Molecular Relaxation Behavior of Fatty Acid-Based Vinyl Ester Resins

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ABSTRACT: The experimental characterization of the time-dependent properties of fatty acid-based vinyl ester resins with reduced styrene content and emissions was conducted and compared with that of various commercial vinyl ester (VE) resins. Constant heating rate and isothermal, multifrequency sweep experiments were conducted over a wide temperature range using dynamic mechanical analysis. Storage and loss modulus master-curves were formed using time–temperature superposition (TTSP) and analyzed to quantify the molecular relaxation behavior using accepted techniques and theories. Special attention was focused on determining the effect of reducing styrene weight percent on the derived viscoelastic properties. The fatty acid-based VE resins were found to have similar or slightly inferior thermomechanical properties and a more pronounced viscoelastic response compared with the commercial resins. However, the research definitively demonstrates that the evaluated fatty acid VE resins are a viable replacement to commercial resins in certain applications with concomitant attractive environmental benefits. © 2008 Wiley Periodicals, Inc.* J Appl Polym Sci 108: 3495–3506, 2008

Key words: viscoelastic properties; thermal properties; relaxation; fatty acid vinyl esters; styrene replacements/alternatives

INTRODUCTION

Vinyl ester (VE) resins are used to make polymer matrix composites for military and commercial civil and infrastructure applications because of their overall good thermal, mechanical, electrical properties, low weight, and low cost compared with conventional materials. These commercial resins typically contain high concentrations (>40 wt %) of reactive diluents, such as styrene (Fig. 1), to decrease viscosity that facilitates the use of conventional room temperature liquid transfer molding techniques to fabricate large scale composites parts and structures. Because styrene is a hazardous air pollutant (HAP) and a volatile organic compound (VOC), the Federal Environmental Protection Agency of the United States of America has introduced legislation that will limit styrene emissions from composite manufacturing.[1] Therefore, replacing all or part of the current reactive diluents in VE resins with nonvolatile reactive diluents, such as fatty acid (FA) monomers, offers a large environmentally green advantage.

Previous work has shown that specially prepared FA monomers can be blended and cured with VE and unsaturated polyester monomers or resins.[2–5] This research presented studies of the glass transition temperature, cure kinetics and viscosity for ternary blends of VE, methacrylated fatty acids (MFA), and styrene (Fig. 2) and compared them with Derakane 411-C50 (now replaced by Derakane 411-350).[2,3] Of particular interest here was the effect of reducing styrene content on monomer and polymer properties and performance. The study found that polymer properties typically decreased with decreasing styrene content with respect to those of the commercial resins. Even so, the observed reduction in properties was minor and reasonably comparable results for room temperature polymer properties such as fracture toughness, flexural strength, and molecular weights of commercial and fatty acid-based VE resins were obtained.[3] The comparable cure and ternary polymer properties are quite encouraging because FA monomers are excellent alternatives to styrene because of their low cost and lower volatility. In addition, fatty acids are renewable resources because they are derived from plant oils. Therefore, not only would the use of fatty acids in liquid molding resins reduce VOC emissions, thereby reducing health and environmental risks, but it also would promote global sustainability.

Commercial Resins

Bisphenol Resins:

Bisphenol A Vinyl Ester

Styrene
33-50+ wt%

Novolac Resins:

Novolac Vinyl Ester
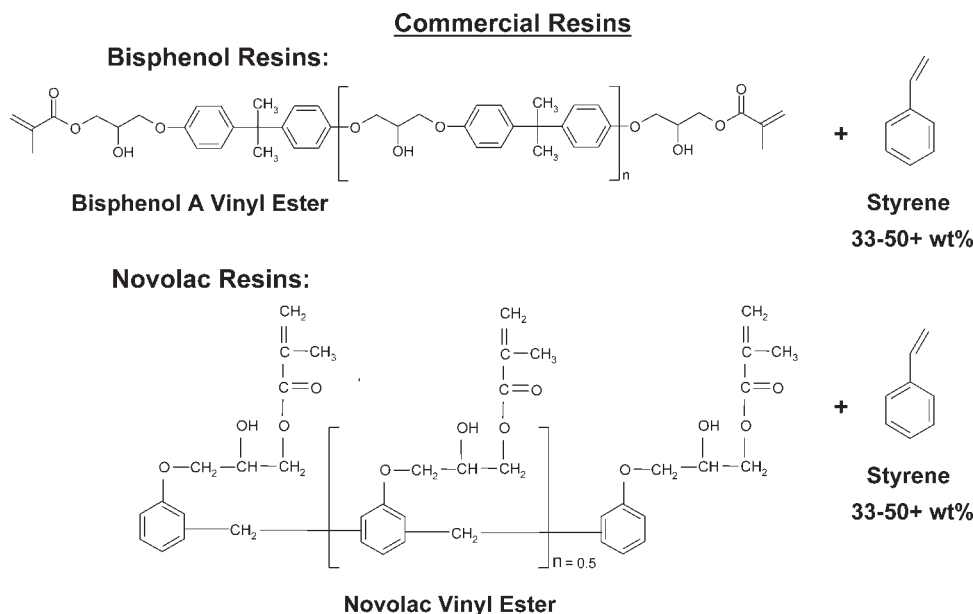
Styrene
33-50+ wt%

Figure 1 The chemical composition of bisphenol A and novolac based vinyl ester resins.

The current research effort will extend the characterization of fatty acid vinyl ester (FAVE) resins and their commercial counterparts to time-dependent polymer properties. This effort will also present a more detailed determination of properties and one-to-one comparison of the commercial and FAVE resins. The commercial and FAVE resins selected here are based on current proposed uses in Department of Defense (DoD) applications for glass reinforced composites such as the Marines HMMWV (i.e.,

FAVE Bisphenol Resins:

Bisphenol A Vinyl Ester

Styrene 10-25 wt%

MFA – methacrylated fatty acid 10-25 wt%

FAVE Novolac/Bisphenol Resins:

Bisphenol A Vinyl Ester

Novolac Vinyl Ester

Styrene

MFA – methacrylated fatty acid
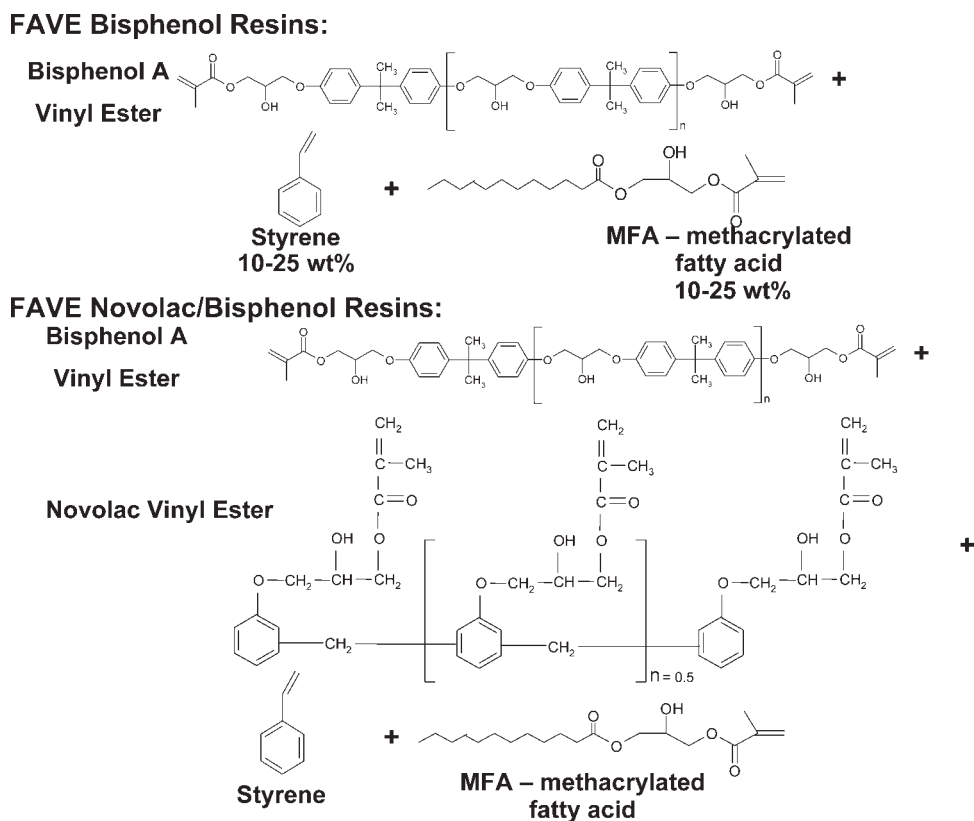
Figure 2 The chemical composition of FAVE resins.

TABLE I
Chemical Formulation of Commercial Resins

		Formulation			
Resin	Type	Bisphenol A VE (wt%)	Novolac VE (wt%)	MFA (wt%)	Styrene (wt%)
Derakane 8084	Toughened Bisphenol A	$\sim 60^a$	0	0	40
Hexion 781-2140	Bisphenol A	54	0	0	46
Corve 8100	Bisphenol A	50.5	0	0	49.5
Derakane 441-400	Bisphenol A	67	0	0	33
Derakane 470-300	Novolac	$\sim 33.5^b$	$\sim 33.5^b$	0	33
Derakane 470HT-400	Novolac	0	67	0	33

[a] An unknown percentage of the non-styrene portion of the resin is an elastomer for toughening.
[b] Approximately half of the Derakane 470-300 vinyl ester is novolac and half is bisphenol A type.

Humvee) helmet hardtops, Air Force T-38 dorsal covers, mine counter measure (MCM) composite rudders for the Navy, and Army tactical vehicles, including HMMWV hoods, HMMWV transmission containers, and M35A3 truck hoods. Although this work focuses on the neat resin viscoelastic characterization, similar testing/validation is currently underway or planned for FAVE glass reinforced composites.

The viscoelastic characterization is performed using data from constant heating rate and isothermal step, multifrequency sweep experiments, and standard techniques. The accelerated characterizations scheme provided by the time–temperature superposition principle (TTSP)[6] is used here to reduce the storage and loss modulus data into time–temperature master-curves. The interdependence of the relaxation times and temperature is determined through a temperature shift factor analysis of the Williams–Landel–Ferry (WLF)[7] type from which the corresponding apparent activation energies can be calculated. The breadth of the relaxation is quantified using the empirical Kohlrausch–Williams–Watts (KWW)[8,9] function. Comparisons of the glass transition temperature, the molecular weight due to crosslinking, and resistance to thermal softening are also presented. The main emphasis of this work is to not only present a comparison of these resin systems but also to determine whether FAVE resins are a viable alternative to commercial resins, thereby defining the effects of reduced styrene content on various viscoelastic properties of these ternary blends.

EXPERIMENTAL AND MATERIALS

Viscoelastic characterization of both commercial and FAVE resins was primarily conducted through dynamic mechanical analysis (DMA) testing. First, DMA samples were prepared for each resin, and then a temperature ramp was conducted to assess the degree of cure, determine the breadth of the glass transition range and the glass transition temperature, T_g. Second, isothermal, multifrequency sweep testing was performed over a broad temperature range carefully focusing on the leathery region of the resin identified by the breadth of the glass transition. Finally, TTSP was used to construct master-curves from the storage and loss modulus data and other analyses were employed to determine relevant viscoelastic properties for characterization and comparison purposes.

Materials

Various commercial VE resins (Table I) were used in this work. The commercial resins Coryzn Corve 8100[10] and Hexion 781-2140,[11] are bisphenol A-based VEs with high styrene contents. Ashland Derakane 441-400 is a bisphenol A-based VE resin with a low styrene content for a commercial resin (33 wt %).[12] Derakane 470HT-400 is a high temperature VE with a high functionality and low styrene content.[13] Derakane 470-300 is a blend of low functionality novolac and bisphenol A VE also with a low styrene content.[14] Derakane 8084 is an elastomer toughened bisphenol A VE resin with 40 wt % styrene.[15]

FAVE resins were formulated to match the properties of commercial VE resins. Table II lists the FAVE formulations and their compositions. The FAVE formulations were prepared using commercial Derakane resins as their basis and through the addition of MFA and pure VE monomers. MFA monomers were prepared by reacting fatty acids with glycidyl methacrylate at moderate temperature.[2–5] Methacrylated lauric acid (MLau) and methacrylated octanoic acid (MOct) were used in this work. MOct produces resins with slightly higher T_g and lower viscosities, but costs more than MLau. Sartomer CN-151 is a

TABLE II
Chemical Formulation of FAVE Resins

Resin	Type	MFA used	Derakane type	Formulation					
				Derakane (wt %)	CN-151 (wt %)	Total Bisphenol A VE (wt %)	Novolac VE (wt %)	MFA (wt %)	Styrene (wt %)
FAVE-L-10S	FAVE, Bisphenol A	Lauric acid	441-400	20.3	44.7	65	0	25	10
FAVE-L-20S	FAVE, Bisphenol A	Lauric acid	441-400	40.6	24.4	65	0	15	20
FAVE-O-20S	FAVE, Bisphenol A	Octanoic acid	441-400	40.6	24.4	65	0	15	20
FAVE-L-25S	FAVE, Bisphenol A	Lauric acid	441-400	50.8	14.2	65	0	10	25
FAVE-O-25S	FAVE, Bisphenol A	Octanoic acid	441-400	50.8	14.2	65	0	10	25
FAVE-O-470-300-25S	FAVE, Novolac/Bisphenol A	Octanoic acid	470-300	50.8	14.2	~ 39.6[a]	~ 25.4[a]	10	25
FAVE-O-HT-25S	FAVE, Novolac/Bisphenol A	Octanoic acid	470HT-400	50.8	14.2	14.2	50.8	10	25

[a] Approximately half of the Derakane 470-300 vinyl ester used to partially formulate the FAVE-O-470-300-25S is novolac and half is bisphenol A type, resulting in a slight uncertainty in the novolac and bisphenol A type vinyl ester fraction of this resin.

low molecular weight bisphenol A VE monomer containing no reactive diluent.[16] The total VE content was targeted at 65 wt % for all FAVE formulations. As an example, FAVE-L-25S was formulated by blending 75.8 wt % Derakane 441-400 (of which 50.8 wt % of the total FAVE resin is VE monomers and 25 wt % is styrene) with 14.2 wt % CN-151 and 10 wt % methacrylated lauric acid (MLau). Because of the high viscosity of CN-151, this monomer was heated to 70°C for 10 min prior to adding to the Derakane/MFA solution and then mixed thoroughly. The ''L'' in ''FAVE-L-25S'' indicates that the MFA used is MLau, and the ''25S'' suffix indicates that the resin contains 25 wt % styrene. FAVE-O-20S indicates uses MOct as the MFA and contains 20 wt % styrene.

Neat resins were cured at room temperature using a mixture of Trigonox 239A (Akzo Nobel Chemicals, Chicago, IL), containing 46% cumene hydroperoxide, and cobalt naphthenate (CoNap) (Aldrich). The Trigonox and CoNap weight percents used were 1.5 and 0.375 wt %, respectively, of the total resin weight; however, for more viscous resins such as FAVE-L/O-20S and FAVE-L/O-25S with lower styrene content, the weight percents were reduced to 1 and 0.2%, respectively, to increase gel time and allow for evacuation of air from the mixture. Neat resins were cured overnight in RTV molds with nominal dimensions of 60 mm × 12 mm × 3 mm and then postcured at 150°C for 2 h. The higher temperature resins such as the Derakane Momentum 470-300 and Derakane 470HT-400 were both cured at 200°C for 2 h. The samples were then wet sanded to ensure uniform cross-sectional area and cut to a length of 50 mm and dried for an additional hour at 40–50°C.

Experimental

All samples were tested on a TA Instruments Q800 DMA using dual cantilever geometry. At least two constant heating rate experiments for each resin were carried out from 30 to 200°C (225°C for the higher temperature novolac-based resins) with a heating rate of 2°C/min and constant oscillatory displacement amplitude of 7.5 μm at 1 Hz. Also, at least two isothermal, multiple frequency sweep tests were conducted over three decades of frequency (0.1 to 30 Hz) at discrete temperatures ranging from 30°C to ~ 170 °C for the bisphenol A type VEs resins and to 200°C for the novolac type VE resins in 5°C steps. The steps were refined to 2 or 3°C in the temperature ranges of the glass transition as identified by the constant heating rate experiments. The oscillatory amplitude was maintained at 7.5 μm to ensure a linearly viscoelastic response over the wide temperature range.

TABLE III
Summary of Thermo-Mechanical and Viscoelastic Properties for Commercial and FAVE Resins

Resin system	n	T_g (°C)	M_c (g/mol)	ΔH_a (kJ/mol)	C_1^0 (°C)	C_2^0 (°C)	f_0 (10^{-2})
Derakane 8084	0.87	101.8 ± 1.4	828 ± 84	633 ± 13	22.8	104.1	1.9
Hexion 781-2140	0.76 ± 0.01	121.8 ± 0.3	895 ± 86	647 ± 14	17.5	55.0	2.5
Corve 8100	0.75	116.4 ± 0.5	1323 ± 103	608 ± 4	18.6	51.7	2.3
Derakane 441-400	0.76	129.1 ± 1.0	632 ± 18	613 ± 32	21.4	71.4	2.0
Derakane 470-300	0.86	151.8 ± 1.0	280 ± 28	809 ± 35	15.6	57.1	2.8
Derakane 470HT-400	0.86	155.9	171	824 ± 31	18.5	74.1	2.3
FAVE-L-10S	0.88	86.7 ± 0.3	346 ± 22	489 ± 4	26.2	132.5	1.7
FAVE-L-20S	0.83	95.9 ± 2.4	409 ± 62	538 ± 21	20.1	84.7	2.2
FAVE-O-20S	0.82 ± 0.01	99.7 ± 2.1	492 ± 62	540 ± 12	20.5	82.7	2.1
FAVE-L-25S	0.8	108.0 ± 1.9	550 ± 4	16.4	16.4	64.1	2.6
FAVE-O-25S	0.8	106.6 ± 0.8	584 ± 2	17.4	17.4	62.9	2.5
FAVE-O-470-300-25S	0.87	110.2 ± 3.4	605 ± 4	23.0	23.0	105.0	1.9
FAVE-O-HT-25S	0.87	124.2 ± 3.8	595 ± 68	25.4	25.4	108.7	1.7

VISCOELASTIC CHARACTERIZATION

Analysis of the constant heating rate experiments

The constant heating rate experiments yielded storage and loss modulus data versus temperature for each resin. The molecular weight between crosslinks, M_c, and the glass transition temperature T_g is calculated from this data and gives a means of assessing the crosslink density and its effect on T_g and the viscoelastic response (both the T_g and M_c are listed in Table III). The theory of rubber elasticity is used to calculate M_c,

$$M_c = \frac{3RT\rho}{E} \qquad (1)$$

Here E is the rubbery modulus, R is the universal gas constant, T is the absolute temperature, and ρ is the sample density.[17,18] The temperature T and rubbery modulus E are determined for the calculation of eq. (1) at $T_g + 40$°C (well into the rubbery region) and the sample density ρ that was taken as 1.07 g/cm^3 (a common value for the VE resins). Typically, rubber elasticity applies only to polymers with low crosslink densities and would not be expected to give completely accurate crosslink density measurements for highly crosslinked VE systems. However, the results tabulated in Table III are the correct order of magnitude based on more accurate crosslink density calculations[17] and certainly provide a relative means of comparison between commercial and FAVE resin systems.

Another important mechanical property of polymers is the ability to resist thermal softening. To assess the residual stiffness versus temperature, the temperature at which the resin lost 20 and 50% of its room temperature storage modulus value was identified. The goal of this calculation was to provide an estimated useful operating temperature range for the resins as well as identify which resins were more vulnerable to thermal softening. The thermal softening performance, of course, figures highly into which applications the FAVE resins are best suited as replacements for their commercial counterparts.

Analysis of isothermal step, multiple frequency sweep experiments

The viscoelastic characterization for the commercial and FAVE resins was primarily derived from an analysis of master-curves of storage and loss modulus data. Storage and loss modulus data from multiple frequency sweeps at discrete temperatures were used to form master-curves using TTSP for the resins over a wide temperature range from the glassy to the rubbery regions. The temperature shift factors were fitted to the empirical and free volume derived Williams–Landell–Ferry (WLF) equation in the leathery to rubbery regions about the distortion temperature. The breath of the distribution of molecular relaxation times was described using a fit to the empirical Kohlrausch–Williams/Watts (KWW) equation.

TTSP is an accelerated characterization scheme that allows for the modeling of long term polymer response to prescribed temperatures and loads using short term data collected over a wide range of temperatures. Multiple frequency sweep storage and loss modulus data was collected over three decades of frequency and shifted into master-curves using time–temperature equivalence. The shifting was performed similar to the reduced variables method described by Ferry[6] in which a vertical shift or

correction due to the flexible chain theory is applied to both storage modulus E'_{Data} and loss modulus E''_{Data} data before horizontal shifting,

$$E'_{\text{MC}} = E'_{\text{Data}} \frac{T_R \rho_R}{T_\rho}$$
$$E''_{\text{MC}} = E''_{\text{Data}} \frac{T_R \rho_R}{T_\rho} \tag{2}$$

where T_R and ρ_R are the reference temperature and density at that reference temperature, respectively, and T and ρ are the temperature and density at the new temperature and is plotted against the reduced frequency. This vertical correction further reduces considering that the densities of most polymers do not change significantly in the temperature range where the time–temperature equivalence is valid and the density ratio is approximately one. The vertical shifting procedure does quite well in the leathery and rubbery regions of the polymer to aid in the formation of smooth master-curves, but may cause too much vertical shifting in the glassy region and thus yield incorrect horizontal shift factors.[6] As a result, shifting of both storage and loss modulus data simultaneously may be required to yield accurate temperature shift factors; an approach that is used for this study.

The temperature shift factor a_T for each resin was analyzed using a WLF type fit to characterize the temperature shift factor versus temperature and calculate the activation energy.[19] The WLF equation is used to characterize the temperature dependence of the distribution of relaxation times in viscoelastic materials.[6,7] All temperature shifts above the glass transition temperature were fit using a rewrite of the WLF equation,

$$\frac{-1}{\log_{10} a_T} = \frac{C_2^0}{C_1^0}\left(\frac{1}{T - T_R}\right) + \frac{1}{C_1^0} \tag{3}$$

where T_R is the reference temperature, C_1^0 is a dimensionless constant, C_2^0 has dimensions of temperature (usually °C), and the superscript "0" indicates that the reference temperature is not T_g. The fractional free volume f_0 is also calculated once C_1^0 is found,

$$f_0 = \frac{B}{2.303 C_1^0} \tag{4}$$

where B is the Doolittle constant and is usually taken to be one.[20,21] The apparent activation energy ΔH_a necessary to initiate the viscoelastic relaxation process was calculated using a direct graphical method from a plot of the natural log of the temperature shift factor at temperatures above the glass transition temperature versus the inverse of the temperature in Kelvin,

$$\Delta H_a = R \frac{d(\ln a_T)}{d(1/T)} \tag{5}$$

The resulting calculated slope multiplied by the universal gas constant gives the activation energy values listed in Table III.

The distribution of relaxation times about the glass transition may be described by calculating the coupling parameter n of the empirical Kohlrausch–Williams/Watts (KWW) function.[8,9] Physically, the coupling parameter reveals the strength of the intermolecular interaction between segmental chains in the polymer and provides a measure of the cooperativity associated with the relaxation process.[22] The coupling parameter was determined using the KWW function $\phi_{\text{KWW}}(t)$ proposed by Williams and Watts,

$$\phi_{\text{KWW}}(t) = e^{-\left(\frac{t}{\tau}\right)^{1-n}} \qquad 0 < n < 1 \tag{6}$$

where τ is the temperature dependent apparent relaxation time, t is time, and n is the coupling parameter. The KWW function is then substituted into an expression for the complex modulus E^*,[23,24]

$$E^* = E'(\omega) - iE''(\omega) = -\int_0^\infty e^{-i\omega t}\left[\frac{d\phi(t)}{dt}\right] dt \tag{7}$$

According to the approach of Weiss et al.,[24,25] the loss modulus E'' is then given by,

$$E''(\omega) = AzQ_\beta(z) \tag{8}$$

where Q_β is given as,

$$Q_\beta(z) = \frac{1}{\pi}\int_0^\infty e^{-u^\beta}\cos{(zu)}du$$
$$\beta = 1 - n$$
$$z = \omega\tau = 2\pi f\tau \tag{9}$$

Here A is an adjustable constant, τ is the same characteristic relaxation time from eq. (6), f is the frequency, z is a dimensionless spatial variable, and Q_β a probability density function. Numerical methods are required to evaluate Q_β[24,25] whose solution may be represented as,

$$Q_\beta(z) = \frac{1}{\pi}\sum_{m=1}^\infty (-1)^{m+1}\frac{\Gamma(1 + \beta m)}{m!z^{1+\beta m}}\sin\left(\frac{\pi m\beta}{2}\right)$$
$$0 \leq \beta \leq 1 \tag{10}$$

The values A, β, and τ of eq. (8) are curve fitted to loss modulus master-curve data until the polymer loss modulus master-curve in the glass transition
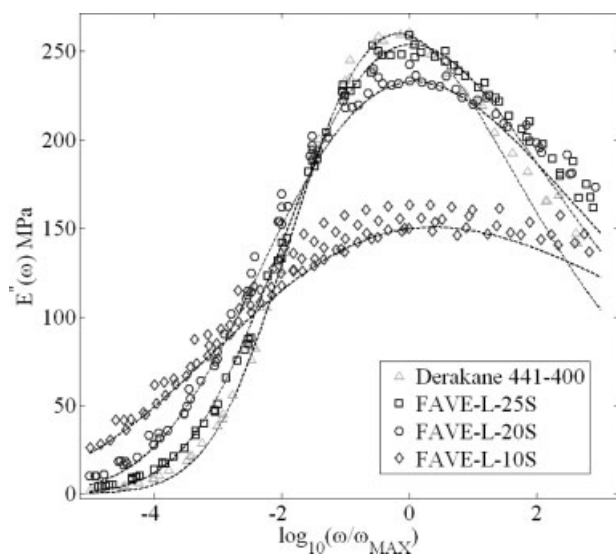
Figure 3 Loss moduli master-curves as a function of frequency normalized at the loss moduli maxima for Derakane 441-400 and FAVE resins based on it in the vicinity of the glass transition temperature along with KWW fit (dashed line).

region is well represented (Fig. 3). The values of the coupling parameter n are listed in Table III.

RESULTS AND DISCUSSION

Thermomechanical polymer properties

Crosslink density is strongly affected by reactive diluent content in the starting resin. From Figure 4, it is clear that the molecular weight due to crosslinking decreased with decreasing styrene content. Although all of the FAVE resins have the same reactive diluent content (35 wt % diluent consisting of styrene and MFA), the molar reactive diluent content increased as the styrene content in the resin increased because MFA monomers have molecular weights 2.75 times (MOct) and 3.3 times (MLau) higher than that of styrene. Therefore, within the FAVE resin, increased styrene content resulted in lower crosslink densities and higher M_c values. The experimental M_c values are listed in Table III and are of the correct order of magnitude for the commercial and FAVE resins.[3] Similarly, M_c of the commercial bisphenol A VE resins (i.e., Derakane 441-400, 8084, Hexion 781-2140, and Corve 8100) increased as the styrene content in the resin increased. Furthermore, the FAVE resins had lower M_c values than the commercial bisphenol A type resins because of the lower styrene content in the bisphenol A resins. Even though Derakane 470-300 and Derakane 470HT-400 have the same styrene weight percent as Derakane 441-400, their M_c values were considerably different. Derakane 470HT-400

had the lowest M_c, followed by Derakane 470-300, whereas Derakane 441-400 had the highest value of M_c. This occurred because Derakane 470HT-400 had the highest novolac content. Novolac resins have higher functionality than bisphenol A type resins (Figs. 1 and 2) and produce resins with high crosslink densities.

As with crosslink density, the glass transition temperature is also affected by the amount of reactive diluent in the polymer resin. In this study, the glass transition temperature T_g was determined as the peak of the loss modulus curve versus temperature at an oscillation of 1 Hz.[26] Overall, the glass transition temperatures for the FAVE resins are slightly lower than those of the commercial resins. Most notable is the significant drop in T_g for Derakane 8084 compared with the other commercial resins caused by the addition of a plasticizing rubber toughening agent. The two high styrene content resins, Hexion 781-2140 and Corve 8100, both have lower T_gs than Derakane 441-400 because of the presence of more lower T_g styrene ($\sim 100°C$) to higher T_g VE ($\sim 170°C$) in the resin's chemical composition. The two novolac type VE resins, Derakane 470-300 and Derakane 470HT-400, have a higher functionality which leads to more crosslinking and thus a higher T_g value. From Figure 5, a decrease in styrene wt % results in a decrease in T_g for the FAVE resins. Though this seems contradictory, it is important to note from Table II that the wt % of reactive diluent (MFA + Styrene) is constant for the FAVE resins at about 35 wt %. The effect here is due to the MFA having a lower intrinsic T_g than the styrene and the VE. As the wt % of MFA increases in the resin chemical composition, the overall T_g of the resin decreases. The difference in T_g between the two novolac type VE resin is more significant for FAVE-O-470-300-25S and FAVE-O-HT-25S than for the commercial resins. Though the "HT" resin is more highly crosslinked
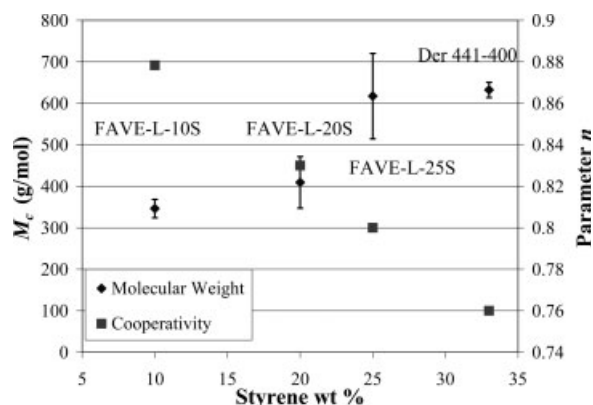

Figure 4 The molecular weight and coupling parameter versus styrene content for Derakane 441-400 and its FAVE resins.
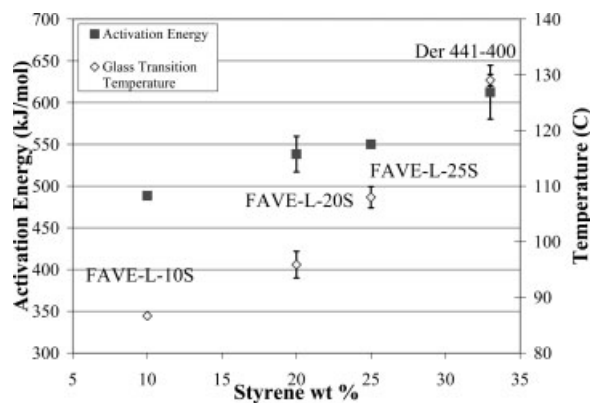
Figure 5 Activation energy and glass transition temperature versus styrene content for Derakane 441-400 and its FAVE resins.

due to a greater novolac wt % (see Table 1 and Table II) and a higher T_g expected, the difference observed here may be due to some experimental error or the unique interaction between the ternary constituents of the FAVE-O-470-300-25S.

The resistance to thermal softening is detailed for the commercial and FAVE resin systems in Figure 6. The temperature at which there is 20% drop in room temperature modulus is reasonably consistent among all the commercial resin systems with the exception of the Derakane 8084 which shows a substantially decreased resistance to thermal softening for both the 20 and 50% drops. Derakane 8084 is toughened with the addition of a proprietary rubber toughening agent which appears to be acting as a plasticizer reducing polymer T_g and thus overall thermal resistance to softening. The Hexion 781-2140 (46 wt % styrene), Corve 8100 (49.5 wt % styrene), and Derakane 441-400 (33 wt % styrene) perform almost identically even though the styrene contents are significantly greater for the Hexion 781-2140 and Corve 8100. This can be explained by noting that increased styrene content leads to a sharper glass transition and thus loss modulus peak versus temperature and a sharper modulus drop in the vicinity of T_g can be expected. Because Derakane 441-400 has less styrene content, its glass transition and peak loss modulus are broader versus temperature and a more gradual modulus drop off is expected; thus, the higher temperature value at 50%. Derakane 470HT-400 and Derakane 470-300 out perform Derakane 441-400 in thermal resistance by about 10°C at the 20% drop-off temperature (glassy region) and a significant 15–25°C at the 50% drop-off temperature (alpha transition region) even though all three resins have the same styrene content. The increase in thermal properties here is given by the higher novolac percent in the Derakane 470 series resins which causes them to be more significantly crosslinked.

The FAVE resins overall had a lower resistance to thermal softening compared with the commercial resins because of the lower styrene content and the presence of long fatty acid groups in the resin. The long aliphatic fatty acid chains pendant to the polymer network increase free volume[3] and reduce the T_g and increase the number of relaxation modes. The Derakane 441-400 based FAVE resins (FAVE-L/O-25S, FAVE-L/O-20S and FAVE-L-10S) with decreasing styrene content showed a noticeable downward trend in resistance to thermal softening, as seen in Figure 6. The best FAVE performers are the FAVE-O-470-300-25S and FAVE-O-HT-25S both based on the two commercial novolac VE resins, respectively. Both of these resins compare well to the non-novolac commercial resins with only a 10–20°C difference in softening temperatures and may be selected as viable replacements in certain applications. Also, it is important to note that most of the FAVE resins with at least 20 wt % styrene content had improved resistance to thermal softening than Derakane 8084.

Extent of cure differences among resins could also result in significantly different thermomechanical properties. However, all resins are postcured at high temperatures to ensure complete cure before testing. In addition, previous results indicate that the overall extent of cure for FAVE resins is similar to that of commercial resins.[3] However, the results also showed that the extent of styrene conversion is higher, indicating that the extent of cure of VE and MFA components are lower in FAVE resins relative to that of commercial resins.[3] However, predicted molecular weight between crosslinks based on the molecular structure of the monomers[3] is similar to what was measured and not systematically different for commercial and FAVE resins. Nonetheless, it is possible that these differences in extent of cure could affect thermal softening behavior.[27] Yet, the reasons previously described are likely the dominating
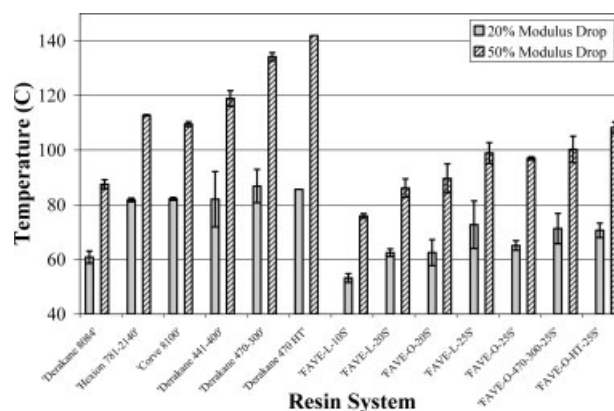

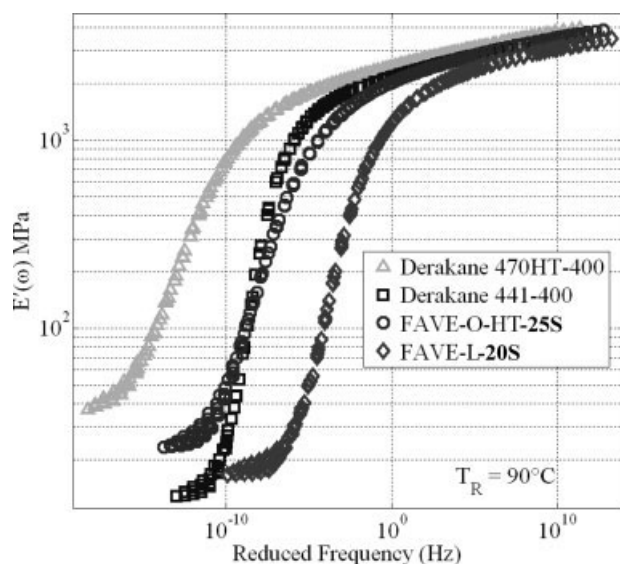**Figure 6** Resin resistance to thermal softening for commercial and FAVE resins.

Figure 7 Storage moduli master-curves for selected commercial and FAVE resins.

reasons for differences in T_g, M_c, and thermal softening behavior for FAVE and commercial resins.

Viscoelastic polymer properties

A sampling of storage and loss modulus master-curves constructed for all resins is given in Figures 7 and 8. As described in the Experimental Section, these master-curves were formed using TTSP and temperature shift factors analyzed using the WLF equation eq. (3). The storage modulus master-curves of Figure 7 illustrate a comparison of the commercial and FAVE novolac based VE resins, Derakane 470HT-400 and FAVE-O-HT-25S, along with Derakane 441-400 and FAVE-L-20S. Figure 7 clearly demonstrates that each of the FAVE resins did not perform as well as their commercial counterparts at higher temperatures and to longer periods of time mainly because of the reduced styrene content. The high temperature novolac VE-based Derakane 470HT-400 maintained its modulus to a higher temperature and longer time falling off more gradually because of its high crosslink density. The FAVE-O-HT-25S did not perform as well as Derakane 470HT-400 because of the addition of $\sim$ 14 wt % bisphenol A VE (refer to Table II) and lower styrene content, that reduced overall crosslink density, but performed comparable to the Derakane 441-400 even though it has 8 wt % less styrene. The Derakane 441-400 and FAVE-L are both bisphenol A based VE systems and are more viscoelastic with lower temperature resistance. The modulus of Derakane 441-400 fell off most sharply in the region of the glass transition and obtained the lowest rubbery region modulus. The steep modulus drop can be explained due to the

increased styrene content of the Derakane 441-400 over the FAVE-L-20S which had a more gradual fall off. Overall, the commercial and FAVE resins all had very similar glass region behavior.

The loss modulus master-curves of Figure 8 were formed in the same way using the same temperature shift factors as the storage modulus master-curves. Figure 8 is meant to clearly illustrate the effect of reduced styrene content on loss behavior and response of Derakane 441-400 and the FAVE resins directly based on it. Derakane 441-400 had the highest peak loss followed by FAVE-L-25S (with 25 wt % styrene), FAVE-L-20S (20 wt % styrene), and FAVE-L-10S (10 wt % styrene). It is generally accepted that as the reactive diluent content decreases, the loss modulus peak decreases and the spectra broadens,[28] which is supported by Figure 8. The breadth of the loss modulus master-curve also significantly increased with reduced styrene content which is quantified by the coupling parameter n of the KWW equation and also represented in Figure 3 and Table III. Most notable was the peak shift to shorter times on the loss modulus master-curves. Viscoelastically, the shift of the distribution of characteristic relaxation times to shorter time intervals implies that the viscoelastic relaxation process will occur more quickly in materials with lower styrene contents, a result that is supported by this data.

The temperature shift factors found from the master-curve shifting were analyzed using a WLF type analysis. The WLF parameters along with the fractional free volume and the coefficient of thermal expansion due to the change in free volume at a specified temperature are listed for each resin in Table III and are consistent with the theoretical values
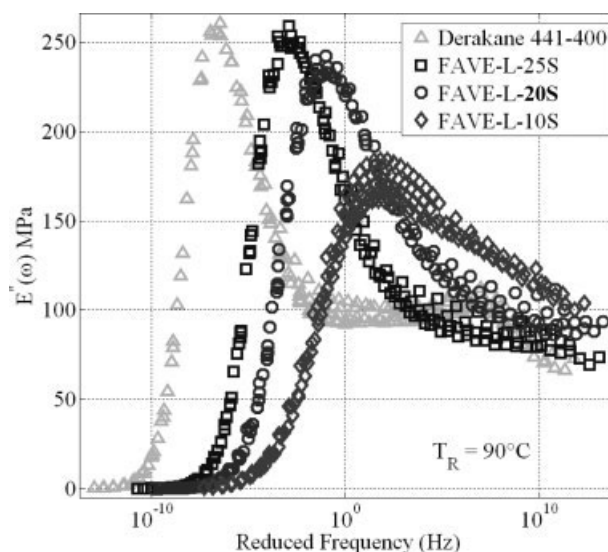

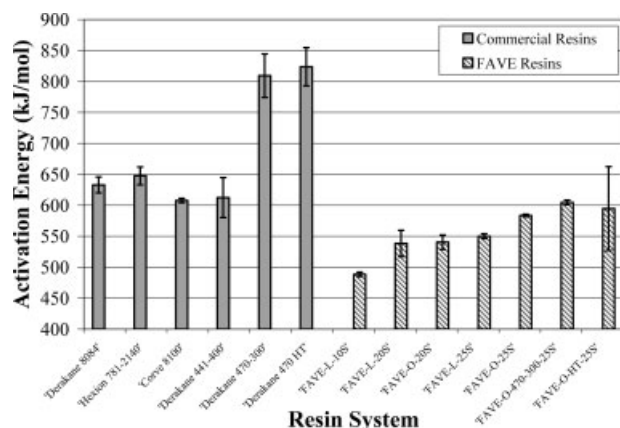**Figure 8** Loss moduli master-curves for Derakane 441-400 and its FAVE resins.

Figure 9 Activation energy comparison for commercial and FAVE resins.

given by Williams et al.[7] The values also indicate that the assumption of a single accelerating mechanism for the viscoelastic process inherent in TTSP is correct or at least adequate for the current analysis.

Apparent activation energies using the WLF temperature shift factor data were calculated graphically using eq. (5) and are listed in Table III and graphed for comparison in Figure 9. The activation energy values are consistent with the results of previous discussions of the influence of crosslink density, styrene content, and resistance to high temperature softening on the viscoelastic response of these resins and compare well to other calculations listed in the literature.[19] The novolac resins, Derakane 470HT-400 and 470-300, had the highest activation energies due to their high crosslink density compared with the other resin systems considered. The other bisphenol A based commercial resin had approximately the same activation energies, which is not surprising since their storage modulus master-curves and T_g values were all very similar. An interesting result here is that the Derakane 8084 had an activation energy which was similar to the other commercial resins yet had the lowest T_g. The proprietary rubber toughening agent added to Derakane 8084 had a demonstrated plasticizing effect lowering T_g (refer to Table III), but also appears to be inhibiting the onset of the viscoelastic relaxation as indicated by the activation energy value of Figure 9 and the larger coupling parameter n of Table III. This indicates that the rubber toughening agent is likely reacting into the polymer network and providing additional crosslinking,[29] but the chemical composition of the rubber toughening agent is nonrigid on the molecular level and thus reduces T_g. The FAVE resins had lower activation energies on average although the two novolac VE-based resins, FAVE-O-470-300-25S and FAVE-O-HT-25S, were comparable to the bisphenol A VE-based commercial resins. The data show that

the activation energy decreased with decreasing styrene content as illustrated in Figure 5 (along with T_g). This occurred because of the resulting broadening of the glass transition.[28] In addition, as the styrene content decreased, the MFA content increased resulting in a higher content of pendant aliphatic chains that increase free volume and allow for additional relaxation modes.

The WLF fit constants, C_1^0 and C_2^0 (Table III), are very highly dependent on the WLF fits to the experimental data. Using or omitting a given data point had a significant effect on particular values of these constants. Nonetheless, the trends in values of these constants were simple functions of the polymer molecular structure. Both C_1^0 and C_2^0 increased as the styrene content decreased, as can be seen the FAVE-L series with varying styrene content, or in general, as the crosslink density increased. Derakane 8084 had WLF fit values that were different than expected based on the other resins. This is likely a result of the rubber toughening agent used in this resin that essentially makes this resin's viscoelastic behavior fundamentally different from the other resins. The fractional free volume also behaved regularly with polymer molecular structure for the most part. The values of f_0 (Table III) especially for the FAVE resins, increased with increasing styrene content and with decreasing crosslink density in general. The results for the commercial resins were more scattered. In particular, Derakane 470-300 had a considerably higher f_0 than expected, whereas Derakane 8084 had a lower f_0 than expected. We attribute this to the toughening additive in Derakane 8084 and the fact that f_0 is calculated directly from C_1^0, which is highly dependent on the WLF fits.

The breadth of the distribution of relaxation times in the viscoelastic process is given by a KWW type analysis. The key parameter is the coupling parameter of eq. (6) which is calculated from a fit of eq. (8) to loss modulus master-curve data as illustrated in Figure 3 (identical to Fig. 8 except with KWW fits and a focus on the glass transition region). This parameter has been used by a number of researchers[19,22,30,31] to characterize the observed broadening of the loss modulus and tan δ curves in neat resins that related to the cooperative motion of the main polymer chains during the glass transition.[22,32] The values of the coupling parameter n calculated for the commercial and FAVE resins are listed in Table III and are in agreement with values provided by other researchers (see Table I in Ref. 32). From Table III, the highest values of n and thus the broadest distribution of relaxation times are given by the novolac VE-based resins, Derakane 470HT-400 and 470-300, their FAVE counterparts and Derakane 8084. The novolac VE resins are more highly crosslinked requiring a greater degree of cooperative movement

among main chains to fully relax. The large coupling parameter value for Derakane 8084 is probable due to the dispersion of the rubber toughening agent within the chain microstructure inhibiting main chain cooperative motion and the onset of the relaxation. The smaller values of n are given by the commercial resins with the higher styrene contents whose glass transition has been demonstrated to be sharper with a steeper fall-off in the modulus. Most of the FAVE resins have a slightly greater value of the coupling parameter compared with the higher styrene content commercial resins probably because the addition of the methacrylated fatty acids slightly increases the crosslink density. Figure 4 clearly shows that the cooperativity measured by n increases with decreasing styrene content for Derakane 441-400 and the FAVE resins which are based on it. Decreasing the reactive diluent content will decrease the length of the polymer chains generating more crosslinks and higher crosslink density, which will slightly increase the degree of cooperativity between neighboring chains.

SUMMARY AND CONCLUSIONS

Research was conducted to characterize and compare the thermomechanical and time dependent properties of commercially available VE resins and lower styrene content FAVE resins which are based upon them. The FAVE resins were found to have similar or slightly inferior properties compared with the commercial resins. The FAVE resins typically had lower glass transition temperatures and lower resistance to thermal softening. The viscoelastic properties were very dependent upon the degree of crosslinking, and the styrene content, methacrylated fatty acid content and type and functionality of the VE monomer played important roles. From the data presented the viscoelastic relaxation process is accelerated not only by temperature but also by reduced styrene content. Although the glassy region response of the commercial versus FAVE resins was very similar, the novolac VE-based resins would be the best choice for higher temperature applications with a low tolerance for viscoelastic behavior. On the opposite end would be low styrene content resins such as FAVE-L-10S and FAVE-L/O-20S which had the least temperature resistance and most pronounced viscoelastic behavior.

The choice of resin depends greatly upon the anticipated use and desired operating temperature; however, the novolac VE-based FAVE-O-HT-25S was a solid performer for both the thermomechanical and viscoelastic criteria considered, and thus a viable alternative to a number of the commercial resins. The FAVE-O-HT-25S resin also has the added environmental benefit of lower styrene content and a corresponding reduced styrene gas emission during processing and postcuring. The methacrylated fatty acids which replace some of the styrene content are also a renewable resource. Future work will consist of manufacturing and testing of several types of glass reinforced FAVE composites panels and structures. These composites will be assessed for applications in numerous DoD proposed projects and are expected to have improved thermomechanical and viscoelastic properties over the neat resins.

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