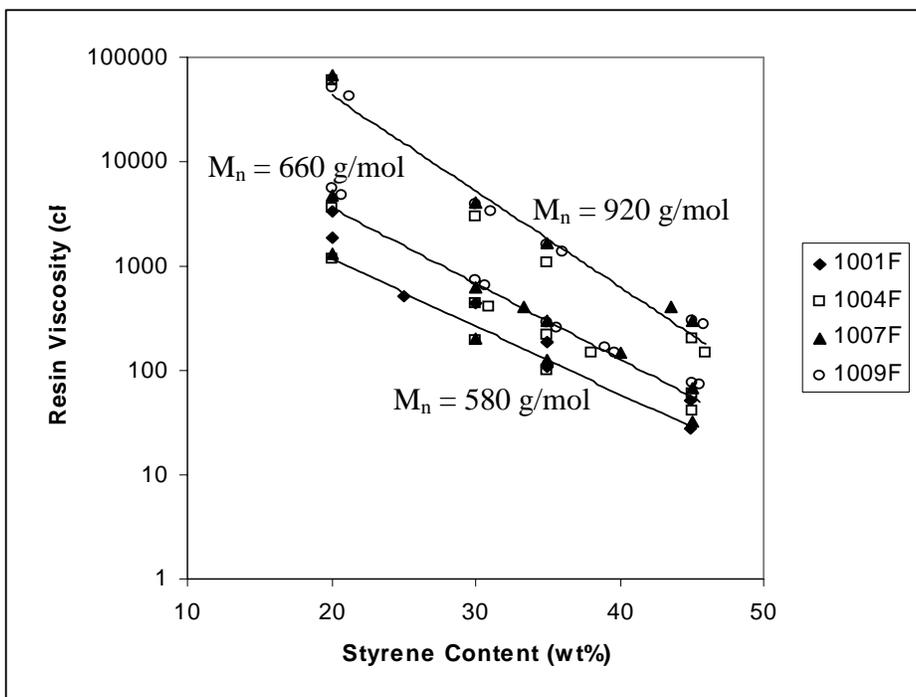


Figure 7. The resin viscosity as a function of styrene content for various VE  $M_n$ , showing that styrene content affected the resin viscosity to the same extent for all bimodal resins with the same  $M_n$ , and the effect of styrene content on resin viscosity decreased as  $M_n$  decreased.

basically acts as a solvent and increases the degrees of freedom and decreases the intermolecular interactions among the larger and more polar vinyl-ester monomers.

The number average molecular weight of the vinyl-ester monomers governed the resin viscosity. For all bimodal blends, the resin viscosity was a single function of the number average molecular weight of the vinyl-ester monomers for constant styrene contents (figure 6). In other words, it did not matter which bimodal blend was used (e.g., 1001F vs. 1009F); only the overall  $M_n$  of the vinyl-ester monomers affected the resin viscosity. On the other hand, similar results were not found when normalizing with the weight average molecular weight (figure 8). Vinyl-ester resins using 1001F, for example, had a different dependence on  $M_w$  than vinyl-ester resins using 1004F.

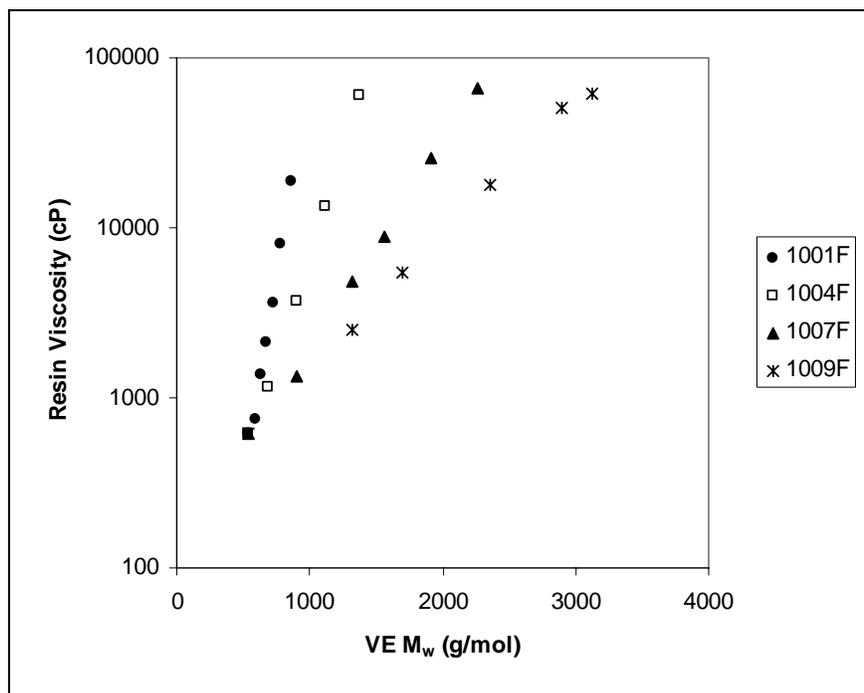


Figure 8. The resin viscosity as a function of VE  $M_w$  for resins containing 20 weight-percent styrene, showing that resin viscosity is not normalized by VE  $M_w$ .

For polymer melts, the viscosity depends on  $M_w$  in a power-law relationship, as shown by Rouse and Reptation theory (33). The Mark-Houwink-Sakurada equation shows that the viscosity of dilute polymer solutions depends on the viscosity average molecular weight, which is between the values of  $M_n$  and  $M_w$ , in a power law-fashion (29, 33). When using a power-law relationship to relate the vinyl-ester resin viscosity to the molecular weight, the power-law exponent had a value between 5 and 10, which is much higher than that for dilute polymer solutions (<1) and for polymer melts (1 or 3.4) (29, 33). The resins tested in this work were monomers or small polymers with a very low degree of polymerization, and they were not in dilute solution. In dilute solution theory, the dissolved polymers interact with the solvent only and increase the

viscosity through these interactions. In concentrated vinyl-ester resins, vinyl-ester monomers interact with styrene and other vinyl-ester monomers to produce frictional forces. Therefore, dilute solution theory is not applicable. The physics and mathematics of concentrated solutions are not well understood (34). Analysis of literature data shows that the bulk viscosities of C5-C16 alkanes and alcohols at 25 °C depend on molecular weight in a power-law relationship with exponents of 2.3 and 1.8, respectively (figure 9) (35), which are considerably higher than the value of 1 Rouse theory predicts for nonentangled melts. Rouse theory failed for the vinyl-esters used in this work because these molecules are Newtonian, and Rouse theory only applies to viscoelastic polymer melts (32, 33). It is possible that the viscosity of these resins will behave according to Rouse theory when no styrene is present in the resin or for higher molecular weight vinyl esters. Reptation is only valid for entangled polymer melts and is not appropriate for these low molecular weight vinyl-ester resins (33). Furthermore, weight average molecular weights only apply to polymeric molecules and would not apply to Newtonian vinyl-ester resins. Therefore, the number average molecular weight should govern the viscosity of vinyl-ester resins.

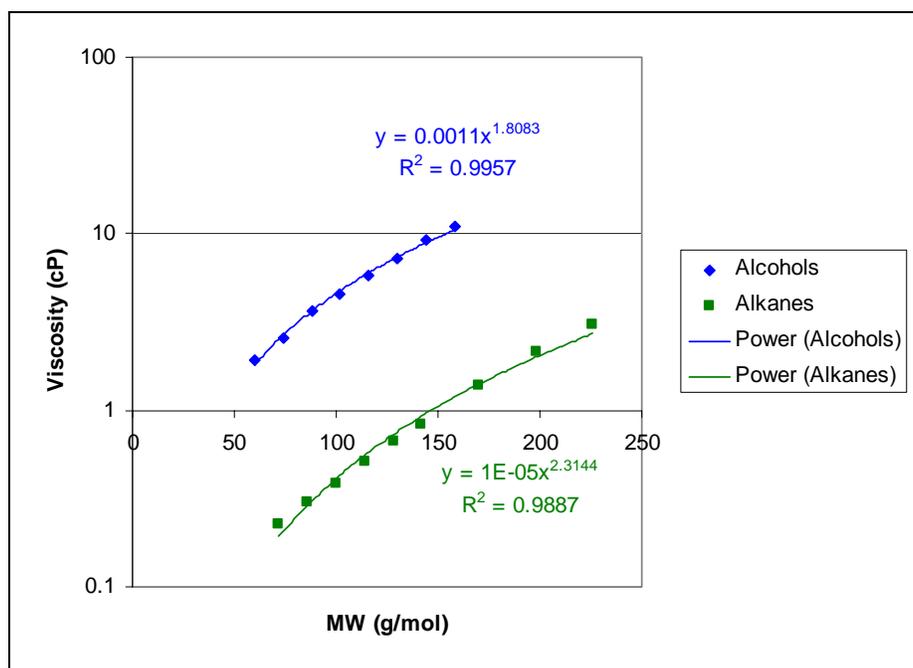


Figure 9. The bulk viscosities of C5-C16 alkanes and alcohols at 25 °C dependence on molecular weight (35).

Styrene affected the resin viscosity in a consistent manner. For different vinyl-ester blends with the same number average molecular weight, the resin viscosity was a single decreasing exponential function of styrene content (figure 7). Styrene content affected all bimodal blends with similar  $M_n$  to the same extent regardless of the molecular weight of the individual components. However, as the overall number average molecular weight decreased, the effect of styrene content on the viscosity decreased, as shown by a less negative slope (figure 7). Most of

the deviation from the best fit lines was due to the fact the various vinyl-ester resins do not have identical  $M_n$  ( $\pm 10$  g/mol), which can affect the viscosity by as much as 15%.

The best fit lines in figure 6 represent a simple expression for the resin viscosity ( $\eta$ ) as a function of number average molecular weight and styrene content. The form of this relationship is

$$\eta_{VE/Sty}(S, M_n) = \eta_{Sty} \cdot \text{Exp}\left[\frac{M_n}{M_e(S)}\right] \quad [\text{cP}] \quad (3)$$

$\eta_{Sty}$  is the viscosity of styrene (i.e., 0.7 cP, the viscosity when the vinyl-ester molecular weight is zero) (35), and  $M_e(S)$  is an effective molecular weight that is a function of styrene content, S. The form of the relationship implies that we are modeling the effect of the addition of a more viscous, higher molecular weight species on the styrene viscosity. As shown in figure 10,  $M_e(S)$  is an exponential function of the styrene content:

$$M_e(S) = 46.7 \cdot \text{Exp}[2.63 \cdot S] \quad [\text{g/mol}]. \quad (4)$$

A linear function of styrene weight fraction with a slope of 292.1 g/mol and an intercept of 17.9 g/mol can approximate this function quite well in the range of the collected data, but its fit was not as good as equation 4. Combining equations 3 and 4 shows that the viscosity of bimodal blends was a predictable function of the  $M_n$  of the vinyl-ester monomers and the styrene weight fraction:

$$\eta_{VE/Sty}(S, M_n) = \eta_{Sty} \cdot \text{Exp}\left[\frac{M_n}{46.7 \cdot \text{Exp}(2.63 \cdot S)}\right] \quad [\text{cP}]. \quad (5)$$

Equation 5 shows that resin viscosity was proportional to the exponential of the number average molecular weight and proportional to the exponential of the inverse of the exponential of the styrene fraction. However, because  $M_e(S)$  can be approximated fairly well by a linear relationship, the viscosity was basically inversely proportional to a single exponential function of styrene content, as shown in figure 7.

Interestingly styrene's molecular weight (104 g/mol) falls right into the range of values of  $M_e(S)$  that increased from 46.7 g/mol at ~0% styrene to 648 g/mol at ~100% styrene. Because of the exponential dependence, small changes in styrene content had a larger effect on the resin viscosity for low values of  $M_e(S)$  than they did for high values of  $M_e(S)$ , as can be seen in figures 6 and 7. The numerical coefficients in equations 4 and 5 are fitting parameters that physically relate how well styrene can reduce the interactions among vinyl-ester monomers and represent the ratio of the pure vinyl-ester viscosity to that of styrene. Rather than examining the effect of polarity, etc.,  $M_e(S)$  allows for an even comparison of vinyl-ester molecular weight to an effective styrene molecular weight. In other words, at high styrene concentrations, the vinyl-ester monomers would need to have at least a molecular weight on the order of 650 g/mol

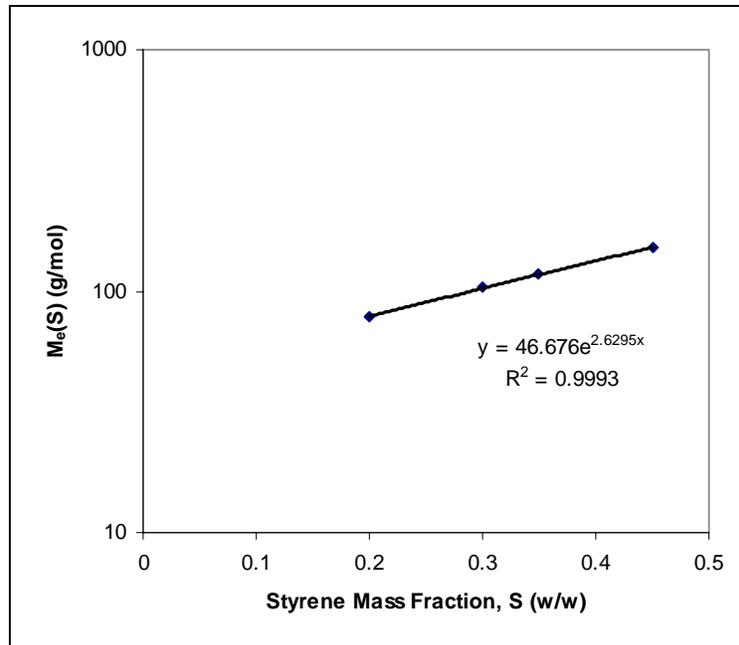


Figure 10. The dependence of  $M_n(S)$  on the styrene weight fraction in bimodal blends of vinyl-ester resins.

for small changes in styrene content to have a significant effect on the viscosity. Because vinyl-ester monomers are more polar in nature than styrene, the value of  $M_n(S)$  at low styrene concentrations was less than the molecular weight of pure styrene. This means that hypothetical vinyl-ester monomers with lower molecular weights than styrene could still raise the viscosity of the resin because of polar interactions.

When the resin viscosity is too high, the pressure driving force in liquid molding operations is not enough to push the viscous resin into all of the gaps in between the fibers (glass, carbon, flax, etc.) before the resin cures. Consequently, viscous resins produce composite parts with high void contents. To reduce the void contents, long production times are necessary. As a result, a viscosity of 500 cP is considered about the maximum for most inexpensive liquid molding techniques (1, 22). Equation 5 can be rearranged to solve for the minimum styrene content required to achieve such a viscosity for given values of  $M_n$ . The minimum styrene content increased approximately linearly with the number average molecular weight of the vinyl-ester monomers. For example, to formulate a resin with only 30 weight-percent styrene, an  $M_n$  of 675 g/mol can be achieved by blending as much as 78 weight-percent vinyl ester 828 with 22 weight-percent vinyl ester 1009F or as little as 62 weight-percent vinyl ester 828 with 38 weight-percent 1001F. In addition, solving equation 8 shows that a minimum styrene content of 20 weight-percent is necessary for the lowest molecular weight DGEBA-based vinyl ester (520 g/mol) to achieve a maximum viscosity of 500 cP. Therefore, there is a significant limit to the amount that bimodal blends can reduce styrene emissions in vinyl-ester resins (i.e., no less than 20 weight-percent styrene in vinyl-ester resins).

### 3.1.2 Effect of Temperature

The viscosity of most chemical species follows an Arrhenius relationship (36):

$$\eta = A \cdot \exp\left(\frac{E}{RT}\right), \quad (6)$$

where  $A$  is the pre-factor,  $E$  is the activation energy for viscous flow,  $R$  is the ideal gas constant, and  $T$  is the absolute temperature. Taking the natural logarithm of both sides of equation 6 yields

$$\ln(\eta) = \ln(A) + \frac{E}{RT}. \quad (7)$$

Therefore, a plot of  $\ln(\eta)$  vs.  $1/T$  should be a line with a slope equal to  $E/R$  and an intercept of  $\ln(A)$ . Figure 11 shows that this plot is indeed linear for vinyl-ester resins. When there was viscosity-temperature hysteresis, the viscosity usually deviated from linearity at 55 °C or so. These points at 55 °C and higher were omitted from analysis because they did not represent the viscosity of the monomeric resin.

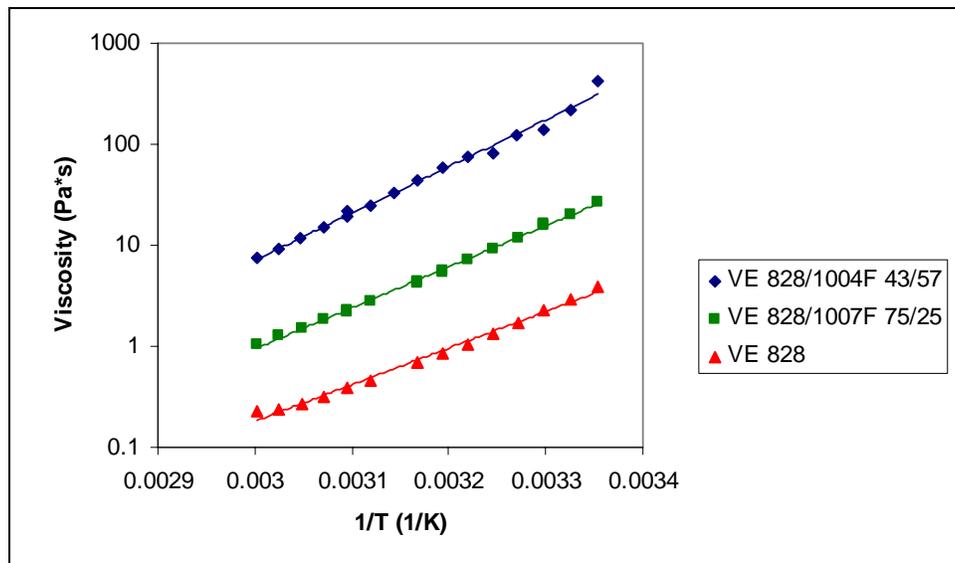


Figure 11. The viscosity-temperature dependence is Arrhenius for vinyl-ester resins with 20 weight-percent styrene.

The activation energy for viscous flow and the pre-factors were calculated from the Arrhenius plots. The activation energy decreased linearly as a function of styrene content (figure 12):

$$E_{VE/Sty} = -186 * S + 114.5 \text{ [kJ]}, \quad (8)$$

where  $S$  is the styrene weight fraction. This indicates the sensitivity to temperature decreased as the styrene content increased. This expression is only valid through 50 weight-percent styrene, considering that over 61 weight-percent styrene, the calculated activation energy is negative. This would indicate that the viscosity should become more dependent on styrene content at

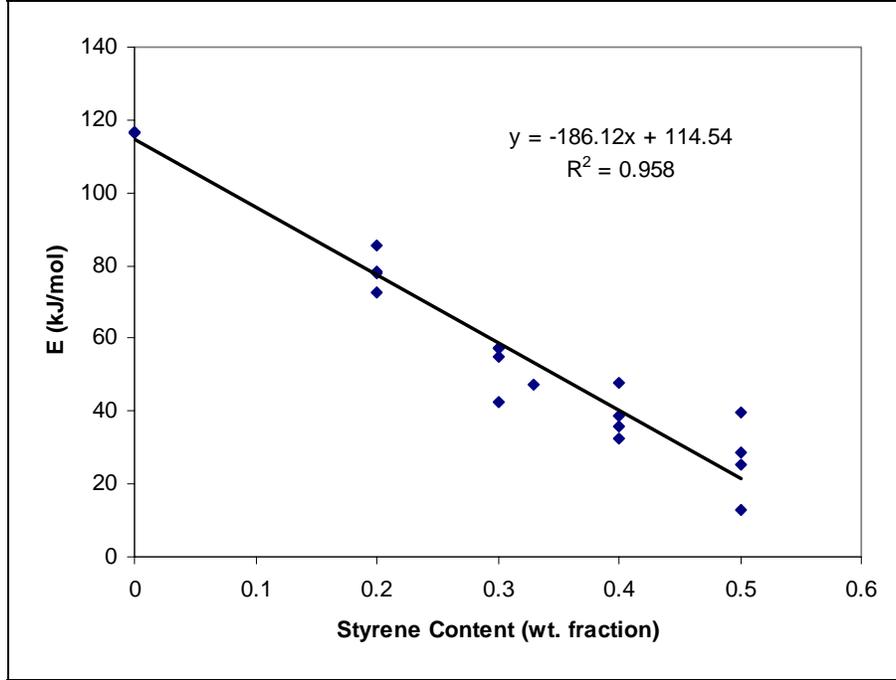


Figure 12. The activation energy for viscous flow as a function of styrene content in vinyl-ester resins.

higher styrene contents, which is not physically reasonable. The activation energy decreased with styrene content because both styrene and temperature reduce viscosity by disrupting intermolecular interactions. As the styrene content increased, it is easier for molecules to slide by each other, thereby reducing the activation energy for viscous flow. The range of activation energies measured is typical for these monomeric resins (37). The pre-factor increased exponentially as a function of styrene content in the resin (figure 13):

$$A_{VE/ Sty} = 3.67 \cdot 10^{-18} \cdot \text{Exp}(59 \cdot S) [\text{Pa*s}]. \quad (9)$$

This factor was expected to increase because it is related to the frequency of interactions, which should increase given that high styrene contents produce resins with lower viscosities. Calculating  $A$  involves extrapolating to infinite temperature. An accurate measurement of this pre-factor is very difficult and is the main cause for the scatter in the results. The activation energy and pre-factor were not functions of vinyl-ester molecular weight (figure 14). Therefore, vinyl-ester molecular weight had no effect on the temperature dependence of the resin, but chemical differences in the resin did affect the temperature dependence of the viscosity (37).

Combining equations 6, 8, and 9 yields the viscosity-temperature model:

$$\eta_{VE/ sty}(S, T) = 3.67 \cdot 10^{-18} \cdot \text{Exp}\left(\frac{-186120 \cdot S + 114540 + 59 \cdot S \cdot RT}{RT}\right) [\text{cP}]. \quad (10)$$

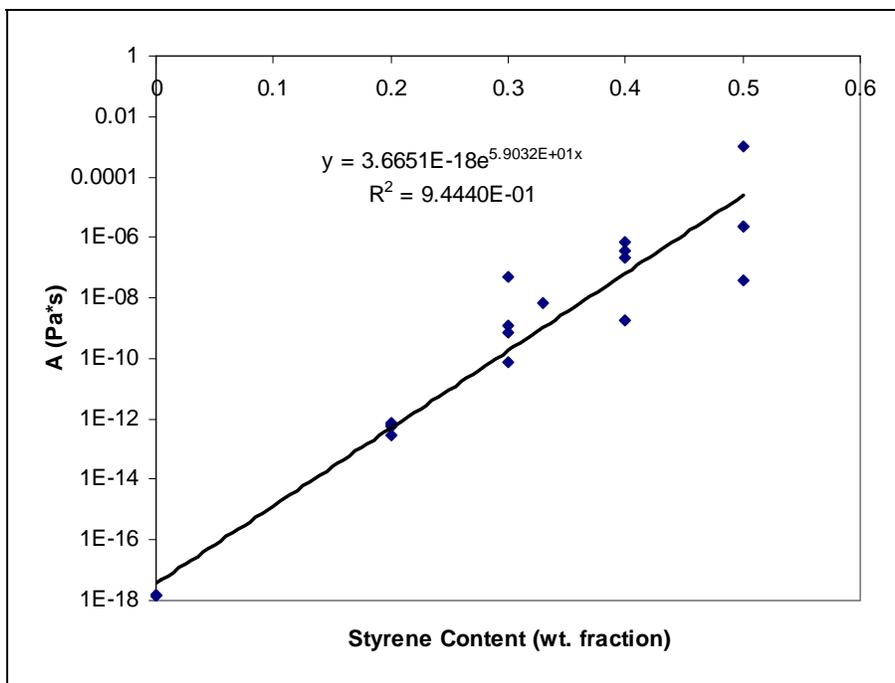


Figure 13. The prefactor as a function of styrene content in vinyl-ester resins.

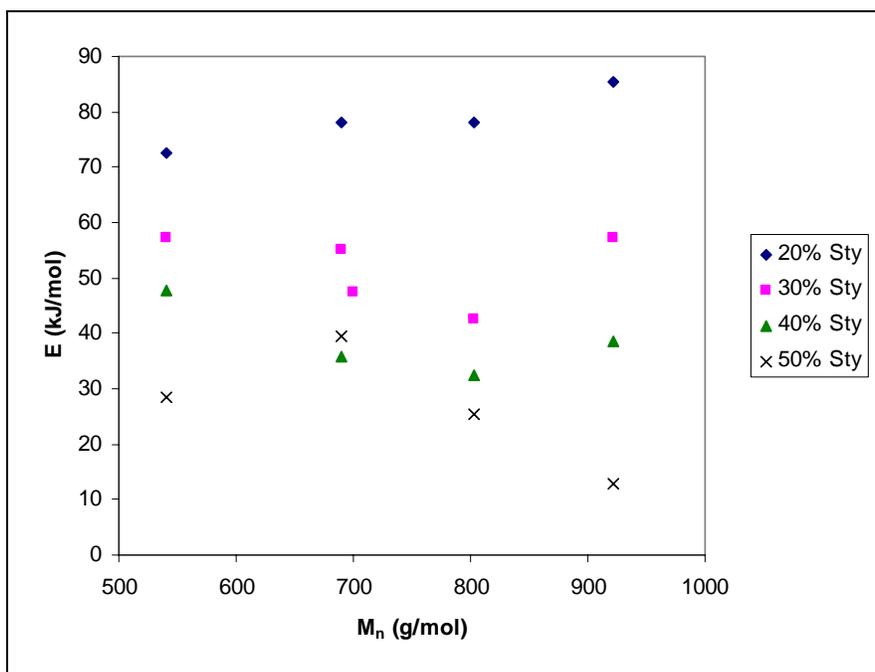


Figure 14. The activation energy for viscous flow as a function of vinyl-ester molecular weight.

Therefore, the viscosity-temperature dependence of vinyl-ester resins was only a function of temperature and styrene content. Specifically, the viscosity was exponentially proportional to the inverse of the temperature. Equation 10 shows the viscosity was both exponentially proportional to the styrene content and to the inverse of the styrene content.

### 3.1.3 Complete Viscosity Model for Vinyl-Ester/Styrene Resins

We already have an accurate working model to predict resin viscosity as a function of styrene content and vinyl-ester molecular weight at 30 °C (equation 5). The viscosity-temperature model only needs to be used to determine the change in viscosity as a result of changing the temperature from 30 °C to a higher or lower temperature. The ratio of the viscosities at temperatures 2 and 1 (303 K) is

$$\frac{\eta_2}{\eta_{1\ VE/Sty}}(S,T) = \text{Exp}\left(\frac{-186120 \cdot S + 114540}{RT_2} + \frac{186120 \cdot S - 114540}{RT_1}\right) \text{ [cP]}. \quad (11)$$

Given the viscosity at 30 °C ( $T_1$ ), the viscosity at an arbitrary temperature 2 is

$$\eta_{2\ VE/Sty}(S,T) = \eta_1 \cdot \text{Exp}\left(\frac{-186120 \cdot S + 114540}{RT_2} + \frac{186120 \cdot S - 114540}{RT_1}\right) \text{ [cP]}. \quad (12)$$

Substituting in the viscosity model at 30 °C for  $\eta_1$  (equation 5) gives the overall viscosity model:

$$\eta_{VE/Sty}(S,T,M_n) = \eta_{Sty} \cdot \text{Exp}\left[\frac{M_n}{46.7 \cdot \text{Exp}(2.63 \cdot S)}\right] \cdot \text{Exp}\left[\frac{-186120 \cdot S + 114540}{R} \left(\frac{1}{T_2} - \frac{1}{303K}\right)\right] \text{ [cP]}. \quad (13)$$

This empirical model allows calculation of the viscosity using only the styrene content, vinyl-ester  $M_n$ , and temperature. This equation is accurate at temperatures ranging from 25 °C to 60 °C,  $M_n$  ranging from 540–950 g/mol, and styrene contents ranging from 0 to 50 weight-percent. This model probably can be extrapolated to other parameter ranges with a good degree of accuracy, but is not valid at styrene contents approaching and above 60 weight-percent because of the zero and negative values of the activation energy calculated at these styrene contents. An advantage of using equation 13 rather than using equation 10 to calculate the resin viscosity as a function of temperature is that the latter equations use the pre-factor, which was calculated with less accuracy than the activation energy or the 30 °C viscosity model. This viscosity model for vinyl-ester/styrene resins can be used to predict the minimum styrene content necessary for a particular liquid molding operation. For example, table 4 shows the required styrene content for given operation temperatures and vinyl-ester molecular weights for a maximum allowable viscosity of 500 cP. Interestingly, 45 weight-percent styrene is only necessary for high molecular weight vinyl esters at fairly low operation temperatures.

Table 4. The calculated styrene content as a function of vinyl-ester molecular weight and temperature that is required to achieve  $\eta = 500$  cP for DGEBA-based vinyl esters.

Temperature (°C)	Required Styrene Content to have $\eta = 500$ cP in Weight-Percent			
	$M_n = 520$ g/mol	$M_n = 650$ g/mol	$M_n = 800$ g/mol	$M_n = 950$ g/mol
20	25.7	33.0	39.8	45.4
25	22.9	30.8	38.1	44.2
30	20.1	28.5	36.4	43.0
35	17.1	26.2	34.6	41.6

## 3.2 Viscosity of Fatty Acid-Based Vinyl-Ester Resins

### 3.2.1 Effect of Fatty-Acid Chemical Structure

The viscosities of the MFA and the reactants used to produce these monomers were measured at 30 °C using a Brookfield digital viscometer. The viscosities of oleic acid and linoleic acid were 24 cP (fatty acids including decanoic acid and longer are crystalline solids at 30 °C), while the viscosity of glycidyl methacrylate was ~1 cP. The viscosities of MFA monomers (figure 15) were higher than their starting materials because MFA contain hydroxy-ester groups, which induce hydrogen bonding (37, 38). The viscosities of MFA monomers increased with chain length and as the level of unsaturation along the fatty acid backbone decreased. At 30 °C, the viscosity was found to be a function of fatty-acid chain length,  $l_f$ :

$$\eta_{MFA} = 0.0111 * l_f^4 - 0.3857 * l_f^3 + 5.145 * l_f^2 - 29.684 * l_f + 92.351 \text{ [cP]}. \quad (14)$$

The level of unsaturation affected the viscosity because these sites put kinks along the fatty-acid chain that increase the intermolecular spacing (39), thereby reducing intermolecular interactions and the viscosity. An unsaturation site is the equivalent of having a fatty-acid with 3.5 fewer carbon atoms according to figure 15:

$$l_f(U) = l_f - 3.5 * U, \quad (15)$$

where U is the level of unsaturation. Initially, the viscosities of polyunsaturated MFAs were similar to that of monounsaturated MFAs. However, the viscosities of polyunsaturated MFAs increase over time. Therefore, it was impossible to quantify the effect of two or more unsaturation sites on MFA viscosity, and equation 15 is only valid for  $U \leq 1$ .

The viscosities of the vinyl-ester resins before cure are shown in figure 16. The viscosities of FA-VE resins are considerably higher than that of vinyl-ester/styrene resins (<100 cP) because fatty-acid monomers have considerably higher viscosities than styrene. The viscosity went through a minimum at 6–8 carbon atoms as the fatty-acid chain length increased. This occurred because two factors are affecting the resin viscosity. At short fatty-acid chain lengths, polar interactions/hydrogen bonding, due to the MFA hydroxyl group, dominate. However, at longer fatty-acid chain lengths, the concentration/effect of this hydroxyl group decreases and chain

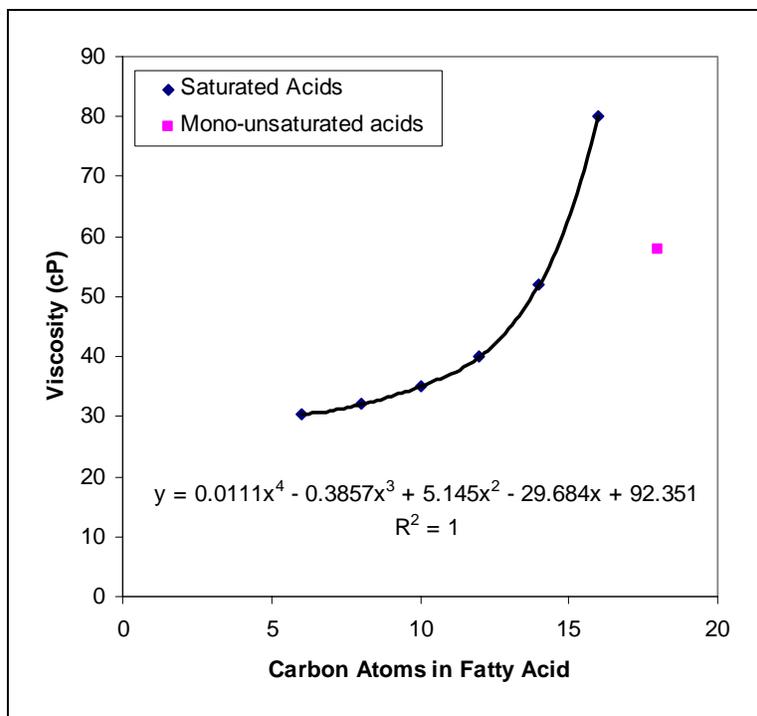


Figure 15. Viscosity of MFA monomers as a function of fatty-acid chain length.

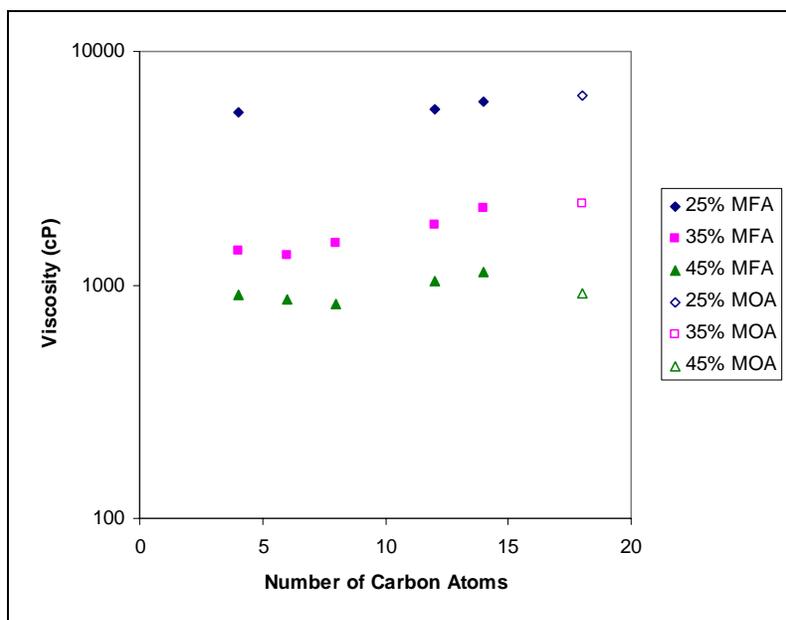


Figure 16. The viscosity of vinyl ester /MFA as a function of fatty-acid chain length at 25 °C.

length effects dominate. Overall, it appears that fatty acids with chain lengths of 6–8 carbon atoms are ideal for producing low viscosity FA-VE resins. The presence of unsaturation sites along the fatty-acid backbone decreased the resin viscosity (figure 16), as they did for MFA monomers alone.

The effect of fatty-acid content on vinyl-ester viscosity was quantified. Figures 17 and 18 show that the resin viscosity decreased exponentially with MFA content. Two functions were used to approximate the effect of MFA content on viscosity. The first was simply an exponential fit of the data (figure 17), which does a good job of fitting the data, except at low MFA contents. A function similar to the vinyl-ester/styrene viscosity model was also used (figure 18). This function does an excellent job of fitting the data with the added benefit of taking into account the effect of vinyl-ester molecular weight. Unfortunately, we are not able to prepare bimodal blends of vinyl-ester monomers with MFA as the only comonomer and therefore cannot verify the effect of bimodal molecular weight in this section. However, using blends of vinyl ester, MFA, and styrene, we will verify the form of this equation in a later section.

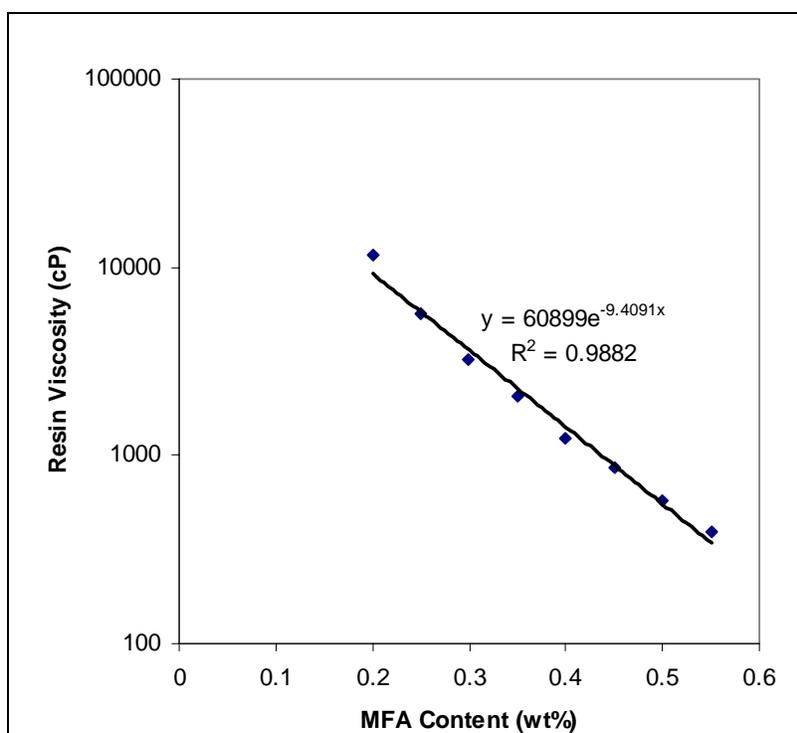


Figure 17. Viscosity of vinyl-ester resin as a function of MFA content for MLau fatty-acids, showing the exponential fit to the data.

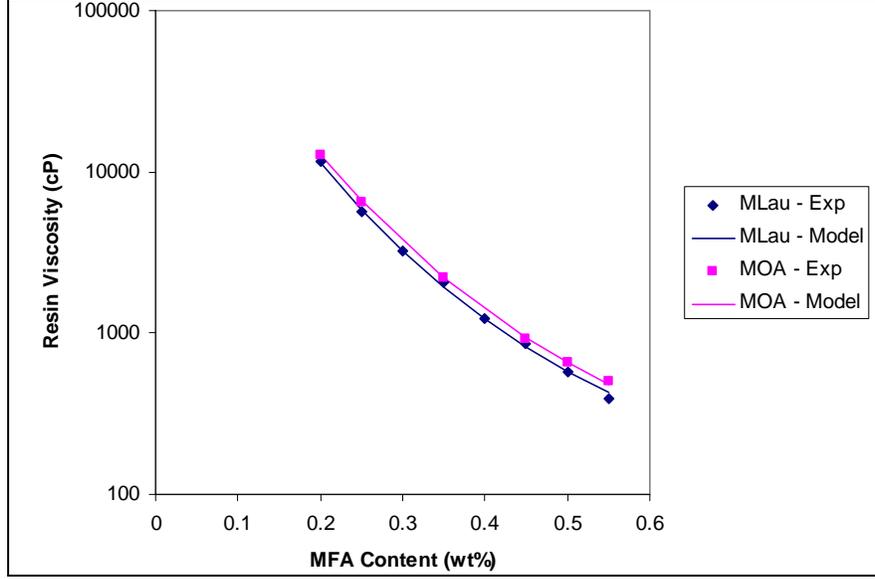


Figure 18. Viscosity of vinyl-ester resin as a function of MLau content, showing the exponential fit to the data.

The best fit curves in figure 18 have the form

$$\eta_{VE/MFA}(MFA, M_n) = \eta_{MFA}^* \cdot \text{Exp}\left[\frac{M_n}{M_e(MFA)}\right] \text{ [cP]}, \quad (16)$$

where  $MFA$  is the weight fraction of MFA monomer and  $\eta_{MFA}^* = 50$  cP, which is the approximate viscosity for all MFA monomers at 30 °C. As for styrene,  $M_e(MFA)$  was an exponential function of the MFA content:

$$M_e(MFA) = 58.5 \cdot \text{Exp}[f(MFA)] \text{ [g/mol]} \quad (17)$$

$f(MFA)$  is an exact linear function of MFA viscosity (figure 19):

$$f(\eta_{MFA}) = (2.9007 - 0.0063 \cdot \eta_{MFA}) \cdot MFA. \quad (18)$$

Combining equations 14 and 18,  $f(MFA)$  can be related to the fatty-acid chain length and unsaturation level:

$$f(\eta_{MFA}) = [2.9007 - 0.0063 \cdot (0.0111 \cdot l_f^4 - 0.3857 \cdot l_f^3 + 5.145 \cdot l_f^2 - 29.684 \cdot l_f + 92.351)] \cdot MFA. \quad (19)$$

Combining equations 16, 17, and 18 gives the overall shows that the viscosity of bimodal blends was a predictable function of the  $M_n$  of the vinyl-ester monomers and the styrene weight fraction:

$$\eta_{VE/MFA}(MFA, l_f, U, M_n) = \eta_{MFA}^* \cdot \text{Exp}\left[\frac{M_n}{58.5 \cdot \text{Exp}((2.9007 - 0.0063 \cdot \eta_{MFA}) \cdot MFA)}\right] \text{ [cP]} \quad (20)$$

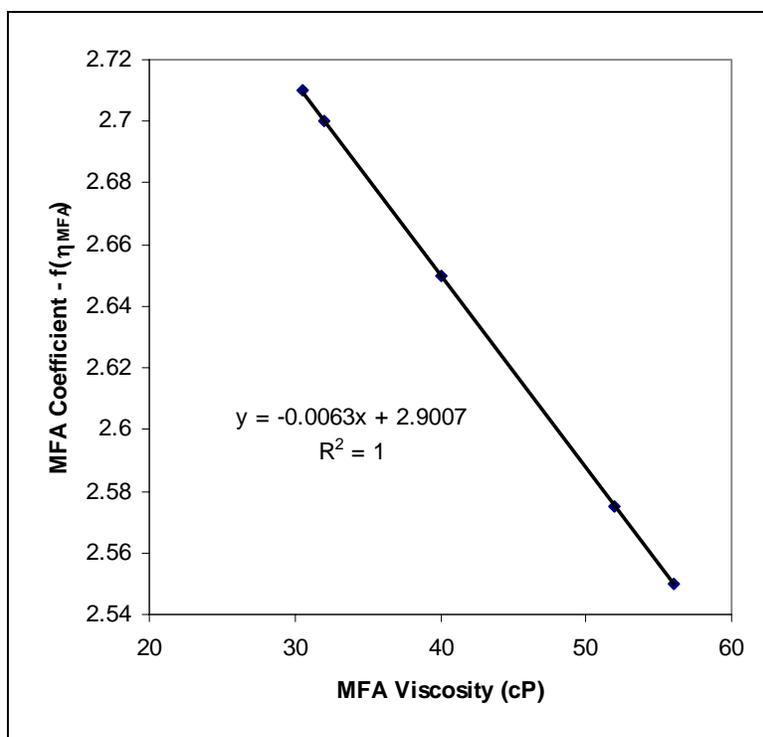


Figure 19. The MFA coefficient in equation 18 is a linear function of MFA viscosity.

Therefore, the resin viscosity was proportional to the exponential of the inverse of the exponential of the MFA. This model is not likely to predict the up-turn in viscosity at short fatty-acid chain lengths as seen in figure 16. Overall, this empirical viscosity model does an excellent job of predicting the viscosity of vinyl-ester/MFA resins as a function of MFA content and MFA type.

### 3.2.2 Effect of Temperature

The viscosities of MFA-based vinyl esters follow an Arrhenius relationship. The activation energy for viscous flow and the pre-factors were calculated from the Arrhenius plots. The activation energy decreased linearly as a function of MFA content (figure 20) as it did for styrene.

$$E_{VE/MFA} = -114.1 * MFA + 114.6 \text{ [kJ]}. \quad (21)$$

This indicates the sensitivity to temperature decreased as the MFA content increased. The three different monomers have very different viscosities alone and in vinyl-ester resins. Therefore, it is expected that all fatty acid-based vinyl esters will have activation energies that fall along this line. The activation energy was higher for a given content of MFA monomer relative to styrene, because of a lower molar content of MFA monomers. Equation 21 indicates that the activation

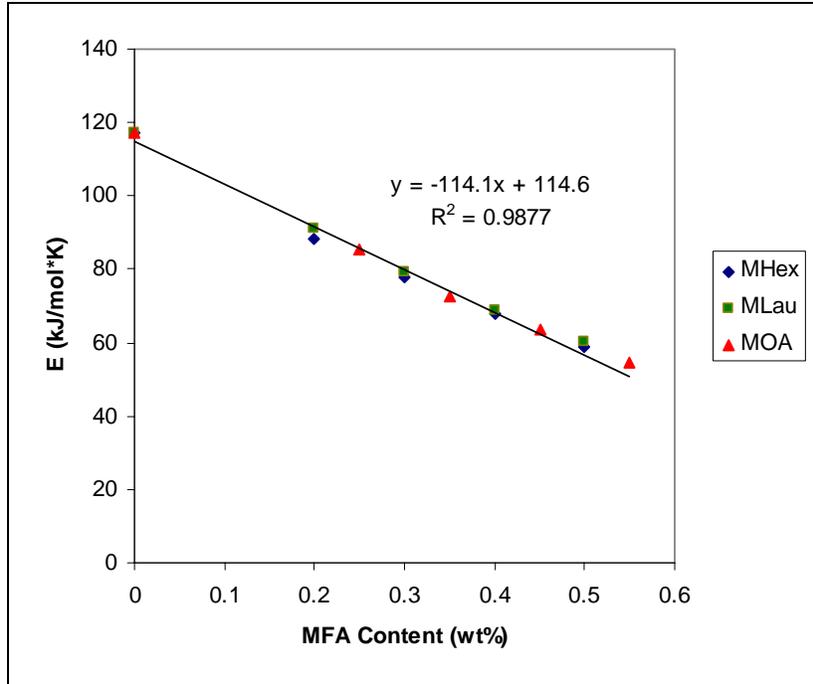


Figure 20. The activation energy as a function of diluent content and fatty-acid type.

energy is  $\sim 0$  for MFA monomers alone, which is not correct. Therefore, we expect this curve to level out as the MFA content is increased above 55 weight-percent.

The pre-factor increased exponentially as a function of MFA content in the resin (figure 21):

$$A_{VE/MFA} = 1.76 \cdot 10^{-18} \cdot \text{Exp}(34.7 \cdot MFA) \text{ [Pa*s]}. \quad (22)$$

This factor was expected to increase because it is related to the frequency of interactions, which should increase given that high MFA contents produce resins with lower viscosities. For this same reason, the value of  $A$  is lower for vinyl-ester/MFA resins relative to vinyl-ester/styrene resins because of the lower molar concentration of MFA monomers used in this work.

Combining equations 6, 21, and 22, we obtain the viscosity of VE/MFA as a function of temperature:

$$\eta_{VE/MFA}(T) = 1.76 \cdot 10^{-18} \cdot \text{Exp}\left(\frac{-114100 \cdot MFA + 114600 + 34.7 \cdot S \cdot RT}{RT}\right) \text{ [cP]}. \quad (23)$$

### 3.2.3 Complete Viscosity Model for Fatty Acid-Based Vinyl-Ester Resins

As for vinyl-ester/styrene resins, the viscosity model for vinyl-ester/MFA resins was a simple combination of the effects of temperature (equation 21) and the effects of monomer content (equation 20), as well as monomer type:

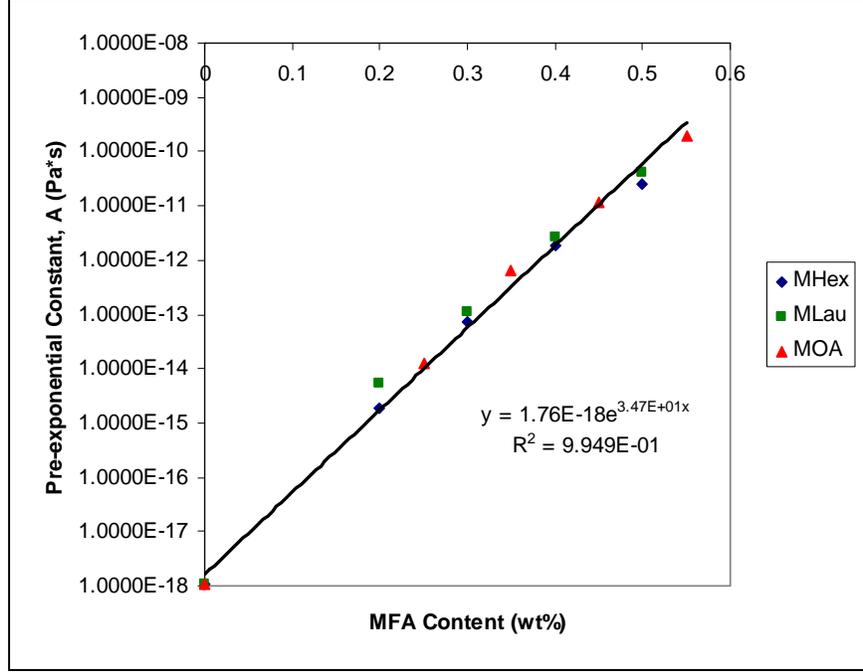


Figure 21. The pre-exponential constant as a function of diluent content and fatty-acid type.

$$\eta_{VE/MFA}(MFA, T, l_f, U) = \eta_{MFA}^* \cdot \text{Exp} \left[ \frac{M_n}{58.5 \cdot \text{Exp}((2.9011 - 0.0063 \cdot \eta_{MFA}) \cdot MFA)} \right] \cdot \text{Exp} \left[ \frac{-114100 \cdot MFA + 114600}{R} \left( \frac{1}{T_2} - \frac{1}{303K} \right) \right] \quad [cP] \quad (24)$$

The model allows for calculation of the vinyl-ester/MFA viscosity for any given temperature, vinyl-ester molecular weight, MFA chain length, MFA unsaturation level, and MFA content. Figure 22 shows the operating window for vinyl-ester/MFA resins as a function of temperature, fatty-acid chain length, and unsaturation level. Increasing temperature reduces the required MFA content, as was expected. Increasing the MFA chain length has little effect on the window until above chain lengths of 12 carbon atoms. Above which, the required MFA content increased severely with chain length. Unsaturation sites decreased the required MFA content, as expected. Interestingly, figure 22 shows that fatty acids of 8 carbon atoms minimize the required MFA content. Therefore, the viscosity model does predict the minimum in viscosity as a function of fatty-acid chain length (figure 16) at 6–8 carbon atoms.

### 3.3 Viscosity of Vinyl-Ester Resins Using Both Fatty-Acid Monomers and Styrene as Reactive Diluents

The viscosities of vinyl-ester resins using MFA were fairly high. Only a small number of formulations achieve viscosities of 500 cP or lower at 30 °C using less than 50 weight-percent MFA. To reduce the viscosity, blends of MFA and styrene were used as the reactive diluent in

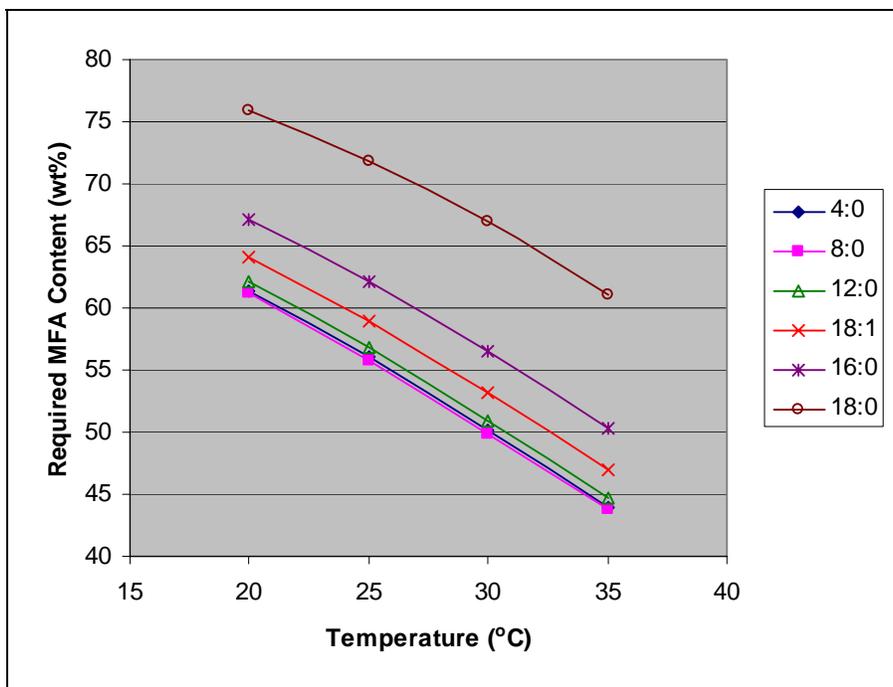


Figure 22. The minimum MFA content required to achieve vinyl-ester resin viscosities below 500 cP as a function of temperature, fatty acid chain length, and unsaturation level. The operating window is any MFA content above the curve. Legend: [carbon atoms: unsaturation sites].

vinyl ester 828. The viscosity of vinyl ester/MFA/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 vinyl-ester 828 resin (figure 23, shown for MHex- based resins). Styrene contents of ~10% or more reduced the viscosity of vinyl-ester resins to the acceptable range (<500 cP is required for most liquid molding processes [1, 22]). Only low styrene contents are necessary to reduce the viscosities of vinyl-ester/MFA systems to acceptable processing conditions at 30 °C.

The best fit curves in figure 23 were derived from a logarithmic rule of mixtures (37):

$$\eta_{VE/MFA/Sty} = \exp\left[w_{S(D)} \cdot \ln(\eta_{VE/Sty}(D)) + w_{MFA(D)} \cdot \ln(\eta_{VE/MFA}(D))\right] \text{ [cP]}, \quad (25)$$

where  $w_{S(D)}$  and  $w_{MFA(D)}$  are the styrene and MFA weight fractions, respectively, of the total diluent content,  $D$ , and  $\eta_{VE/Sty}(D)$  and  $\eta_{VE/MFA}(D)$  are the viscosities of vinyl-ester/styrene and vinyl ester/MFA, respectively, evaluated at the total diluent weight fraction. This logarithmic rule of mixtures does an excellent job of predicting vinyl-ester/MFA/styrene resin viscosity as a function of composition. On the other hand, a simple rule of mixtures does not accurately fit the data, nor does the Fox equation (41). Furthermore, this model is able to accurately predict the effect of vinyl-ester molecular weight (figure 24) and temperature (figure 25) on resin viscosity.

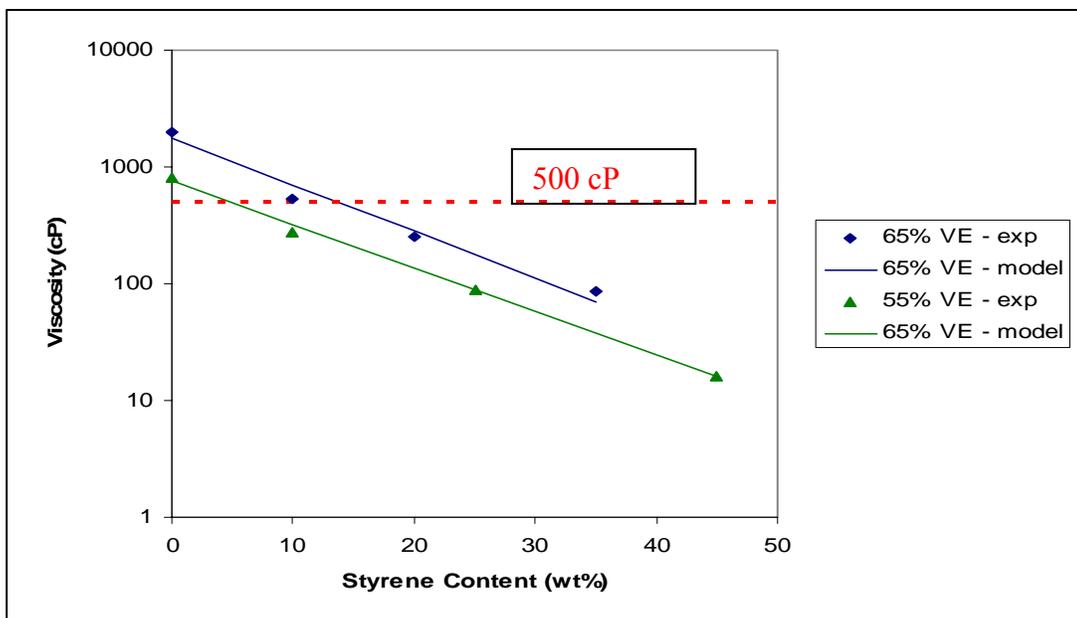


Figure 23. The viscosity of vinyl ester/MHex/styrene as a function of styrene content in the resin for resins containing 55 weight-percent and 65 weight-percent vinyl ester 828, along with model predictions.

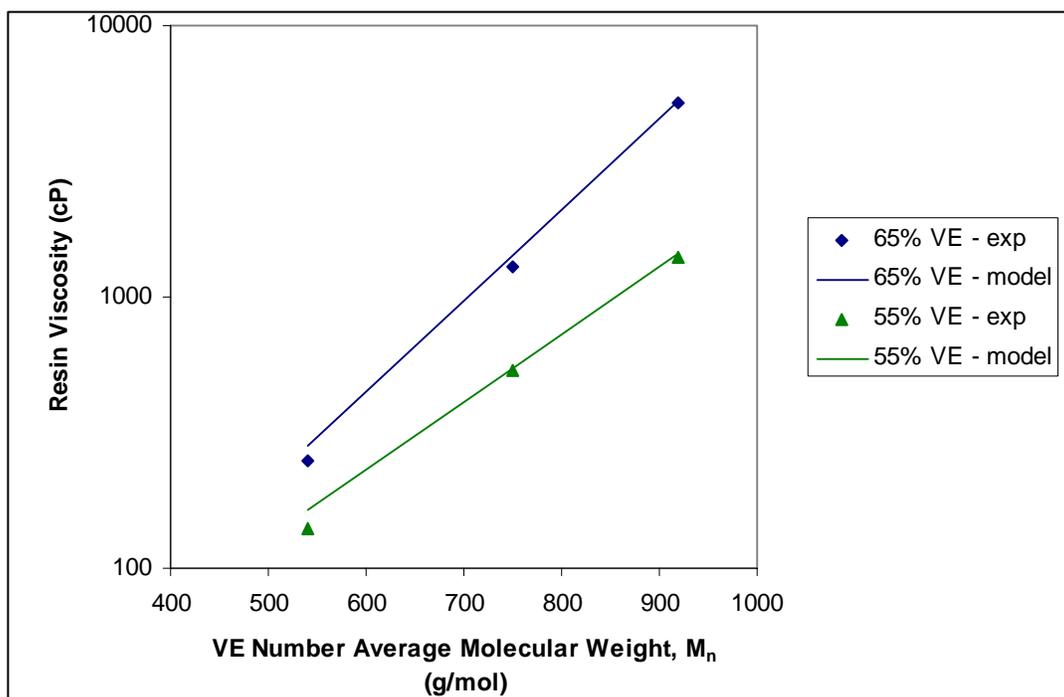


Figure 24. The experimental and model viscosities of vinyl ester/MHex/styrene as a function of vinyl-ester molecular weight and vinyl-ester content for resins containing 20 weight-percent styrene.

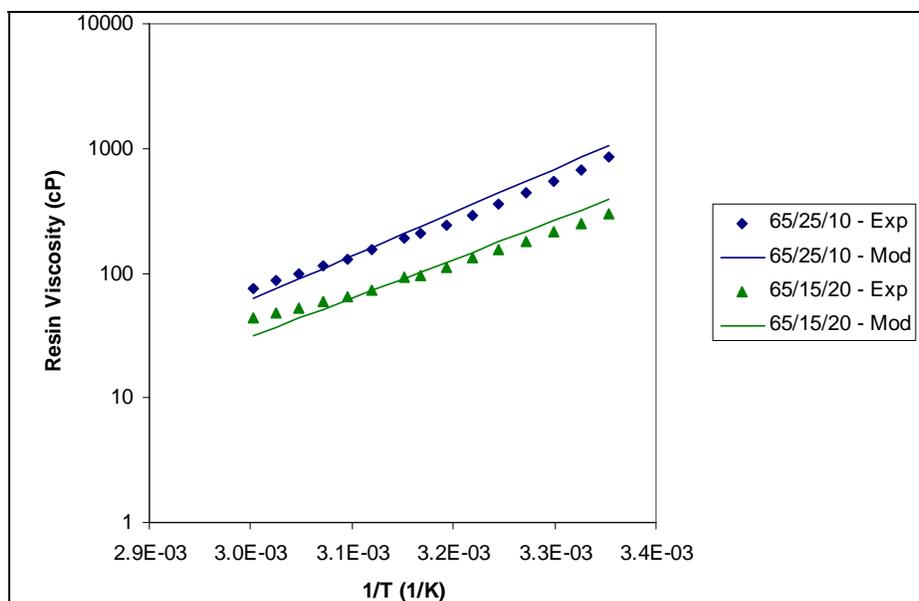


Figure 25. The experimental and model viscosities of VE/MLau/styrene as a function of temperature.

Therefore, this overall viscosity model allows prediction of the viscosity of vinyl-ester resins based on the vinyl-ester molecular weight, styrene content, MFA chain length, MFA unsaturation level, MFA content, and temperature.

Using this overall viscosity model, an operating window (i.e., viscosity below 500 cP) can be determined for a single variable while keeping the other variables constant. For instance, at 30 °C, the required styrene content in vinyl-ester/MFA/styrene resins increases as the vinyl-ester molecular weight increases (figure 26). However, fatty-acid chain length does not have a strong affect until effective fatty acid lengths of 14 are reached. Therefore, using lauric acid to make fatty acid-based vinyl-ester resins will not result in significantly higher viscosities than hexanoic acid-based resins.

## 4. Conclusions

The viscosities of DGEBA-based vinyl-ester resins are predictable functions of reactive diluent content, type, temperature, and vinyl-ester molecular weight. The viscosity decreased exponentially with reactive diluent content. Therefore, changes in the diluent content have a larger effect on the resin viscosity at low diluent contents than they do at higher diluent contents. Two different types of reactive diluents affected the viscosity in the same manner, but not to the same extent. The viscosities of resins using both diluents were accurately predicted using a logarithmic rule of mixtures from the two-component viscosity functions. The viscosity increased exponentially and predictably as a function of the vinyl-ester number average molecular weight. Increasing the temperature decreased the viscosity in an Arrhenius manner.

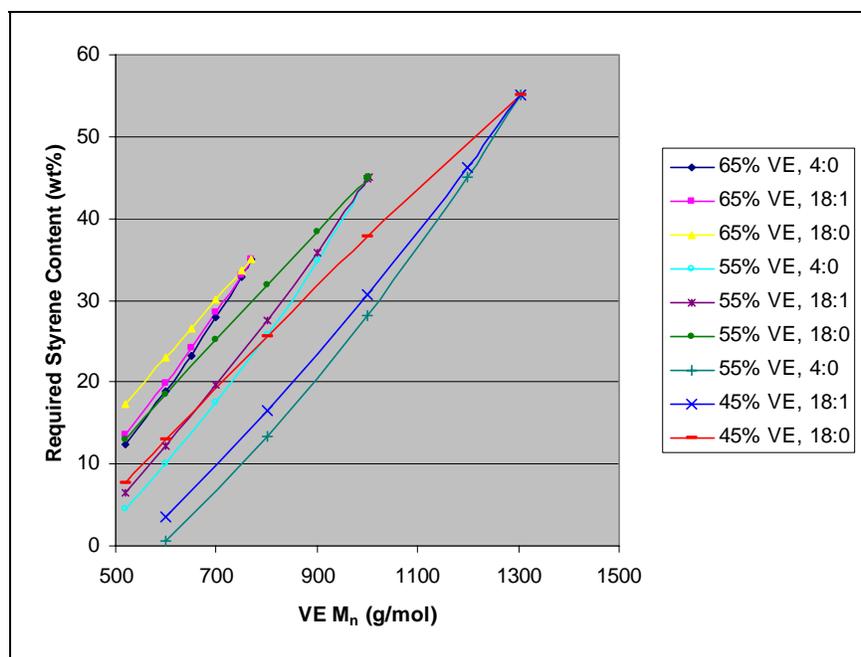


Figure 26. The minimum styrene content required to achieve vinyl-ester resin viscosities below 500 cP as a function of fatty acid chain length, vinyl-ester content, and vinyl-ester molecular weight at 30 °C. The operating window is any styrene content above the curve for any molecular weight along the curve. Legend: [carbon atoms: unsaturation sites].

The activation energy for viscous flow decreased linearly as the diluent content increased, but was unaffected by vinyl-ester molecular weight, fatty-acid chain length, and unsaturation level. Overall, the resin viscosity can be modeled as simple functions of the resin temperature, vinyl-ester molecular weight, styrene content, MFA content, MFA chain length, and MFA unsaturation level, which are all known quantities for a formulated resin.

This work has a number of potential applications:

- determining the minimum VOC/HAP content for liquid molding operations,
- design of low VOC/HAP resins, and
- emissions modeling.

Because of Environmental Protection Agency regulations, minimizing VOC/HAP emissions is a priority for facilities that work with composite materials. This work allows a predictive method for doing so. Considering that this work allows for viscosity prediction of bimodal blends of vinyl esters and fatty acid-based vinyl esters, this model can be used to determine the set of formulations that would meet the viscosity processing requirements. Emissions modeling work so far has shown that styrene emission rates from vinyl-esters are dependent on resin viscosity. Therefore, this model allows for better emissions modeling predictions.

Although styrene is damaging to the environment, there is a minimum styrene content required in vinyl-ester/styrene resins to achieve acceptable viscosities for liquid molding. At 30 °C, 20 weight-percent styrene is required in vinyl-ester/styrene resins. The minimum styrene content is much lower in fatty-acid-based resins because of the viscosity reduction associated with MFA monomers. The exact styrene content required is dependent on the processing temperature, fatty-acid monomer used, fatty-acid content, and vinyl-ester content used, but 5–10% is a typical minimum styrene content required. Therefore, both bimodal blends of vinyl-ester resins, and especially fatty-acid-based vinyl esters, can be used to reduce VOCs, maintaining low resin viscosities.

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