Emission and Mechanical Evaluations of Vinyl-Ester Resin Systems

by James M. Sands, Chad A. Ulven, and Uday K. Vaidya

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Emission and Mechanical Evaluations of Vinyl-Ester Resin Systems

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1. Introduction

Vinyl-ester (VE) resins are frequently used in liquid molding of composite materials for several applications including naval and army structures, commercial boat manufacturing, and building construction. Currently, commercially available VEs contain a hazardous styrene monomer, a reactive diluent, which allows liquid molding of VE and provides linear chain extension during cure. The styrene monomer is released during mixing, processing, curing, and service life of the VEs. As federal emission standards continue to regulate the release of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs), alternatives or modifications to VEs must be ascertained.

Currently, steps are being taken towards developing low-cost, alternative composite resin systems comprised of lower VOC monomer concentrations. These resin systems will prove an effective means to reduce or eliminate VOC release during processing, service life, or repair of composite structures. These efforts will provide an environmentally preferred composite resin system applicable for liquid molding techniques.

In the current study, commercially available VEs are tested for both emissions and mechanical properties to act as a baseline for comparing VEs being developed. VEs cure via free radical bulk copolymerization. Several processing parameters control the curing kinetics, network structure, and total conversion of VEs, which, in turn, effect total emissions and mechanical properties. These parameters include initiator/catalyst concentration, temperature, styrene concentration, glass fiber sizing, and processing conditions. An extensive literature search was implemented to determine proper parameters needed to process VE composite materials with vacuum-assisted resin transfer molding (VARTM).

Several studies sought to determine characteristics and cure kinetics of VEs while controlling certain processing parameters. These studies employed experimental methods such as differential scanning calorimetry, Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and dynamic mechanical thermal analysis to evaluate VEs. Mathematical models were also implemented to approximate the rate of polymerization.

These studies infer that certain processing parameters must be manipulated in order to process VEs/glass fiber composites with infusion technology at room temperature. Decreasing concentrations and manipulating ratios of initiator and catalyst can increase gel times and effect total conversion [1–5]. By increasing the amount of styrene, the viscosity decreases, yet reaction rates increase [2, 6–8]. An increase in VE molecular weight results in higher toughness yet increases viscosity [7]. An inhibitor can be added to increase gel time of VEs [3, 9]. Room-temperature cured VEs will have lower glass transition temperatures (T_g) resulting from a low final degree of reaction [1, 3, 10]. Low degree of reaction can be remedied with postcuring at
temperatures slightly above the T_g [2, 9]. The type of fiber sizing used strongly influences the cure kinetics along with the mechanical and thermal properties of the composite [11, 12]. Considering these parameters, processing with VARTM is easily accomplished.

In the past, emission of styrene during processing has received little attention. Due to growing concern from the U.S. Environmental Protection Agency, restrictions have been issued to decrease the release of VOCs and HAPs by composite manufacturers [13]. Measurement of styrene emissions during processing can be accomplished using several different techniques. Luong and Walewski [14] developed a procedure for evaluating low styrene emission resins that has generally been accepted as a standard in the industry. A British standard [15] has also been established as a mass emission test.

In this study, emission of styrene is measured using gravimetric analysis in a controlled environment. In order to understand and predict the rate of styrene emission from VEs, classic diffusion models are consulted [16, 17]. The diffusion coefficients of styrene in certain commercial VEs are determined from these diffusion models.

2. Experimental Procedure

2.1 Mass-Loss Measurement

2.1.1 TGA

Thermogravimetric analysis (TGA) was used to measure microscale sample weight loss (<40 mg) in the VEs as a function of time, initial mass, and temperature under a controlled atmosphere. A TA Instruments model TGA-2950 hi-resolution thermogravimetric analyzer was used to carry out each microscale mass-loss experiment. To create isothermal conditions, temperature was held constant for each run. Three types of studies were conducted using TGA with different VEs. One study varied the initial mass of each sample while the same temperature was used for each run. In the second study, the temperature was changed for each run while maintaining the equivalent initial mass for each sample. In the third study, the temperature and initial mass were maintained while using VEs with different concentrations of styrene.

Each VE sample was dispensed in an Omnitherm 1021 pan with the intent to maintain a constant surface area of 32 mm² throughout the multiple experiments. The empty pans in the TGA were equilibrated before each run, ensuring that the mass of each sample was precisely measured. A simple program was created in the TA Instruments software to ramp the temperature of each sample from room temperature to isothermal equilibrium in 4 min for each run. Preliminary studies indicated that due to the overshoot associated with a faster ramp rate, a ramp rate of 4 min was critical to maintain during each run in the TGA. Samples were purged with a constant
60 mL/min of nitrogen during each run. Results were written to a spreadsheet file and analyzed using Microsoft Excel. Mass-loss measurements were recorded in milligrams.

2.1.2 Macroscale Mass Loss

A mass balance/oven apparatus was engineered to accommodate measurements of macroscale sample weight loss (1 g < x < 50 g) in the VEs as a function of time, initial mass, and temperature under a controlled atmosphere. A Mettler AE 240-S mass balance was used in conjunction with a modified Blue M Stabil-Therm gravity oven to carry out each experiment. The two TGA studies previously explained were also carried out with the macroscale mass measurement apparatus.

An aluminum holder, large enough to hold a sample tray, was hung from the bottom of the mass balance through a hole into the oven. The sample trays used were made of thin aluminum, with a constant diameter to ensure an equivalent surface area of 3765 mm$^2$ for each sample during the experiment. The mass balance was connected to a central processing unit through an eight-pin serial port. A LabVIEW program was created to record mass and time at specified intervals to a specified file created by the user. For each run, temperature was held constant to create isothermal conditions. Mass-loss measurements were recorded in grams.

2.2 DMA

Dynamic mechanical analysis (DMA) was used to measure the $T_g$ and mechanical properties of the VEs as a function of time, temperature, and frequency. A TA Instruments model 2980 dynamic mechanical analyzer was used to carry out each experiment. Neat VE samples were cast and tested in DMA. Cast specimen dimensions were 20 mm long, 11.5–12.6 mm wide, and 2.2–3.4 mm thick. A simple program was created in the TA Instruments software to equilibrate each sample at 40 °C and ramp the temperature of each sample 5 °C/min up to 175 °C while maintaining a dynamic amplitude of 5 μm. Each specimen was tested twice to ensure final conversion. Results for each specimen were denoted as first heat and second heat accordingly. Storage and loss modulus measurements were recorded in megapascal.

2.3 Brookfield Viscometer

A Brookfield viscometer was used to measure the viscosity of various VEs as a function of speed and temperature. A Brookfield CAP 2000 viscometer with CAPCALC software was used to carry out each experiment. The viscometer was used with a plate and cone at 60 Hz. Temperature was varied between 25° and 45 °C for each VE. Speed was varied between 50 and 150 rpm for each VE. Specimens of 67 µL were required to wet out the area between the cone and plate. Viscosity measurements were recorded in centipoise.
3. Processing

3.1 VEs

Table 1 shows the types of VEs used in this study. The Styrid product indicated in this table is a styrene emission suppressant. Derakane 510A-40 was mixed with 1.0 weight-percent of Styrid. Each VE was cured using the same initiator and catalyst, with concentrations adjusted for the processing temperature and required gel time. The type of initiator used was Trigonox 239 A, produced by Akzo Nobel. This initiator contained 45% cumyl hydroperoxide, 45% carboxylic ester, and 10% cumyl acid. The concentration of initiator used in the various VEs ranged from 1 to 2 weight-percent. Cobalt napthenate (CoNap), containing 6% cobalt, was used as the catalyst. The concentration of catalyst used in the various VEs ranged from 0.1 to 0.2 weight-percent.

Table 1. VEs used for processing.

<table>
<thead>
<tr>
<th>Company</th>
<th>Resin Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dow Chemical</td>
<td>Derakane 411-45</td>
</tr>
<tr>
<td>Dow Chemical</td>
<td>Derakane 510A-40</td>
</tr>
<tr>
<td>Dow Chemical</td>
<td>Derakane 441-400</td>
</tr>
<tr>
<td>Verdant Technologies</td>
<td>Verdant Infusion VE</td>
</tr>
<tr>
<td>Specialty Products Co.</td>
<td>Styrid used w/Derakane 510A-40</td>
</tr>
</tbody>
</table>

3.2 Neat Resin Plaques

Neat resin plaques were cast using aluminum molds at room temperature. Molds were coated with Dexter Frekote 700-NC release agent. Four differently shaped molds created DMA, three-point bend, fracture toughness, and tensile specimens. Table 2 shows the types of VEs cast for subsequent tests. Concentrations of initiator and catalyst were selected such that each system exhibited a gel time of 40–60 min.

Table 2. VEs cast test specimens.

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>DMA</th>
<th>Three-Point Bend</th>
<th>Tensile</th>
<th>Fracture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Derakane 411-45</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Derakane 510A-40</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Derakane 441-400</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Verdant Infusion VE</td>
<td>X</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Derakane 510A-40 w/Styrid</td>
<td>X</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

3.3 Composite Panels

Composite panels were processed using VARTM at room temperature. VARTM is of interest in low-cost processing as it uses one-sided tooling and vacuum bag technology. Large structural
parts with high-fiber volume fractions (50%-60%) can be produced rapidly using VARTM. Another advantage of VARTM is good process repeatability and low/controlled volatile emissions during processing.

The fiber used in the manufacturing of composite panels, shown in Figure 1, was a Burlington Glass Fabrics Industries plain-woven E-glass (16,700 kg/m$^3$, 0.3912 mm, 16 × 14 count) with all-purpose organically bound silanes sizing.

![Figure 1. Plain-woven E-glass fabric.](image)

Table 3 shows the VE/E-glass composite panels processed and their dimensions. Concentrations of initiator and catalyst were selected such that each system exhibited a gel time of 40–60 min. The composite panels completely solidified in 120–180 min for each of the VEs.

Table 3. Specifications for composite panels.

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Fiber</th>
<th>Layers</th>
<th>Thickness (mm)</th>
<th>L × W (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Derakane 411-45</td>
<td>E-glass</td>
<td>16</td>
<td>6.4</td>
<td>300 × 300</td>
</tr>
<tr>
<td>Derakane 510A-40</td>
<td>E-glass</td>
<td>16</td>
<td>6.4</td>
<td>300 × 300</td>
</tr>
<tr>
<td>Derakane 441-400</td>
<td>E-glass</td>
<td>16</td>
<td>6.4</td>
<td>300 × 300</td>
</tr>
</tbody>
</table>

4. Results and Discussion

4.1 Mass-Loss Measurement Results

In both the macroscale and microscale mass-loss experiments, styrene was assumed the only diffusing material causing mass loss in the VEs tested. The molecular weight of the vinyl-ester monomer (>520 g/mol) was significantly greater, and the vapor pressure was significantly lower than that of the styrene monomer (104 g/mol, 12.4 mm/hg at 37 °C). Because of a low molecular weight and a high vapor pressure, the styrene monomer was allowed to move easily around the vinyl-ester monomer, which led to the ease of diffusion through the VEs.
The initial linear slope in each figure was considered the short-time mass loss in the system, which dominated the total mass loss observed in the VEs tested. The slow exponentially decreasing slope in each figure was considered the long-time mass loss in the system and contributed much less to the total loss observed.

The characteristic elbow observed in each of the mass-loss trends was considered the transition between the short-time and the long-time mass loss in each system. At the point of transition, the rate at which the styrene diffused from the VEs began to decrease exponentially. If data was collected for an infinite amount of time, the concentration of styrene would eventually reach equilibrium with the VE, and the slope of the long-time mass loss would be zero, as diffusion would cease.

The short-time (high percentage) total mass loss was found to be a function of time, temperature, initial weight percentage of styrene, and total initial mass of the VEs. The short-time (high percentage) rate of mass loss was found to be a function of time, temperature, and total initial mass of the VEs. The long-time (low percentage) total mass loss was negligible in comparison to the short-time total mass loss. The long-time rate of mass loss for each VE became a function of time only. The calculated rate of mass loss was normalized for each VE tested.

### 4.1.1 Mass-Dependent Emissions

Macroscale mass-loss experiments were performed using the mass balance/oven apparatus explained previously. Samples of 4.46, 6.69, 8.92, and 11.15 g were suspended from the bottom of the balance, inside the oven, at isothermal 60 °C conditions. The percentage of mass loss plotted vs. the square root of time for Derakane 411-45 and Derakane 510A-40 are shown in Figures 2 and 3.

Both VEs tested illustrated a short-time mass loss followed by a transitional elbow, continuing into a long-time exponentially decreasing mass loss. These characteristic curves were separated only by the initial mass.

Table 4 shows the rate of mass loss for each VE tested at 60 °C. The short-time rates of mass loss reported in Table 4 were derived from a linear fit to the percentage of mass loss vs. square root of time. As the total initial mass of the sample increased, the short-time rate of mass loss decreased.

For Derakane 411-45, the 6.69-, 8.92-, and 11.15-g samples exhibited decreased rates of mass loss 18%, 28%, and 35% lower than that of the 4.46-g sample, respectively. For Derakane 510A-40, the 6.69-, 8.92-, and 11.15-g samples exhibited decreased rates of mass loss 13%, 28%, and 34% lower than that of the 4.46-g sample, respectively. These findings proved that initial total mass influenced the total amount of emissions and the rate of emissions from VEs.
4.1.2 Temperature-Dependent Emissions

For comparison purposes between the results of the microscale and macroscale temperature experiments, the ratio of initial mass to surface area was maintained for both scales of samples.

4.1.2.1 TGA

Microscale mass-loss temperature experiments were performed using the TGA previously indicated. Samples with an initial mass of 38 mg were dispensed in aluminum pans, immediately placed inside the microbalance, and measured in isothermal conditions at temperatures of 30°, 40°, 50°, 60°, and 70°C. The percentage of mass loss plotted vs. the square root of time for Derakane 411-45 is shown in Figure 4.

The trends plotted for the mass loss in the TGA experiments changed as the temperature increased. The transition from short- to long-time mass loss for the samples held at 60° and 70°C occurred much earlier than the samples run at lower temperatures. This phenomenon may be attributed to the shape of the meniscus formed by the resin in the pan or simply an inconsistency in the microbalance measurements. Further investigation of this occurrence must be pursued.
Figure 3. Mass loss of Derakane 510A-40 at 60 °C.

Table 4. VE's rate of mass loss at 60 °C.

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Temperature (°C)</th>
<th>Mass (g)</th>
<th>Rate (%/t^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Derakane 411-45</td>
<td>60</td>
<td>4.46</td>
<td>0.567</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.69</td>
<td>0.463</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.92</td>
<td>0.409</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.15</td>
<td>0.368</td>
</tr>
<tr>
<td>Derakane 510A-45</td>
<td>60</td>
<td>4.46</td>
<td>0.495</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.69</td>
<td>0.429</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.92</td>
<td>0.358</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.15</td>
<td>0.325</td>
</tr>
</tbody>
</table>
Figure 4. Mass loss of Derakane 411-45 at 38 mg.

Table 5 shows the rate of mass loss for Derakane 411-45 tested at five isothermal temperatures. As the temperature of the sample increased, the short-time rate of mass loss increased. For Derakane 411-45, the 40°C, 50°C, 60°C, and 70°C samples exhibited increased rates of mass loss 37%, 90%, 127%, and 215% higher than that of the 30°C sample, respectively.

Table 5. Derakane 411-45 rate of mass loss at 38 mg.

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Mass (mg)</th>
<th>Temperature (°C)</th>
<th>Rate (% / t^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Derakane 411-45</td>
<td>38</td>
<td>30</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>1.64</td>
</tr>
</tbody>
</table>
4.1.2.2 Macroscale Mass Loss

Macroscale mass-loss experiments were conducted with Derakane 411-45, maintaining an initial mass of 4.46 g at isothermal temperatures of 30°, 40°, 50°, 60°, and 70 °C. The percentage of mass loss plotted vs. the square root of time for Derakane 411-45 is shown in Figure 5.

![Image of a graph showing mass loss percentage over time for different temperatures](image)

Figure 5. Mass loss of Derakane 411-45 at 4.46 g.

Unlike the microscale experiments, the trends plotted for mass loss in the macroscale experiments retained the same shape as the isothermal temperatures increased. The difference in trends may be attributed to isothermal conditions preexisting in the macroscale experiments before the samples were placed in the oven and isothermal conditions being reached in the microscale experiments after the samples were placed in the oven.

Table 6 shows the rate of mass loss for Derakane 411-45 tested at five isothermal temperatures. As the temperature of the sample increased, the short-time rate of mass loss increased. For Derakane 411-45, the 40°, 50°, 60°, and 70 °C samples exhibited increased rates of mass loss 45%, 104%, 148%, and 214% higher than that of the 30 °C sample, respectively.
Table 6. Derakane 411-45 rate of mass loss at 4.46 g.

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Mass (g)</th>
<th>Temperature (°C)</th>
<th>Rate (% / t^1/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Derakane 411-45</td>
<td>4.46</td>
<td>30</td>
<td>0.229</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>0.333</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>0.467</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>0.567</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>0.718</td>
</tr>
</tbody>
</table>

4.1.3 Styrene-Dependent Emissions

Microscale and macroscale mass-loss experiments were performed for Derakane 411-45 and Derakane 510A-40, maintaining constant initial mass and isothermal temperature. These experiments were conducted to show the effect of styrene concentration on mass loss in each of the VEs. From the Dow Company data sheets, the initial concentration of styrene for Derakane 411-45 was ~45 weight-percent and 40 weight-percent for Derakane 510A-40.

4.1.3.1 TGA

Microscale mass-loss styrene concentration experiments were performed using 17 mg of Derakane 411-45 and Derakane 510 at an isothermal temperature of 40 °C. The true mass loss plotted vs. the square root of time for the two VEs is shown in Figure 6.

It can be seen from Figure 6 that the short-time and long-time decreasing slopes at which styrene diffuses from the VEs was nearly identical for the two Derakane resins. The actual short-time rates of mass loss only deviated by 18% between the two resin systems. This was a negligible percentage difference when compared to the influence of temperature and mass. Such insignificant deviations can be attributed to the accuracy of the initial mass dispensed and any slight variation in the microbalance equipment.

4.1.3.2 Macroscale Mass Loss

Macroscale mass-loss styrene concentration experiments were performed using 7 g of Derakane 411-45 and Derakane 510 at an isothermal temperature of 60 °C. The true mass loss plotted vs. the square root of time for the two VEs is shown in Figure 7.

It can be seen from Figure 7 that the short-time and long-time decreasing slopes at which styrene diffuses from the VEs is nearly identical for the two Derakane resins. The actual short-time rates of mass loss only deviated by 6% between the two resin systems. This difference was even smaller than that of the small-scale TGA experiments further proving that the short-time rate of mass loss was not a function of styrene concentration. Only the total mass loss was dependent on the concentration of styrene within each VE.

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This finding becomes important when considering the design or modifications of new VEs. Since styrene diffuses through VEs at a constant rate when temperature and initial mass is fixed, a lower emission VEs would need to include a diluent that would diffuse at a slower rate or not at all.

4.1.4 Diffusion Modeling

The data collected from the mass-loss experiments just mentioned was used in the modeling of styrene diffusion through the VEs. The model used for the diffusion of styrene though VEs was the classical diffusion in a plane sheet, described by a one-dimensional continuity equation shown in equation 1.

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}.
\]  

(1)
Figure 7. Mass loss for VEIs at 7 g at 60 °C.

This model assumed that the diffusion out of the plane sheet of material was so thin that all the diffusing substance effectively left through the plane faces and a negligible amount through the edges.

For this model, initial distribution was assumed uniform, and surface concentrations were equal. This case was also described as desorption by a membrane. The initial and boundary conditions are as follows:

\[
c = c_i \quad 0 \leq x \leq h \quad t < 0, \\
\]
\[
c = c_a \quad x < 0; x > h \quad t \geq 0, \\
\]

where \(c_i\) is the initial concentration in the material, \(c_a\) is the material concentration in the atmosphere, and \(h\) is the material thickness.

The resulting complete solution for classic Fickian diffusion (equation 1) with the initial and boundary conditions previously defined in terms of mass concentration of diffusing material is shown in equation 2.
\[
\frac{M - M_t}{M_m - M_t} = 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp \left[ -(2j+1)^2 \pi^2 \left( \frac{D_t}{h^2} \right) \right]}{(2j+1)^2},
\]

where \(M\) denotes mass concentration of styrene, \(M_i\) denotes initial mass concentration of styrene, and \(M_m\) denotes mass concentration of styrene at time equal to infinity.

Since a high percentage of styrene desorbs at early experimental times, a short-time solution to equation 2 was used. At short times, the diffusion coefficient can be determined from the slope of the experimental desorption curves with equation 3.

\[
D = \pi \left( \frac{h}{4M_m} \right)^2 \left( \frac{M_2 - M_1}{\sqrt{r_2} - \sqrt{r_1}} \right)^2.
\]

The mass loss or desorption curves shown previously were characteristic of Fickian diffusion and modeled accordingly. From the analytical models, diffusion coefficients were regressed for each of the Derakane resins tested. The accuracy of these models and the resulting diffusion coefficients will become increasingly important as steps toward the design or modification of new VEs are initiated. The short-time diffusion coefficients calculated from equation 3 for the VE mass-loss data is shown for two Derakane resins in the next subsections.

4.1.4.1 Influence of Mass on Diffusion

In Figure 8, diffusion coefficients were calculated for different initial total masses of Derakane 411-45 and Derakane 510A-40 at equivalent isothermal temperatures.

The diffusion coefficients for both Derakane resin systems increased linearly with increasing initial total mass. For Derakane 411-45, the diffusion coefficient increased by 165% from the 4.46-g sample to the 11.15-g sample. For Derakane 510A-40, an increase in the diffusion coefficient of 161% from the 4.46-g sample to the 11.15-g sample was observed. Due to the large differences in diffusion coefficients from one initial total mass to another, the model used for these VEs may not accurately describe the desorption process of styrene from VE.

4.1.4.2 Influence of Temperature on Diffusion

In Figure 9, diffusion coefficients were calculated for different temperatures at two equivalent initial total masses of Derakane 411-45.

The diffusion coefficients for Derakane 411-45 increased linearly with increasing temperatures. For the 38-mg sample of Derakane 411-45, the diffusion coefficient increased by 791% from the 30 °C sample to the 70 °C sample. For the 4.46-g sample of Derakane 411-45, an increase in the diffusion coefficient of 888% from the 30 °C sample to the 70 °C sample was observed.
Figure 8. Short-term solution for mass-influenced diffusion coefficients of styrene in VEs.

Figure 9. Short-term solution for temperature-influenced diffusion coefficients of styrene in VEs.
From the results shown for both the temperature-dependent and mass-dependent diffusion coefficients, it was seen that temperature had a greater effect on the diffusion coefficient for styrene through VEs than initial total mass. However, the change in the diffusion coefficient due to change in initial total mass for the VEs was significant enough that it could not be ignored.

Further investigation of the diffusion modeling in VEs must be executed to accurately describe the desorption process of styrene from VE. As mentioned earlier, the modeling of this process will become important when comparing the emissions of commercially available VEs to newly developed VEs.

4.2 DMA Results

Dynamic mechanical analysis was used to determine two material characteristics for various VEs—glass transition temperature and storage modulus. These measurements gave insight as to how the various VEs would perform mechanically. Glass transition temperature measurements indicated the state at which rigid-to-elastic transition occurred. Storage modulus measurements depicted the amount of energy effectively stored in the material dependent on frequency. The tests were mainly used to indicate how one VE contrasts to another mechanically.

4.2.1 \( T_g \)

The glass transition temperature for each of the VEs was recorded from the peak of the loss modulus curve. The glass transition temperature was measured for three processing conditions—room-temperature cure (first heat), DMA cured at a rate of 5 °C/min up to 175 °C (second heat), and room-temperature cure followed by an oven cure at 140 °C for 1 hr. The glass transition temperature for each VE for each processing condition is represented in Figure 10.

For each of the Derakane resin systems, the glass transition temperature increased from room-temperature cured, to DMA cured, to oven cured, respectively. For the Verdant infusion resin, the glass transition temperature was less for the oven-cured sample than for the DMA-cured sample. This may be a result from polymer degradation due to overheating.

The glass transition temperatures for the Derakane resin systems were comparable. On average, the difference in glass transition temperature between each of the Derakane resins without styrene emission suppressant was 1.5%. The addition of the Styrid (styrene emission suppressant) decreased the glass transition temperature of Derakane 510A-40 by an average of 5%. The Verdant infusion resin had an average glass transition temperature 77% lower than Derakane 510A-40.

4.2.2 Storage Modulus

The storage modulus for each of the VEs was measured for two processing conditions—DMA cured (second heat) and room-temperature cure followed by an oven cure at 140 °C for 1 hr. The storage modulus for each VE for each processing condition is represented in Figure 11.
Figure 10. Glass transition temperature of VEs.

Figure 11. Storage modulus of VEs.
The storage modulus data indicated which VEs were able to store more energy when subjected to dynamic loading, which directly related to mechanical performance. On average, the specimens postcured in the DMA exhibited a 23% higher storage modulus than those oven cured. This increase in storage modulus may have been the result of a difference in degree of cure or polymer degradation from postcuring the samples at a high temperature.

Derakane 441-400 exhibited the highest storage modulus compared to the rest of the Derakane resins. When postcured in the DMA, the storage modulus of Derakane 441-400 was 22%, 25%, and 45% higher than that of the Derakane 411-45, 510A-40, and 510A-40 with Styrid, respectively.

The influence of the styrene suppressant Styrid proved to decrease the storage modulus of Derakane 510A-40 by 16% when mixed at 1.0 weight-percent. This result indicated that the use of suppressants might decrease the amount of styrene emissions but adversely affect the mechanical performance of certain VEs.

4.3 Brookfield Viscometer

The viscosity measurements obtained from a Brookfield viscometer were used to indicate which VEs could be used effectively in the VARTM process. A VE with a dynamic viscosity in the range of 100–500 cP can flow quite readily through dry fabric under high vacuum, resulting in good fiber wet-out. A VE with a viscosity higher than 500 cP may not completely wet out dry fabric preform or may require longer infusion times to achieve wet-out, thereby compromising the process. Figure 12 illustrates the viscosity measured from various VEs under different temperature and speed conditions.

The viscosity of each VE was measured at temperatures of 25°, 35°, and 45 °C and cone speeds of 50, 100, and 150 rpm. Temperature had a large influence on the dynamic viscosity of VEs. Increasing the temperature by 10–20 °C decreased the viscosity in each of the VEs represented. The reduced viscosity, caused by the increase in temperature, was low enough to easily flow in VARTM. By heating a VE, which exhibited a high viscosity at room temperature, VARTM processing could be accomplished with ease.

From the viscosity data, Derakane 411-45 was the only VE which exhibited a value drastically higher than 500 cP. A viscosity of 950 cP did not allow complete fiber wet-out in VARTM processing. The large difference in viscosity between Derakane 411-45 and the other Derakane resins was not consistent with Dow Plastics literature. This phenomenon may have been a result from long-time, room-temperature storage conditions, which further testing will clarify.
5. Conclusions

Initial tests conducted on various commercially available VEs provided a good baseline for comparing upcoming modified and new VEs exhibiting lower emissions of styrene. These preliminary tests indicated emission rates, mechanical properties, and viscosities for each of the VEs tested. The properties exhibited in these tests gave a general sense of the overall characteristics of VEs.

Mass-loss experiments indicated the amount of emissions released during the measurement and mixing of VEs as well as the mechanism of styrene diffusion. Desorption curves for the mass loss of styrene appeared Fickian in nature. Short-time diffusion models were used to calculate diffusion coefficients for Derakane 411-45 and 510A-40 as a function of temperature and initial mass. Further investigation must be conducted to verify the accuracy of these models and diffusion coefficients obtained. Further, the impact of mass variation on the diffusion is of interest for scale-up efforts. A future analysis should address this issue.

DMA experiments measured the storage modulus and glass transition temperature for each of the VEs, indicating how each would perform mechanically. From the results, Derakane 441-400 exhibited the highest storage modulus at room temperature over the rest of the VEs tested.
Derakane 510A-40 exhibited the highest glass transition temperature. The storage modulus and glass transition temperature measurements gave a general indication that Derakane 441-400 would mechanically perform better than the other VEs tested.

Viscosity experiments gave insight to the ability of VEs to be processed using VARTM. Derakane 411-C-50 exhibited the lowest viscosity at room-temperature processing conditions. Only the measured viscosity of Derakane 411-45 proved unfit for large-part VARTM processing. Continual measurement of viscosity for each of the commercially available VEs will determine long-term effects of storage in relation to processability.

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6. Ongoing Studies

Several more commercially available VEs will be obtained and tested similarly to the tests explained as a screening process. As companies continue to develop and advertise low-emission VEs, testing must be done to compare performance to VEs modified and developed in-house.

Composite processing will also continue, as more VEs are obtained. Mechanical testing will be conducted with several of the VEs/E-glass composites processed to compare performance. A complete study on the commercially available VEs will provide a benchmark for in-house modifications and developments of new VEs for a gamut of different applications.

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7. References


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14. ABSTRACT  Vinyl-ester resins (VE) are frequently used in liquid molding of composite materials for several applications including naval and army structures, commercial boat manufacturing, and building construction. Currently, commercially available VE products contain large amounts of styrene monomer, which is released as a hazardous air pollutant (HAP) during mixing, processing, curing, and fielding of VE-based composite structures. As federal emission standards continue to regulate the release of volatile organic compounds (VOCs) and HAPs, alternative low-emission reactive diluents or low-styrene concentration VEs must be designed to meet emission limits without financial penalties. Currently, steps are being taken to develop low-cost, alternative composite resin systems comprised of lower styrene concentrations. These resin systems will prove an effective means to reduce or eliminate VOC release. In this study, commercial VE formulations are tested for both emission and mechanical properties to establish a baseline for comparing new VE performances. A method of evaluating the emission rate is developed using mass loss of VOC as a function of time and temperature. The impact of selected parameters on the observed rate of mass loss is evaluated using a preliminary model to compare resin systems. Finally, the material performance of commercial VEs is evaluated using thermal-mechanical evaluation methods to provide material targets for new formulations.

15. SUBJECT TERMS  vinyl ester, styrene emission, emission kinetics, thermal-mechanical analysis

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