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The use of bimodal blends of vinyl ester monomers to improve resin processing and toughen polymer properties

John J. La Scala[a,b], Joshua A. Orlicki[b], Cherise Winston[b], E. Jason Robinette[a],
James M. Sands[b], Giuseppe R. Palmese[a,*]

[a]Department of Chemical Engineering, Drexel University, Philadelphia, PA 19104, USA
[b]Army Research Labs, 4600 Deer Creek Loop, Aberdeen Proving Grounds, MD 21005-5069, USA

Abstract

Vinyl ester (VE) monomers with bimodal molecular weight distributions were prepared by reacting methacrylic acid with blends of monodisperse epoxy resins ranging in molecular weight from 350–7000 g/mol. Monodisperse vinyl ester monomers were prepared from epoxy resins of a single molecular weight. The extent of vinyl ester formation was found to be near complete and side reactions, such as etherification, did not occur to a significant extent. The viscosities of these vinyl ester resins were measured as a function of styrene content. It was found that resin viscosity, η, increased exponentially and predictably as both the styrene content (S) decreased and as the number average molecular weight (M_n) of the vinyl ester monomers increased: $\eta \sim \exp(M_n)/\exp(S)$. Cure kinetics studies showed that the vinyl ester reactivity ratio decreased to 0.1 from 0.6 for bimodal blends relative to monodisperse resins while the styrene reactivity ratio increased from 0.4 to 0.6. Thus, the microgels in bimodal blends were smaller than in monodisperse resins. Emissions studies proved that decreasing the styrene content reduced the VOC emission rate and total emissions. Higher VE molecular weights decreased the overall emissions due to a reduction in monomer mobility. T_g decreased from 143 to 125 °C as M_n of the VE monomers increased from 540 to 920 g/mol; yet, T_g of these bimodal blends were still equal to or greater than that of commercial VE resins (~ 125 °C). The fracture toughness of bimodal blends increased from ~ 100 to ~ 330 J/m^2 as VE M_n increased from 540 to 920 g/mol because of matrix toughening. The fracture properties did not improve as the styrene content increased from 35 to 45 wt% because of corresponding changes in the morphology. Yet, there were numerous low VOC bimodal formulations with fracture properties in excess of the low VOC Dow Derakane 441–400 (110 J/m^2) and even the industry standard Derakane 411–350 (240 J/m^2).
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1. Introduction

Vinyl ester (VE) 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 (UPE) systems and are less expensive and easier to process than epoxy systems [1]. Vinyl ester resins contain VE monomers and a reactive diluent, such as styrene. The VE monomers have two terminal free-radically polymerizable unsaturation sites, enabling the resin to cross-link. Reactive diluents, such as styrene, have a single vinyl group, and act as linear chain extenders. The reactive diluent is used because it severely reduces the resin viscosity and improves overall polymer 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.

VOC emissions 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. Composite parts typically have very large surface to volume ratios, which allows 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 a HAP and a VOC, the Federal Environmental Protection Agency of the United States of America introduced legislation to limit styrene emissions from composite manufacturing [4]. Therefore, liberation of VOC emissions must be mitigated not only during composite processing, but also during curing and fielding of the composite part. Thus, a means of reducing the styrene emissions from VE resins is desired. Current low VOC VE systems do exist, such as Dow Derakane 441–400 [6]. However, the use of these resins is limited because of their low fracture toughness (~ 100 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, fracture toughness values above 200 J/m^2, and slightly lower costs [5–8].

Unfortunately, decreasing the styrene content in VE 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.

Styrene vapor suppressants have been used to reduce emissions from vinyl ester resins. These suppressants are typically a surfactant or paraffin wax that segregates to the air interface and reduces the styrene evaporation rate [11, 12]. Unfortunately, these suppressants also tend to segregate to the resin–fiber interface, which decreases fiber–matrix adhesion and the mechanical properties of the composite [13].

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 [9,14]. High molecular weight VE monomers yield resins with high fracture properties via matrix toughening. However, low styrene contents cannot be used because the resin viscosity increases severely and processing becomes unacceptably difficult [15]. On the other hand, using a mixture of low and high molecular weight vinyl ester monomers (i.e., bimodal blend) could be used to maintain low resin viscosities and low styrene contents while achieving high fracture toughness. This method has been successful for UPE resins, but the target resin viscosities were an order of magnitude higher than that which is allowable for inexpensive liquid molding techniques [16,17]. Here, we examine the effect of using bimodal blends of VE monomers on resin and polymer properties. Furthermore, this paper presents empirical models that detail how resin and polymer properties are affected by VE molecular weight.

2. Experimental

2.1. Vinyl ester preparation

Vinyl ester monomers were prepared via methacrylation of diglycidyl ether of bisphenol A (DGEBA) (Fig. 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 [18]. 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) [15].

Pure VE was prepared via methacrylation of Epon 828, 834, or 836 (Fig. 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

Table 1
Epoxy equivalent weight as determined by epoxy titration and literature values [15]

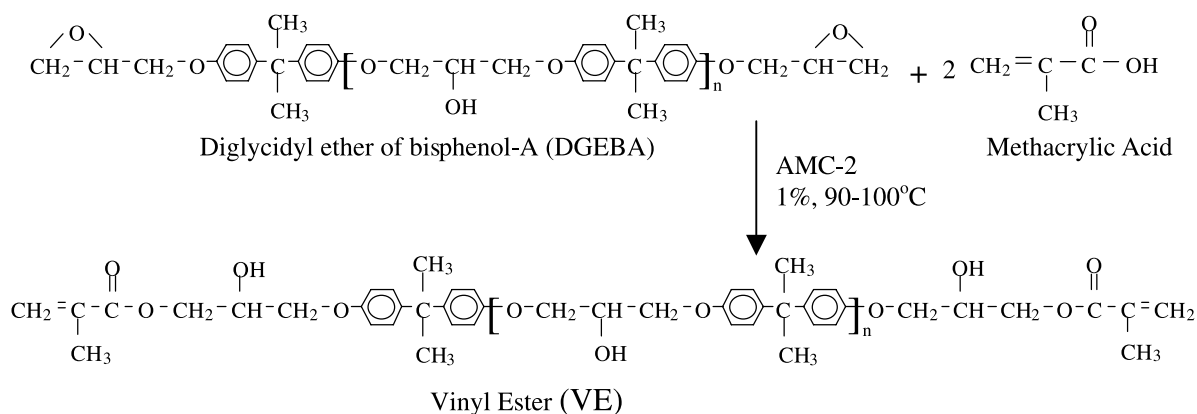| Epon Resin	Literature EEQ (g/mol)	Experimental EEQ (g/mol)	Calculated MW (g/mol)
828	185–192	186±3	372±6
834	230–280	255±4	510±8
836	290–335	307±3	614±6
1001F	525–550	548±3	1096±6
1004F	800–950	900±5	1800±10
1007F	1700–2300	1990±7	3980±14
1009F	2300–3800	2770±8	5550±16

Fig. 1. The methacrylation of DGEBA to form vinyl ester monomer.

for the reaction and to prevent epoxy homopolymerization [19] in the amount of 1 wt%. The reaction was run at $\sim 90\,^{\circ}C$, but because of the exothermicity of this reaction, water was periodically flowed through cooling coils within the reactor to keep the temperature below $95\,^{\circ}C$. Acid number titration was used during the course of the reaction to measure the amount of free (unreacted) acid in the VE system. The acid number tests were performed in accordance with ASTM D1980-87 [20]. Approximately 1 g of the VE reaction mixture was dissolved in 5 g acetone. Three drops of 0.5 wt% 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 $\sim 2\%$ 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 numbers were below 5. Although the VE 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 VE monomers 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 VE reaction, even at $100\,^{\circ}C$. Therefore, these resins were blended with Epon 828 to prepare bimodal VE blends. Unfortunately, the solid contents were just too high for only Epon 828 and the required amount of methacrylic acid to dissolve, even at $100\,^{\circ}C$. Therefore, low styrene (Aldrich, 99%) contents (<20 wt%) 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 wt%) was added to the reaction vessel. The reaction vessel was sealed and stirred vigorously with the mechanical mixer. While heating to $90\,^{\circ}C$, the desired content of Epon 100XF was added to the reactor in aliquots over the course of one hour to prevent excessive clumping of the solid Epon 100XF. In addition, 1.01 times the stoichiometric amount of methacrylic acid along with 1 wt% AMC-2 catalyst (based on Epon and methacrylic acid masses only) were added to the solution. The reaction temperature was kept in the range of $90–95\,^{\circ}C$, while using the cooling coils for cooling as needed. Once the acid number was approximately 5, the reaction was ended.

Bimodal blends of VE were prepared with the specific mass ratios of 828/1001F 29/71, 828/1004F 42/58, 828/1007F 52.5/47.5, 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 VE resins is listed as weight percentage of the entire resin. Bimodal blends with higher VE 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 VE 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. A Thermo Nicolet Nexus 670 FTIR was used in absorbance mode, taking 16 scans per spectrum with a resolution of $4\,cm^{-1}$. The raw FTIR spectra of these resins showed that the peaks representing the epoxide groups (6066, 4530, and $917\,cm^{-1}$) were no longer visible after reaction, and

methacrylate groups (6160 and 942 cm^{-1}) were present in the resin [7,21]. 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 VE molecular weight and styrene content in the bimodal blends. A Waters 515 GPC was used with two 30 cm long, 7.5 mm diameter, 5 μm styrene-divinyl benzene columns in series. The columns were equilibrated and run at 45 °C using tetrahydrofuran (THF) (Aldrich) as the elution solvent at a flow rate of 1 mL/minute. The column effluent was monitored by two detectors operating at 25 °C: a Waters 2410 refractive index detector and a Waters 2487 dual absorbance detector operating at 270 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 [22]. Fig. 2 shows that these blends do indeed have bimodal molecular weight distributions. The peak at 14.5 min represents the VE 828 fraction of the resin, while the peak at lower elution times represents the higher molecular weight VE 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

Fig. 2. SEC chromatographs of VE 828 and representative VE bimodal blends. The curves are vertically offset for clarity.

that if a significant amount of epoxy homopolymerization occurred, a broad peak appearing at 10 min and lower elution times would appear [22,23]. 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 VE/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 VE 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 VE resins using SEC, the molecular weight as a function of retention time was calibrated using Epon resin samples [24]. 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 VE 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) (Eq. (1) and (2)):

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

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

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 experiment and literature values [15]. 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 VE 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.

SEC shows that pure styrene had a single peak at 18.0 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 18.0 min relative to the area of the VE peaks from 12–16 min (Fig. 2). However, pure VE 828 also had a small peak at 18.0 min as a result of catalyst and unreacted
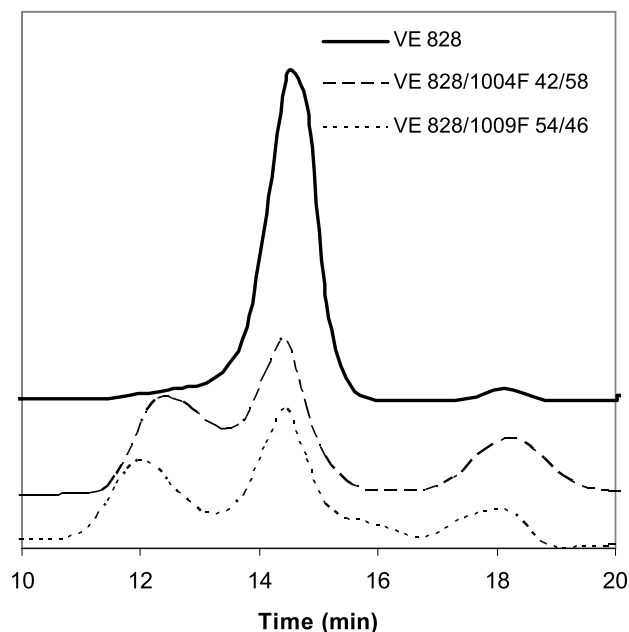
Table 2
The VE molecular weights and styrene contents as determined using NMR and SEC along with literature/known values

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

The styrene contents listed for the bimodal blends of VE 828/100XF are the experimentally determined values and the initial weight fraction styrene (known) in the reaction mixture of the prepared VE.

methacrylic acid. The effect of these components were small, but were removed anyway using a calibration procedure. VE 828 standards with 30–50 wt% styrene were prepared and tested to calibrate SEC results. Using this calibration curve, the styrene content in commercial resins was measured. In all cases, the results agreed within 1% of the amount of styrene added to the bimodal resin system (Table 2).

Nuclear magnetic resonance spectroscopy (NMR) was run on the Epon resins, the prepared vinyl esters, and commercial VE resins to verify the extent of methacrylation, styrene content, and VE molecular weight. A Bruker 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 VE is described in the literature [5,7]. The internal standards for VE are the four methylene protons and the six methyl protons of the methacrylate groups per VE. The area per proton for these standards should be in agreement. The value of n for the VE (Fig. 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 [21,25] 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 conversions greater than 99%, verifying the FTIR results.

Derakane 411–350 and 441–400 were analyzed in this manner along with the VE 828 and bimodal blends of VE resins. The experimental results for Derakane resins and the VE 828 resin were similar to the literature results (Table 2) [5–7]. Furthermore, VE 828 with 30 wt% styrene was

determined to have 29 wt% styrene using NMR, which proves the validity of this method.

2.2. Resin viscosity

The viscosities of the resins were measured using a Brookfield digital viscometer in Couette geometry (i.e., concentric cylinders). Approximately 8 ml of the sample were placed into the sample holder. 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 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 (e.g. 828/1001F) was also tested using two higher VE 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 wt%. The viscosities of selected samples were also measured using a TA instruments (New Castle, DE) AR2000 rheometer in steady shear flow experiments to prove that the resins have Newtonian behavior. The shear rate was increased from 1 to 3000 s^{-1} and then decreased back to 1 s^{-1}, and 10 measurements were taken per decade. At a given shear rate, the shear stress was measured every two seconds. The shear rate and viscosity were recorded when the shear rate stabilized to within 5% tolerance for three consecutive points.

2.3. Resin cure

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 (e.g. 828/1001F) was also tested using higher VE 828 weight fractions. For each resin

system, styrene contents as low as 28 wt% and as high as 45 wt% were used. All resins were initiated using trigonox 239A (Akzo Nobel Chemicals, Chicago, IL), containing 45% cumeme hydroperoxide, and cobalt napthenate (CoNap) (Aldrich) as a catalyst to promote room temperature cure. The trigonox and CoNap masses used were 1.5% and 0.375%, respectively, of the total resin mass. All resins were allowed to cure at room temperature for 16 h. Fracture toughness samples were also post-cured at 130 °C for 3 h.

2.4. Cure kinetics

A Nicolet Magna 860 Fourier FTIR operating in transmission mode with $4 \, cm^{-1}$ resolution was used. The set-up of the FTIR cell is explained elsewhere [7]. A drop of the resin was sandwiched between two 25 mm diameter NaCl disks (International Crystal Labs) separated by a 0.025 mm thick Teflon™ spacer (International Crystal Labs). One sodium chloride disk was 2 mm thick while the other was 4 mm thick. The salt plate assembly was placed in a cell holder. The temperature of the cell holder can be controlled to within ± 0.1 °C of the set-point. When the cell holder equilibrated to the reaction temperature, the salt plate assembly was placed in the holder, and the first FTIR scan was taken. All resin mixtures were cured at 30 °C for 16 h and post-cured at 120 °C for an additional 2 h. The resin mixtures were also cured at 90 °C for 4 h and post-cured at 120 °C for an additional 2 h. An FTIR spectrum comprised of 16 scans was taken every 30 s during the cure reaction. All vinyl ester resins were prepared and tested with 20–60 wt% styrene.

The conversion, α, was calculated by measuring the height of the peak relative to an internal standard (i.e. a group that is not affected by the reaction) (Eq. (3)):

$$\alpha = 1 - \left(\frac{ABS(t)_{peak}}{ABS(t=0)_{peak}}\right)\left(\frac{ABS(t=0)_{standard}}{ABS(t)_{standard}}\right) \qquad (3)$$

The cure kinetics were fit to an autocatalytic model [7]. VE monomers contain methacrylate groups that appear at $942 \, cm^{-1}$. The methacrylate conversion was calculated by measuring the height of the peak relative to the vinyl ester aromatic C–H stretch at $828 \, cm^{-1}$ [7,21]. The styrene conversion was calculated by measuring the styrene carbon-carbon double bond peak height ($910 \, cm^{-1}$) relative to the styrene aromatic C–H stretch ($700 \, cm^{-1}$) [7,21].

The differences in the conversion profiles can be explained by the reactivity ratios. Reactivity ratios are a measure of the ratio of the likelihood of one component polymerizing with itself vs. the other component (Eq. (4)):

$$r_1 = k_{11}/k_{12} \quad r_2 = k_{22}/k_{21} \qquad (4)$$

r_1 is the reactivity ratio of component 1, k_{11} is the rate constant for propagation of a radical of type 1 with a monomer of type 1, and k_{12} is the rate constant for propagation of a radical of type 1 with a monomer of type 2.

When $r_1 = 0$, component 1 will only polymerize with monomer 2. When $r_1 = 1$, a radical of component 1 is equally likely to polymerize with either monomer. As $r_1 \rightarrow \infty$, radicals of component 1 will only polymerize with monomer 1. Reactivity ratios were calculated using the Mayo–Lewis and the Fineman–Ross methods [26]. The results were similar for both methods and were averaged to remove the effect of the calculation method.

2.5. Polymer properties

The thermo-mechanical properties of vinyl esters were measured using dynamic mechanical analysis (DMA). Rectangular samples with approximate dimensions of $25 \times 9 \times 3 \, mm^3$ were tested using a TA Instruments 2980 DMA in single cantilever geometry. The samples were tested at 1 Hz with a deflection of 15 μm while ramping the temperature from 30 to 200 °C at a rate of 5 °C/min. Three temperature ramp experiments were run for each sample. The first ramp completely post-cured the polymer, as verified using near-FTIR. Near-FTIR was performed using a Thermo Nicolet Nexus 670 FTIR in transmission mode, taking 32 scans per spectrum between 4000 and 8000 cm^{-1} with a resolution of 8 cm^{-1}. The FTIR experiments showed that the relative height of the vinyl group at 6160 cm^{-1} did not change after the first temperature ramp. Furthermore, the DMA traces for the second and third ramps were nearly identical, showing that the resulting polymers are thermally stable at least for limited durations up to 200 °C.

The temperature at which the peak in the loss modulus occurred in the fully post-cured polymer was considered the glass transition temperature of the material [27]. The experimental error in T_g was ± 3 °C. The point at which the modulus in the rubbery plateau began to increase with increasing temperature was used to calculate the molecular weight between cross-links, M_c. The theory of Rubber Elasticity was used to calculate M_c (Eq. (5)):

$$E = 3RT\rho/M_c \qquad (5)$$

E is the rubbery modulus, R is the ideal gas constant, T is the absolute temperature, and ρ is the sample density [28,29]. Rubber elasticity applies to polymers with low cross-link densities and would not be expected to give completely accurate cross-link density measurements for highly cross-linked vinyl ester systems. However, the calculated numbers are on the correct order of magnitude based on cross-link density calculations [3] and provide a means for comparing and quantifying whether one sample is more cross-linked than another.

Flexural tests, in accordance with ASTM 790M, were performed to determine the modulus of elasticity and flexural strength [30]. The samples had approximate dimensions of $10 \times 80 \times 64 \, mm^3$ and were measured prior to testing. The samples were tested flat-wise on a support span, resulting in a support-to-depth ratio of 16. All tests

were performed at ambient conditions, which were approximately 22 °C and 40% relative humidity. The samples were tested using an Instron at a crosshead speed of 0.17 mm/min. The flexural modulus, elongation at failure, and flexural strength were calculated according to the ASTM standard [30].

Three-point single-edge notch bend (SENB) specimens were used for fracture toughness measurements. ASTM 5045-93 specifies that approximate sample dimensions of $2.00 \times 0.50 \times 0.25$ in^3. should be used to assure plain strain conditions [31]. A notch was placed in the samples equal to half the sample depth. The actual sample dimensions were measured after testing, so that the notch length could be accurately measured. A sharp razor blade was used to initiate a crack at the base of the notch. The samples were tested using an Instron 4505 in flexural mode at a crosshead speed of 0.05 inch/min. An un-notched sample was run in the same manner twice during the course of the experiment to account for system compliance, loading pin penetration, and sample compression. All tests were performed at ambient conditions, which were approximately 22 °C and 40% relative humidity. 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.

2.6. Styrene emissions

An emissions test apparatus and methodology were developed based on the British Standard 2782, Part 4-Method 432D: Determination of Styrene Evaporation from Unsaturated Polyester Resins [32]. The apparatus consists of a small convection oven with attached mass balance to directly measure VOC mass loss in samples less than 50 g as a function of time at specified temperatures. A direct measurement technique is most applicable for sources that have a large emission rate and fast decay, especially for 'wet' materials. A Blue M Stabil-Therm gravity oven was modified by installing an electronic temperature controller (Omega Model: CN137MV-DC-AL1) to maintain specified isothermal conditions. A Mettler (Model: AE 240-S) mass balance was attached to the top of the oven and used to measure the mass as a function of time.

A steel holder, large enough to hold a sample tray, was hung from the bottom of the mass balance through a small hole in the top of the oven. The sample trays used were made of thin aluminum, with a constant diameter (70 mm) to ensure an equivalent surface area (3848.45 mm^2) for each sample during the experiment. Uninitiated and uncatalyzed liquid VE resin in the amount of 10 g was added to the sample tray and tested at 40 °C. The mass balance was connected to a central processing unit through an eight-pin serial port. A LabVIEW program was created to record mass in grams and time in seconds at specified intervals to a specified file created by the user.

As an extension of thermo gravimetric analysis (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 instrument was found to be reliable and reproducible, even more so than micro-TGA studies of the emissions from these liquid resins [8].

3. Results and discussion

3.1. Resin viscosity

Both the viscometer and rheometer showed that the viscosity of the resins did not depend on the shear rate and no shear history was observed. Therefore, the VE resins used in this work are Newtonian, non-polymeric fluids [33].

The viscosity decreased as the molecular weight of the bimodal blend decreased (Fig. 3). This result was expected because the viscosity of epoxy resins increases with the molecular weight of the monomer [15]. A decrease in the degrees of freedom of the vinyl ester monomers caused this viscosity increase with molecular weight [34]. The viscosity decreased exponentially with styrene content for all bimodal blends (Fig. 4). Styrene is a non-polar small molecule that 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 VE 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 (Fig. 3). In other words, it did not matter which bimodal blend was used (e.g. 1001F vs. 1009F); only the overall M_n of the VE monomers affected the resin viscosity. On the other hand, similar results were not found when normalizing with the weight average molecular weight. VE resins using 1001F, for example, had a different dependence on M_w than VE resins using 1004F.

For polymer melts, the viscosity depends on M_w in a power-law relationship, as shown by Rouse and Reptation theory [34]. 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 [24,34]. When using a power-law relationship to relate the VE 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) [24,34]. 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 VE resins, VE monomers interact with styrene and other vinyl ester monomers to
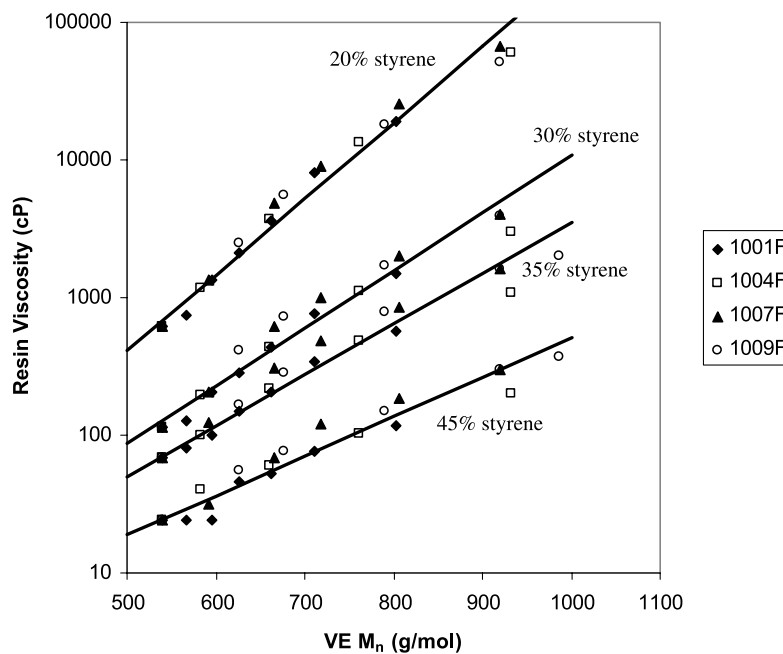
Fig. 3. The resin viscosity as a function of VE M_n for different styrene contents, showing that resin viscosity is normalized by VE M_n.

produce frictional forces. Therefore, dilute solution theory is not applicable. The physics and mathematics of concentrated solutions are not well understood [35]. 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 [36], which are considerably higher than the value of 1 Rouse theory predicts for non-entangled 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 [33,34]. 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 VE resins [34]. Furthermore, weight average molecular weights only apply to polymeric molecules, and would not apply to Newtonian VE resins. Therefore, the number average molecular weight should govern the viscosity of vinyl ester resins.

Styrene affected the resin viscosity in a consistent manner. For different VE blends with the same number average molecular weight, the resin viscosity was a single decreasing exponential function of styrene content (Fig. 4). 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 (Fig. 4). 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 (± 10 g/mol), which can affect the viscosity by as much as 15%.

The best fit lines in Fig. 3 represent a simple expression for the resin viscosity (η) as a function of number average molecular weight and styrene content. The form of this relationship is (Eq. (6)):

Fig. 4. 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.

$$\eta = \eta_{\text{styrene}} \times \exp\left[\frac{M_n}{M_e(S)}\right] \quad [\text{cP}] \qquad (6)$$

η_{styrene} is the viscosity of styrene (i.e., 0.7 cP, the viscosity when the vinyl ester molecular weight is zero) [36], and $M_e(S)$ is an effective molecular weight that is a function of
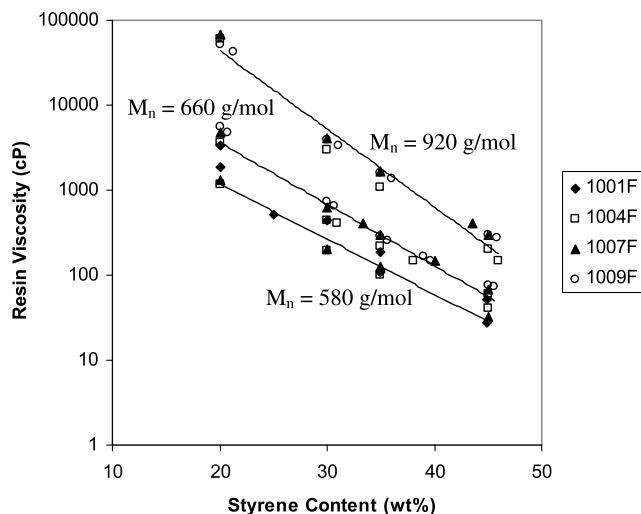
styrene content, S. The form of the relationship implies that we are modeling the effect of the addition of a more viscous, higher molecular weight species on the styrene viscosity. $M_e(S)$ is an exponential function of the styrene content (Eq. (7)):

$$M_e(S) = 46.7 \times \exp[2.63 \times S] \quad [\text{g/mol}] \tag{7}$$

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 Eq. (7). Combining Eq. (6) and (7) shows that the viscosity of bimodal blends was a predictable function of the M_n of the VE monomers and the styrene weight fraction (Eq. (8)):

$$\eta = \eta_{\text{styrene}} \times \exp\left[\frac{M_n}{46.7 \times \exp(2.63 \times S)}\right] \quad [\text{cP}] \tag{8}$$

Eq. (8) shows that resin viscosity was proportional to the exponential of the number average molecular weight and proportional 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 Fig. 4.

Interestingly, styrene's molecular weight (104 g/mol) falls right into the range of values of $M_e(S)$, which 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 Figs. 3 and 4. The numerical coefficients in Eq. (7) and (8) are fitting parameters that physically relate how well styrene can reduce the interactions among VE monomers, and represent the ratio of the pure VE viscosity to that of styrene. Rather than examining the effect of polarity, etc. $M_e(S)$ allows for an even comparison of VE molecular weight to an effective styrene molecular weight. In other words, at high styrene concentrations, the VE monomers would need to have at least a molecular weight on the order of 650 g/mol for small changes in styrene content to have a significant effect on the viscosity. Because VE monomers are more polar in nature than styrene, the value of $M_e(S)$ at low styrene concentrations was less than the molecular weight of pure styrene. This means that hypothetical VE 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 [1,37]. Eq. (8) 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 VE monomers. For example, to formulate a resin with only 30 wt% styrene, an M_n of 675 g/mol can be achieved by blending as much as 78 wt% VE 828 with 22 wt% VE 1009F or as little as 62 wt% VE 828 with 38 wt% 1001F. In addition, solving Eq. (8) shows that a minimum styrene content of 20 wt% is necessary for the lowest molecular weight DGEBA-based VE (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 wt% styrene in VE resins).

3.2. Cure kinetics

Commercial vinyl ester polymers have a microgel morphology [1,5,7]. Microgels are highly cross-linked phase-separated regions of the polymer. These occur when vinyl ester monomers react to a high degree with themselves to produce highly cross-linked regions. It was found that the sizes of the microgel regions depended on the reactivity ratios and cure temperature [1,5,7]. At low cure temperatures, the microgel regions were large and $r_{\text{VE}} > 1$ while $r_{\text{styrene}} < 1$ [5]. At high cure temperatures, the microgel regions were small and the reactivity ratio of each component was ∼0.5 [5]. Therefore, it was concluded that microgel morphology was affected by the reactivity ratio of the polymers, and microgels were more prominent as the reactivity of the VE monomer increased relative to the reactivity of styrene [5]. Furthermore, it was found that the fracture toughness of these polymers increased as the size of the microgel regions increased [5].

The conversion profiles of the VE 828, VE 834, VE 836, and the commercial resins were similar, but the cure of bimodal blends was significantly different. Fig. 5 shows the conversion as a function of time at 30 °C for monodisperse VE 828 and bimodal blends, respectively. There were a few differences between the conversion profiles. First, the extent of cure of the vinyl ester monomers was always lower in the bimodal blend for identical styrene contents. Also, varying the styrene content had more effect on the styrene conversion in VE 828. Lastly, the bimodal resin cured more slowly than the other resins, which was likely due to the extra inhibitor added during the preparation of bimodal resins. On the other hand, when cured at 90 °C, the cure rates of the bimodal and other resins were comparable.

Cure of the bimodal blends was affected for resins containing different styrene contents. The extent of cure of styrene monomer was higher but the VE monomer extent of cure was lower in the resin containing low styrene contents. For example, in VE 828/1004F 43/57, the final conversion of styrene at 30 °C increased from 0.61 to 0.65, while the VE conversion decreased from 0.52 to 0.49 as the styrene content was decreased from 50 to 35 wt%. It is well known
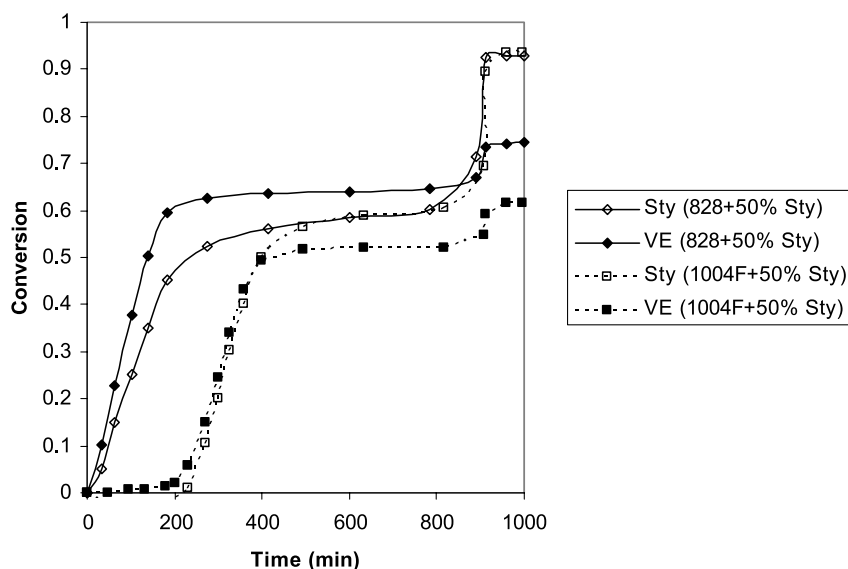
Fig. 5. The component cure profiles of VE 828 + 50 wt% styrene relative to a representative bimodal blend (VE 828/1004F 43/57 + 50 wt% styrene).

that styrene facilitates the cure of vinyl ester, a major reason for styrene's wider use in these resins over methyl methacrylate. This indicates that bimodal blends with low styrene contents should have lower than expected cross-link densities based on the cure of high styrene content-resins.

The sudden increase in conversion in Fig. 5 at ∼900 min is due to post-cure at 120 °C. The conversion of both monomers increased very fast, although the styrene conversion increased more than the vinyl ester monomers because of styrene's high mobility. Again, the final vinyl ester monomer conversion was lower in the bimodal resins, indicating that these resins should have lower cross-link densities than expected based on the cure of monodisperse resins. Also, the styrene conversion was higher for resins with lower styrene contents.

The reactivity ratios for these systems are listed in Table 3. All of the measured reactivity ratios were below 1, meaning that the initial polymer formed had a propensity to be alternating in nature (i.e. VE prefers to polymerize with

styrene and styrene prefers to polymerize with VE). The reactivity ratios of vinyl ester and styrene became more similar as the cure temperature increased. This indicates that the microgels decreased in size as cure temperature increased, as was found in the literature [5]. At both temperatures tested, the reactivity ratio of the vinyl ester was near zero for the bimodal blends, while it was higher for styrene. Furthermore, the reactivity ratio of vinyl ester was lower and the styrene reactivity ratio was relatively higher in the bimodal blends relative to the monodisperse and commercial resins. The added inhibitor during the preparation of the bimodal blends did not cause this effect because cure studies of VE 828 and VE 834, synthesized using 1000 ppm hydroquinone, indicated that the reactivity ratios were unaffected by the presence of the hydroquinone.

According to the reactivity ratios, the initial polymers formed of the bimodal resins should have a higher percentage of styrene and a lower percentage of vinyl ester than the monodisperse and commercial resins. We would therefore expect these bimodal resins to have small microgels. We cannot automatically assume there will be a reduction in the fracture toughness due to decreased microgel size because the cross-link density decreased for the bimodal blends, which should improve the fracture toughness via matrix toughening [9]. Furthermore, a direct measurement of the size of the microgels in bimodal blends has yet to be done.

3.3. Polymer properties

Fig. 6 shows the storage modulus and loss modulus as a function of temperature for VE 828 and a bimodal blend. DMA results indicated that phase separation did not occur as there was only one loss modulus peak for each sample. However, the width of the glass transition region width did

Table 3
The reactivity ratios of vinyl ester and styrene for monodisperse VE resins, bimodal resins, and commercial resins

Resin type	Cure tempera-ture (°C)	r_{VE}	$r_{styrene}$
VE 828, 834, 836	30	0.6 ± 0.1	0.4 ± 0.1
Bimodal	30	0.1 ± 0.1	0.6 ± 0.1
Derakane 411-C50 [5]	30	1.54 ± 0.02	0.45 ± 0.00
VE 828, 834, 836	90	0.3 ± 0.1	0.3 ± 0.1
Bimodal	90	0 ± 0.1	0.3 ± 0.1
Derakane 411-C50 [5]	90	0.61 ± 0.1	0.47 ± 0.01

These reactivity ratios do not represent intrinsic rates, but instead represent the actual cure reaction that is occuring.
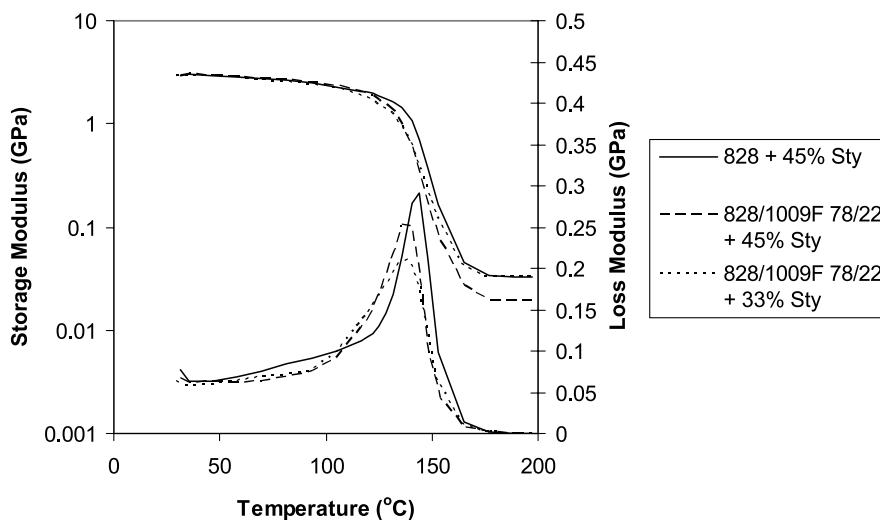
Fig. 6. The storage modulus (monotonically decreasing) and loss modulus (maximum) of VE 828 + 45 wt% styrene and representative bimodal blends of VE 828/1009F 78/22 with 33 and 45 wt% styrene.

increase as the disparity in molecular weights of the two components increased (Fig. 6). This indicates that micro-phase separation may have occurred in these resins. As was expected, the glass transition width also increased as the styrene content decreased [1]. The temperature at which the loss modulus peak occurred shifted depending on VE M_n and styrene content. The values of the storage modulus at room temperature were within experimental error. Other-wise, the appearance of the DMA traces were unaffected by the bimodal blend.

Dynamic mechanical properties were affected by the molecular weight of the bimodal blends and the styrene content. In general, as the number average molecular weight of the bimodal resin increased, T_g decreased because M_c increased (Fig. 7). In general, samples with the same M_n and styrene content had T_g within 3 °C of each other, which is within experimental error. In fact, bimodal resins with M_n of
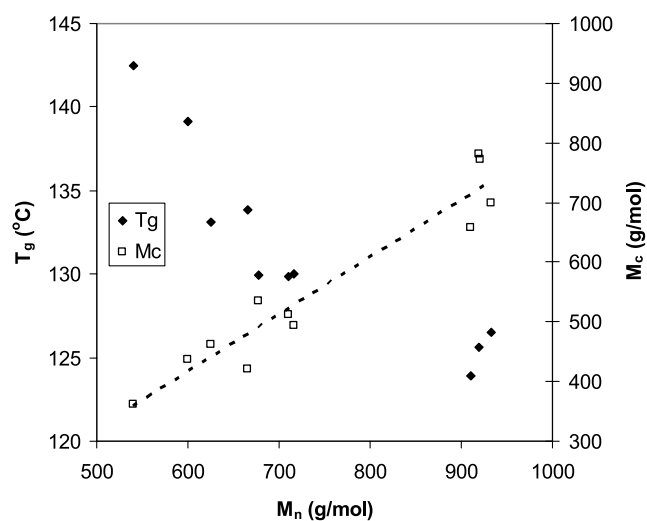

Fig. 7. T_g and M_c as a function of M_n for bimodal VE blends with 45 wt% styrene.

~ 910 g/mol had T_g very similar to that of Derakane 411–350 (~ 125 °C). As the molecular weight of the resin increased, the distance between cross-links increased causing the network to become less rigid. However, the effect of bimodal blend molecular weight on polymer properties was fairly small, as T_g decreased only from 142 to 125 °C as M_n increased from 540 g/mol to 950 g/mol. For the same reasons, T_g decreased and M_c increased as the styrene content increased (Fig. 8). As M_n increased, the effect of styrene content on T_g was less pronounced. This indicates that T_g of pure VE with no styrene is a stronger function of VE molecular weight than at 45 wt% styrene. As shown by the Fox equation [38] and other equations relating T_g of a blend to that of its components, the blend T_g is always greater than that of the lower T_g component. As the styrene content increased and T_g of 100 °C (i.e. T_g of styrene) [39] was approached, the effect of increasing styrene content decreased. Overall, the results show that bimodal blends can be used to achieve T_g values higher than that of Derakane 411–350. T_g and M_c were not functions of M_w. The storage modulus was not significantly affected by the molecular weight of the VE monomers or the styrene content.

The flexural strength and modulus were not significantly affected by the styrene content and vinyl ester molecular weight. The flexural strength was 130 MPa ± 5 MPa and the flexural modulus was 3.5 ± 0.2 GPa for all samples, including the commercial resins. Because the chemical nature of styrene and the high and low molecular weight vinyl esters are similar, the flexural properties were expected to remain constant. Therefore, bimodal blends of vinyl esters produce resins with similar modulus and strength relative to commercial resins.

The fracture toughness increased with the number average molecular weight of the vinyl esters (Fig. 9) because of matrix toughening [9]. Fracture toughness
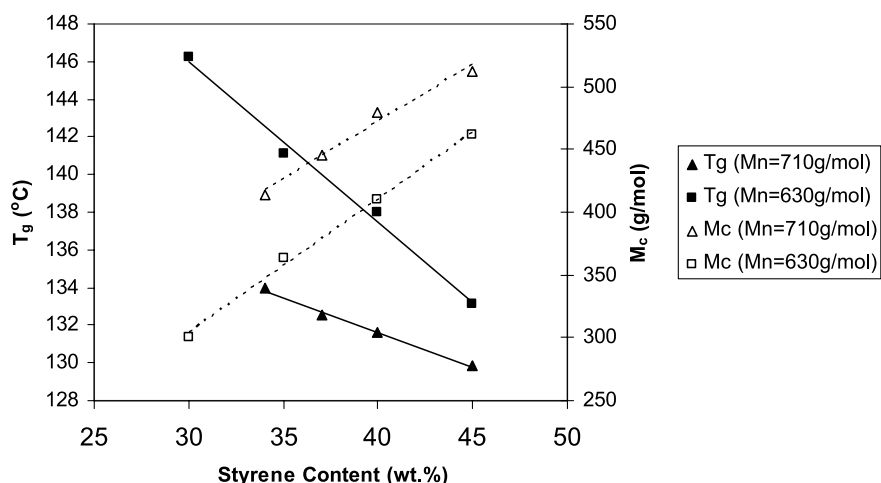
Fig. 8. T_g and M_c as a function of styrene content for VE 828/1001F 48/52 ($M_n = 710$ g/mol) and VE 828/1009F 84.9/15.1 ($M_n = 630$ g/mol).

increased linearly at low values of M_n but then leveled off at values of M_n greater than 800 g/mol. G_{IC} of the commercial resins were considerably lower than that of the bimodal blends with the same molecular weight. Therefore, bimodal blends of vinyl esters can be used to improve fracture properties. However, the fracture properties of VE 834 and VE 836 were within experimental error of the bimodal blends. This indicates that other factors may be influencing the fracture properties of these resins. Styrene content did not have a significant effect on the fracture properties (Fig. 9). Therefore, low VOC vinyl esters can be prepared using bimodal blends of vinyl esters while having excellent fracture properties.

There are a number of possible reasons why the low VOC bimodal resins had better than expected fracture properties.

First, the results indicated that the morphology of the vinyl esters was different in the bimodal blends relative to monodisperse and commercial resins. In addition, the cross-link density was lower for bimodal blends relative to commercial resins. Although increasing the styrene content results in lower cross-link densities, the fracture properties need not increase. Cure studies showed that the extent of cure, and therefore the network strength, was affected by the styrene content. Lastly, polystyrene zones, which were more likely to occur in resins with high styrene contents, are brittle and should reduce the fracture properties [5]. Hydroquinone did not have a significant effect on fracture toughness, as VE 828, VE 834, and Derakane resins with added hydroquinone (1000 ppm) had similar fracture properties.
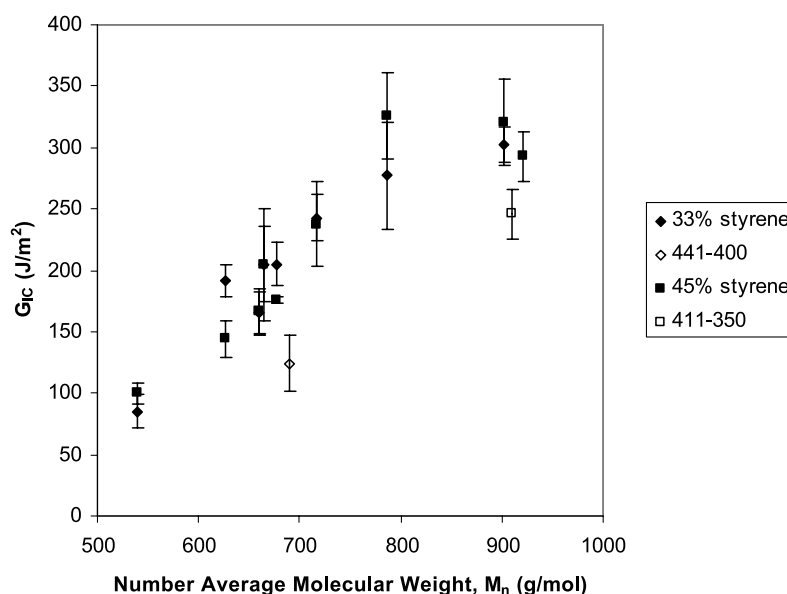

Fig. 9. Fracture toughness as a function of vinyl ester number average molecular weight for VE 828, 834, 836, bimodal, and Derakane resins containing 33 and 45 wt% styrene.

3.4. Styrene emissions

EPA guidelines show that VOC emissions can be reduced from composite resins simply by reducing the volatile content in the resin (i.e., styrene content) [4]. To prove that styrene emissions can be reduced using bimodal blends of vinyl esters, the styrene emissions from these resins were measured as a function of styrene content and vinyl ester molecular weight. During early stages of the emission process (<6 h), the styrene emission rate was high and was linear with time (Fig. 10). After the initial linear emission region, the styrene emission rate decreased. At long times, the styrene emission rate dropped to near zero, even for samples with substantial styrene contents remaining (Fig. 10). This implies that VE systems which contain a lower percentage of styrene will have lower initial emission rates, as is also shown Fig. 10. However, when the resin mass is normalized by the styrene content, the initial emission rate was the same regardless of the styrene content or vinyl ester M_n. Yet, the emission rates decreased sooner and the overall emissions were lower for samples with higher VE M_n. This occurred because the viscosity was greater for the higher molecular weight samples, reducing the mobility of styrene in the resin and limiting its ability to diffuse to the surface. For resins with the same styrene content and vinyl ester M_n, regardless of which bimodal blend was used (i.e. 828/1001F or 828/1009F), the emission profiles were the same (Fig. 10). Therefore, emissions from vinyl ester resins can be reduced by using higher VE M_n and lower styrene contents, such as in bimodal blends.

The reported emission results are for uninitiated and uncatalyzed liquid resins that do not polymerize during the course of the experiment. The cure time of VE resins (typically <2 h) is within the linear portion of the emissions profile. The emission profiles of curing samples thus only depend on the styrene content, which only affects the initial emission rate. As Fig. 10 shows, resins with lower styrene

contents, again such as bimodal resins, will produce less styrene emissions. Analysis of styrene emissions from resins during cure will be examined in a future publication.

4. Conclusions

Bimodal VE blends were prepared using styrene as a solvent to help dissolve the high molecular weight epoxy monomers along with the addition of hydroquinone to inhibit polymerization. The viscosity of the bimodal blend increased exponentially as the styrene content decreased and VE molecular weight increased. Furthermore, the number average, rather than the weight average, molecular weight of the bimodal VE governed the resin viscosity. An empirical model was developed that allowed determination of the resin viscosity solely based on the VE M_n and styrene content. Polymer properties were affected by the VE molecular weight. T_g decreased slightly as M_n of the bimodal blend increased and as the styrene content increased because the molecular weight between cross-links increased. Cure kinetics results indicated that bimodal blends of vinyl esters had a different morphology than monodisperse vinyl ester resins. The fracture toughness increased with VE M_n but was not affected by styrene content. Emissions results proved that decreasing the styrene content reduced VOC emissions and showed that bimodal blends are useful in reducing overall emissions. Therefore, bimodal blends of vinyl ester monomers can be prepared with low resin viscosities with improved fracture toughness while using lower styrene contents than commercial resins.
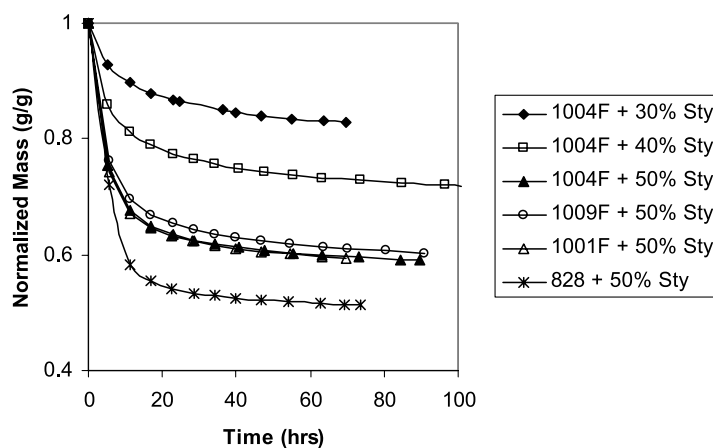
Fig. 10. The emissions profiles for uninitiated resins as a function of time showing that resins with decreasing styrene content and increasing M_n decreased the styrene emissions. 1004F resins are VE 828/1004F 43/57 with $M_n=921$ g/mol. 1001F resin is VE 828/1001F 29/71 with $M_n=902$ g/mol. 1009F resin is VE 828/1009F 54/46 with $M_n=920$ g/mol.

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