The Synthesis of 9–10 Dibromo Stearic Acid Glycidyl Methacrylate and Its Use in Vinyl Ester Resins

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ABSTRACT: In this study, 9–10 dibromo stearic acid glycidyl methacrylate (Di-BrSAGMA) was synthesized from oleic acid and used as a replacement for styrene in vinyl ester (bisphenol A type VE (VE 828) and Novalac type VE (VE160)) to introduce fire retardance to these systems and to decrease the volatile organic compound (VOC) emissions caused by styrene. When the Di-BrSAGMA was used as the comonomer, these resins exhibited too high viscosities, reduced modulus and glass transition temperature (T_g) values compared to those of the styrene based systems. Thus, the Di-BrSAGMA was used in the presence of styrene in these resins. The viscosities of the resins with various Di-BrSAGMA contents were determined and the modulus and the T_g values of the resulting polymers were measured via dynamic mechanical analysis (DMA) to determine the ideal formulations for each resin system. Similar analysis was performed, with similar oleic acid glycidyl methacrylate (OAGMA) contents, to determine the effect of the introduction of the bromine groups onto the network. Reactive diluent blends of the fatty acid based monomers with styrene, at styrene contents as low as 15–20 wt % at 35–45 wt % total comonomer content, in VE formulations were shown to have processable viscosities for liquid molding processes, and modulus and T_g values that are comparable to those of the commercial VE-styrene systems. The effect of the replacement of styrene by the Di-BrSAGMA monomer on the thermal degradation behavior of the VE 828 and VE 160 networks was also explored by thermal gravimetric analysis (TGA). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3833–3842, 2007

**Key words:** resins; flame retardance; halogenated; monomers; thermal properties

INTRODUCTION

Vinyl ester (VE) and unsaturated polyester (UPE) resins and their composites have applications in transportation and infrastructure. They are widely used in automobiles, boats, and navy vehicles as body panels and also as furniture.[1] UPE resins are also widely used as coatings. In all of these areas, fire safety is of major importance. VE and UPE resins are low molecular weight prepolymers with reactive functional groups. They are generally dissolved in a reactive diluent, such as styrene, to reduce the viscosity. Lowering the viscosity improves the processability by allowing the resins to infuse the gaps between fibers before polymerizing into a crosslinked network when preparing composites. However, styrene and other commonly used reactive diluents are hazardous air pollutants (HAP) and volatile organic compounds (VOC), and their use results in significant risks to the environment and to people working in this industry. Thus, the replacement of styrene with less volatile alternative monomers is an area of active research. In

this context, our group has reported the use of methacrylated fatty acids as replacements for styrene in VE resins. The ternary blends of the VE, methacrylated-fatty-acid-based monomers, and styrene gave properties comparable to those of the commercial VE formulations with significantly reduced VOC emissions.[2,3] Thus, the main objective of this research was to develop a fatty-acid-based monomer for fire resistant resins and their composites.

One of the most common practices for providing fire retardancy in polymers involves the use of halogenated species. Among the halogenated chemicals, brominated chemicals are the most commonly used chemicals. The *ortho*-tetra bromo diglycidyl ether of bisphenol A is the most commonly used starting chemical for fire retardant epoxy and VE resins. Tetra-bromo phthalic anhydride and dibromo neopentyl glycol are the most commonly used monomers in fire resistant UPE formulations.[4,5] Other than the halogenated chemicals, phosphorus-based chemicals and silicon-based flame retardants are also commonly used. Triethyl phosphate and dimethyl methyl phosphonate both enhance flame retardancy and enable viscosity reduction.[5] Among the silicon based systems, polyhedral oligomeric silesquioxanes (POSS) are new generation materials that can be used as flame retardants in thermosetting resins.[6] These materials, which are chemically modified
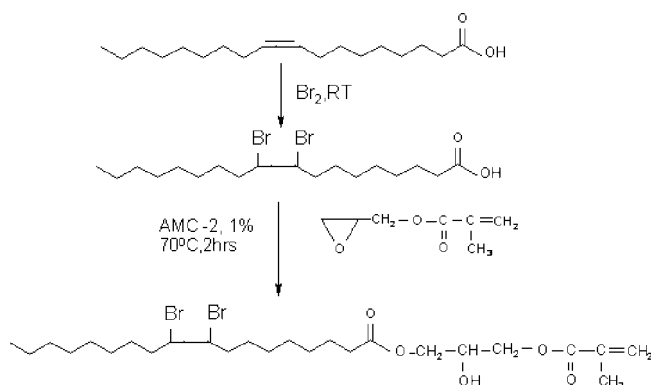
Figure 1 The reaction scheme for the synthesis of 9–10 dibromo stearic acid glycidyl methacrylate (Di-Br SAGMA) from oleic acid.

particles of silica, have dimensions at the nanometer scale. Their inorganic (silicon based) structure provides thermal stability and fire resistance whereas their organic (carbon based) structure provides compatibility and/or reactivity with the resins. Inorganic (metal) hydroxides and oxides are also commonly used as flame retardants. Antimony trihydroxide (ATH) is a popular flame retardant in UPE resins. Antimony trioxide, on the other hand, is generally used with the halogenated resins, as a synergist to improve the fire retardancy of these materials. For translucency, colloidal antimony pentoxide is preferred.[5]

Currently, bromine-containing fire retardants have the highest market share among the major families of fire retardants in US.[4] Although smoke toxicity is suspected to be associated with the use of halogenated chemicals, debates on this issue still continue, and brominated chemicals maintain their position as effective fire retardants in the plastics industry. Thus, in this study, a brominated-fatty-acid-based monomer was synthesized and used as a replacement for styrene in VE formulations to provide fire retardancy to these resin systems. The synthesis of bromoacrylated methyl oleate by bromoacrylation of methyl oleate in the presence of *N*-bromosuccinimide and acrylic acid in one step was recently reported.[7] The resulting monomer was copolymerized with styrene, methyl methacrylate, and vinyl acetate; however, no attempt was made to use this monomer in VE or UPE resins.[7,8] In our study, a different synthetic route was used. Oleic acid, which can be obtained from triglyceride oils, was first brominated at room temperature (RT) to form dibromo stearic acid and then reacted with glycidyl methacrylate to form 9–10 dibromo stearyl glycidyl methacrylate (Di-BrSAGMA) as shown in Figure 1.

Because the final resins were intended to be used in liquid molding processes and the Di-BrSAGMA exhibited a high viscosity at RT (830 cP), this monomer was used in the presence of styrene in VE resins. The viscosities of the resins with various Di-

BrSAGMA content were determined, and the modulus and the glass transition temperature (T_g) values of the resulting polymers were screened via DMA to determine the ideal formulations for each resin system. Similar analysis was performed, with similar oleic acid glycidyl methacrylate (OAGMA) contents, to determine the effect of the introduction of the bromine groups onto the network.

It was expected that the OAGMA and the Di-BrSAGMA comonomers would decrease the glass transition temperature (T_g) and modulus of the bisphenol A type VE resins (VE 828) when used as replacements for styrene, as discussed above. In an effort to increase the T_g and the modulus of these systems, a bisphenol F type Novalac resin, VE 160, which typically has better thermal properties, was used instead of the bisphenol A type vinyl ester resin VE 828.

Lastly, the thermal degradation behaviors of the VE-Di-BrSAGMA polymers were analyzed via thermal gravimetric analysis (TGA). This allowed determination of how effective the brominated fatty acids are in improving fire retardance.

EXPERIMENTAL

Instrumentation

Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopic techniques were used to characterize the synthesized monomers. For the FTIR analysis of the samples, a Thermo Nicolet Nexus 670 FTIR was used in absorbance mode, taking 16 scans per spectrum with a resolution of 4 cm^{-1}. Samples were prepared for NMR analysis by dissolving $\sim$ 0.1 g sample in $\sim$ 1 mL deuterated chloroform (CDCl$_3$). A Bruker AM300, 300 MHz spectrometer with a spectral window of $\pm$2000 Hz, 0.427 Hz/pt digital resolution, was used to analyze samples. A pulse width of 90° was used in all cases. The samples were analyzed at 293 K, and 16 scans of each sample were taken.

The viscosities of the resins were measured using a Brookfield digital viscometer in Couette geometry. Approximately 8 mL of the sample was placed into the sample holder. The viscosities were measured at 25°C, using the appropriate spindle and shear rate to maximize the allowable torque. For resins which possess high viscosities at RT, the temperature dependence of the viscosity was determined using a Brookfield Model 84 type temperature controller, connected to the sample holder.

Dynamic mechanical analysis (DMA) was used to determine the thermomechanical properties of the polymers. The tests were performed using a TA Instruments DMA 2980 DMA in single cantilever geometry. The rectangular samples with approximate dimensions of 25 × 10 × 2.8 mm^3 were tested at 1 Hz
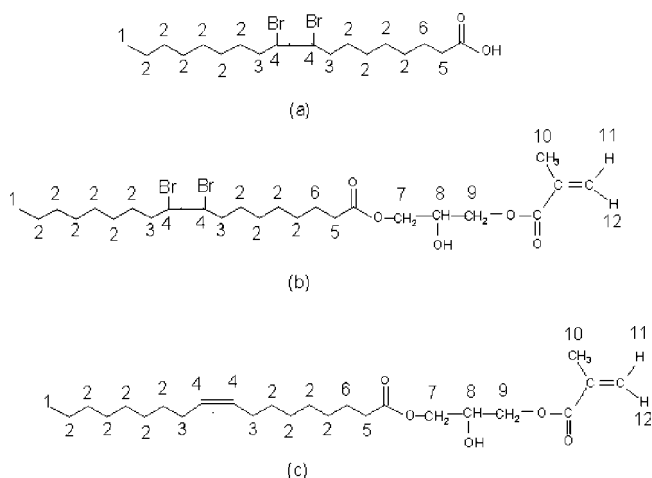
Figure 2 The different types of protons of (a) Di-BrSA (b) Di-BrSAGMA and (c) OAGMA monomers as determined from ^{1}H-NMR analysis.

with a deflection of 15 μm while ramping the temperature from 30°C to 200°C at a rate of 10°C/min. Two temperature ramps were performed for each sample. The results of the first test were taken as the properties of the RT-cured samples and the results of the second test were taken as the properties of the postcured samples. A TA Q0500 TGA was used to evaluate the thermal oxidative stability of 8–10mg of the samples in air. The samples were analyzed in platinum pans from 30°C to 800°C at 10°C/min heating rate.

Monomer Synthesis

Synthesis of the Di-Br SAGMA and OAGMA monomers

The oleic acid (80%), Br$_2$ (100%), and glycidyl methacrylate (97%) used for the synthesis of the fatty-acid-based monomers were all purchased from Sigma-Aldrich (Milwaukee, WI) and used without further purification. Hydroquinone (99%; Sigma-Aldrich) was used as a radical inhibitor in the methacrylation reactions. AMC-2 (Aerojet Fine Chemicals, Rancho Cordova, CA), which is a chromium-based esterification catalyst, was used as a catalyst in the methacrylation reactions.

The Di-BrSAGMA monomer was synthesized in two steps. In the first step, oleic acid was reacted with an equimolar ratio of Br$_2$. Bromine was added in aliquots to oleic acid cooled in an ice bath to prevent the excessive heating caused by the exothermic addition reaction. The red brown color of bromine instantly disappeared as bromine was added leading into a light orange colored solution. The solution was stirred at RT for an hour to ensure the completion of reaction. This solution was than ether extracted and washed two times with distilled water to wash away any unreacted bromine. The ether extract was then dried

over anhydrous sodium sulfate to eliminate any residual water. Finally, the sodium sulfate was filtered out and the excess ether was evaporated in a rotatory evaporator. The remaining product was a light orange colored liquid. The ^{1}H-NMR spectral analysis of this product indicated the disappearance of the 5.35 ppm peaks that represent the olefinic protons of oleic acid and the appearance of the 4.10–4.50 ppm peaks that represent the methylene protons attached to Br, confirming the complete reaction of the double bonds of oleic acid with Br$_2$. ^{1}H-NMR (CDCl$_3$, 300 MHz), δ ppm: 0.9 (3H, H$_1$), 1.3 (20H, H$_2$), 1.5 (2H, H$_6$), 1.7–2.2 (4H, H$_3$), 2.35 (2H, H$_5$), 4.1–4.3 (2H, H$_4$), [Fig. 2(a)].

In the second step of the synthesis, the 9–10 dibromo stearic acid was reacted with an equimolar ratio of glycidyl methacrylate in the presence of 1 wt % AMC-2 catalyst and 0.01 wt % hydroquinone for 2.5 h at 70°C to yield 9–10 dibromo stearyl glycidyl methacrylate (Di-BrSAGMA). The carboxylic acid of the fatty acid undergoes a catalyzed addition reaction with the epoxide group of glycidyl methacrylate to form a single product as shown in Figure 1. The mid-IR spectrum of the product showed the disappearance of the 917 cm^{-1} epoxide peaks and also the replacement of the broad carboxylic acid band of stearic acid by the 3468 cm^{-1} hydroxyl band, confirming the completion of the reaction. The ^{1}H-NMR spectral analysis of this product showed the absence of the epoxide methylene peaks at 2.7 ppm and 2.9 ppm indicating the addition of the acid group to the epoxy ring of glycidyl methacrylate. Protons that indicate the connection of the glycidyl methacrylate and the fatty acid appear at around 4.3 ppm. ^{1}H-NMR (CDCl$_3$, 300 MHz) δ ppm: 0.9 (3H, H$_1$), 1.3 (20H, H$_2$), 1.5 (2H, H$_6$), 1.7–2.0 (4H, H$_3$). 1.8 (3H, H$_{10}$), 2.35 (2H, H$_5$), 3.7 (1H, H$_8$), 4.05–4.3 (6H, H$_{4,7,9}$), 5.6 (1H, H$_{11}$), 6.2 (1H, H$_{12}$), [Fig. 2(b)].

The OAGMA monomer was synthesized in a similar manner by reacting equimolar ratios of oleic acid and glycidyl methacrylate in the presence of 1 wt % AMC-2 catalyst and 0.01 wt % hydroquinone inhibitor for 2.5 h at 70°C. The completion of the reaction was confirmed both by FTIR and ^{1}H-NMR as explained for the methacrylation of the dibromostearic acid (Di-BrSAGMA). ^{1}H-NMR (CDCl$_3$, 300 MHz) δ ppm: 0.9 (3H, H$_1$), 1.3 (20H, H$_2$), 1.5 (2H, H$_6$), 2.0 (4H, H$_3$).1.8 (3H, H$_{10}$), 2.35 (2H, H$_5$), 3.7 (1H, H$_8$), 4.05–4.3(4H, H$_{7,9}$), 5.35 (2H, H$_4$), 5.6 (1H, H$_{11}$), 6.2 (1H, H$_{12}$), [Fig. 2(c)].

Synthesis of VE 828 and VE 160 resins

VE 828 was prepared via methacrylation of diglycidyl ether of bisphenol A (DGEBA) (Epon 828) as shown in Figure 3. Epon 828 was purchased from Tec Epon resins and had an epoxy equivalent weight of 186 g/mol. Approximately 150 g Epon resin was reacted with 1.01
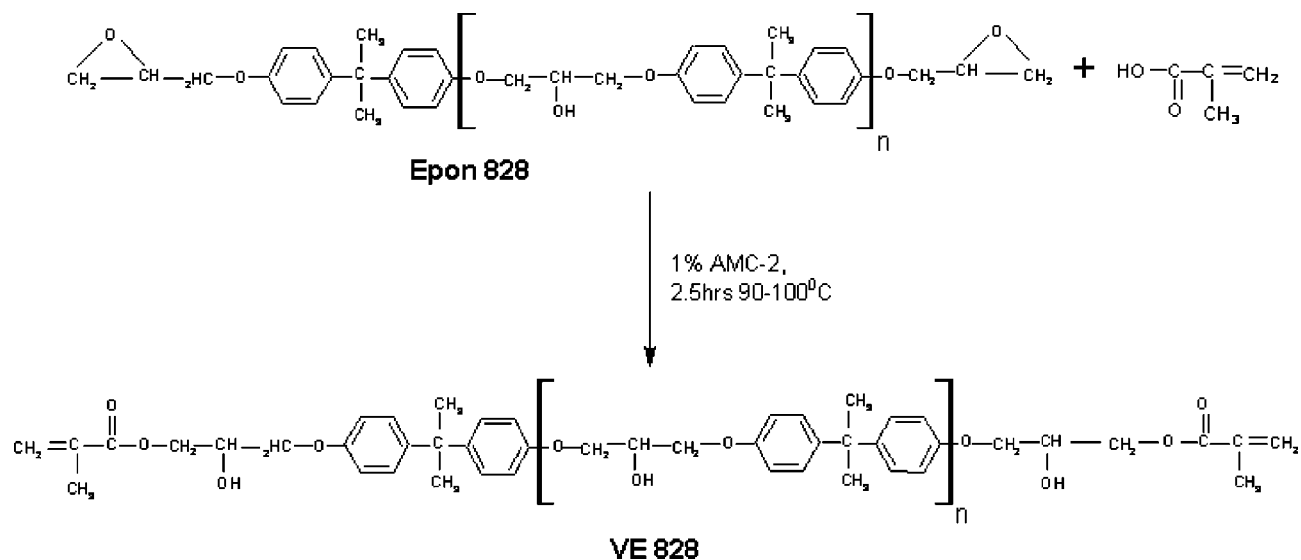
Figure 3 The synthesis of VE 828 from Epon 828 and methacrylic acid.

times the stoichiometric amount of methacrylic acid (70.05 g) necessary to convert all the epoxies to methacrylates. The reaction was run in the presence of 1 wt % AMC-2 catalyst and 0.01 wt % hydroquinone for 2.5 h at 90°C. At the end of this time an acid number titration was performed to measure the amount of free acid in the reaction mixture in accordance with the ASTM standard D1980–87. 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 and the solution was titrated with 0.5N sodium hydroxide until the solution remained
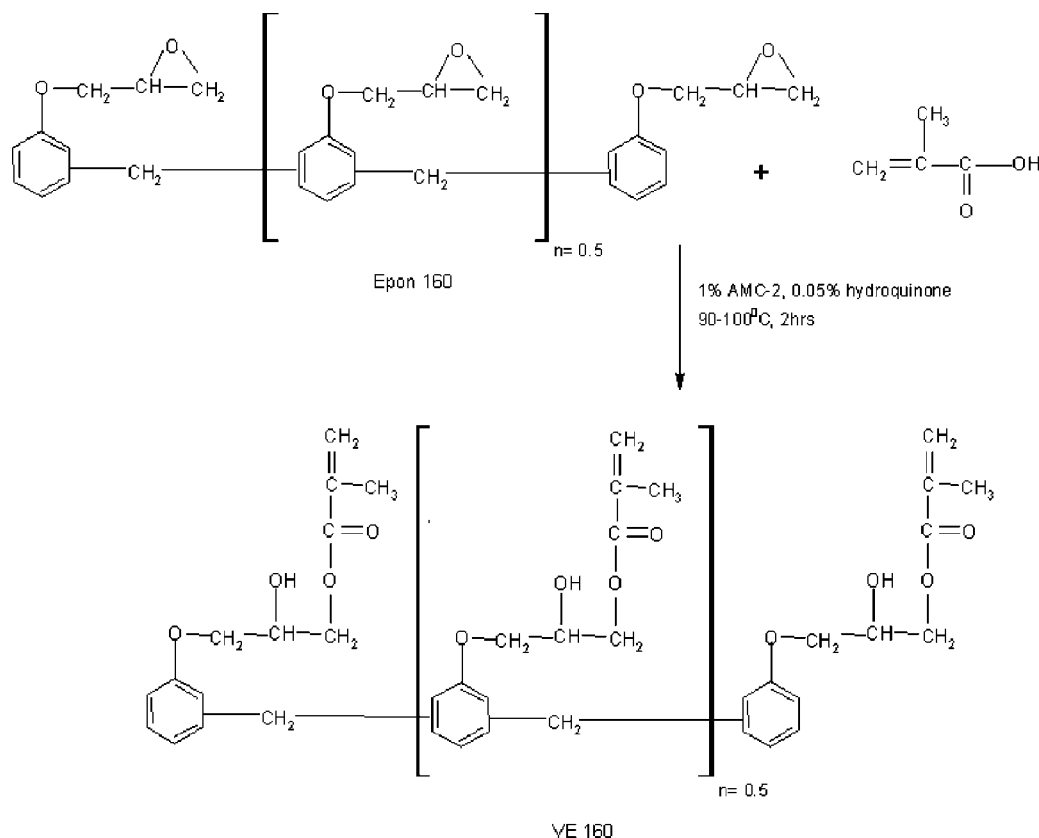
Figure 4 The synthesis of VE 160 from Epon 160 and methacrylic acid.

slightly pink in color for 30 s. The acid number was then calculated according to the following equation:

$$\text{Acid number} = \frac{VN \times MW_{\text{NaOH}}}{m}$$

where V is the volume in mL of NaOH solution used, N is the normality of the NaOH solution, and m is the VE mass in grams. An acid number (mg NaOH/g VE) of 10, corresponding to $\sim 3\%$ free acid, was the maximum allowable acid number. The acid number of the VE mixture was 6 at the end of 2.5 h. The mid-IR analysis of the product showed the disappearance of the 917 cm^{-1} epoxy peak and the presence of the 940 cm^{-1} methacrylate peak confirming the conversion of the epoxies of Epon 828 to methacrylates.

VE 160 was prepared via methacrylation of Epon 160, which is a bisphenol F/Epichlorohydrin type epoxy resin, as shown in Figure 4. Epon 160 was also received from Tec Epon resins and had an epoxy equivalent weight of 174 g/mol. For the preparation of VE 160 resin, 200 g Epon 160 resin was reacted with 1.01 times the stoichiometric amount of methacrylic acid (99.84 g) necessary to convert all the epoxies to methacrylates. The reaction was run in the presence of 1 wt % AMC-2 catalyst and 0.05 wt % hydroquinone for 2 h at 90°C. At the end of this time, the mid-IR spectrum of the product showed no epoxy peak at 917 cm^{-1} confirming the conversion of all the epoxy functional groups to methacrylates. The acid number of the VE 160 product was 4 as determined in accordance with the ASTM D1980–87.

Polymerization

For all the formulations, the total reactive diluent content of the resins was fixed at 35 or 45 wt % (65 or 55 wt % VE content). For the preparation of the VE-OAGMA-Di-BrSAGMA-styrene blends, the VE resin was first heated to 60–70°C and then the comonomers were added and mixed at RT with magnetic stirring for about 2 h. The VE was soluble in all the fatty-acid-based monomers and its styrene blends at every concentration. VE-Di-BrSAGMA, OAGMA, styrene blends were cured at RT in the presence of Trigonox 239A and cobalt naphthanate (CoNap) initiator-catalyst system. The Trigonox 239A initiator containing 45% cumene hydroperoxide was obtained from Akzo Nobel Chemicals, Chicago, IL, and the CoNap catalyst (6% solution) was obtained from Aldrich (Milwaukee, WI). After the addition of the initiator and the catalyst, the resins were poured into round plastic molds with 3 mm height and cured at RT. The VE 828 resins were cured in the presence of 1.5 wt % Trigonox 239A and 0.375 wt % CoNap. The resins containing 35 wt % Di-BrSAGMA did not cure at RT completely at the end of

24 h. This was attributed to the presence of hydroquinone used in the preparation of the Di-BrSAGMA and to the presence of bromine functional groups which may cause further inhibition effect on radical polymerization. Thus, this resin was postcured at 120°C for 2 h and 160°C for 2 h. Because a higher amount of hydroquinone was used in the synthesis of VE 160 resin (0.05 wt %) as compared to that of the VE 828 resin (0.01 wt %), higher initiator-catalyst concentrations were used to cure the VE 160 resins. The VE 160 resins using styrene and OAGMA as the reactive diluent (45 wt %) were cured in the presence of 1.5 wt % Trigonox A and 0.8 wt % CoNap. The VE 160 resins with 10–45 wt % Di-BrSAGMA content were cured in the presence of 2.5 wt % Trigonox A and 0.8 wt % CoNap. All the other VE 160 resins were cured in the presence of 3 wt % Trigonox A and 0.8 wt % CoNap.

No phase separation was observed in any of the formulations. The polymers obtained had a green color caused by the AMC-2 catalyst used in the methacrylation reaction. The polymers containing the Di-BrSAGMA had a distinct brown-green color caused by the presence of bromine. The cured samples were demolded and cut to desired dimensions for dynamic mechanical analysis (DMA).

The RT-cured VE 828 and VE 160 samples used for TGA analysis were postcured at 160°C for 2 h.

RESULTS AND DISCUSSION

Monomer viscosity

Table I shows the RT viscosities of Di-BrSAGMA monomer, its precursors and the oleic acid glycidyl methacrylate (OAGMA) analogue. As can be seen, the viscosity of Br-OA is considerably higher than that of oleic acid. The viscosity of the Di-BrSAGMA monomer shows a tremendous increase compared to the OAGMA monomer. This huge increase in the viscosity of the Di-BrSAGMA monomer is attributed mainly to the polar interactions brought to the OAGMA structure by the highly polar Br- functional groups and also to the considerable molecular weight increase caused by the addition of two Br atoms (+159.8 g). Additionally, the decrease in the level of unsaturation of fatty acids or triglycerides is expected to increase the viscosity because the unsaturation sites put kinks

TABLE I
Room Temperature Viscosities of Di-BrSAGMA and OAGMA Monomers and Their Precursors

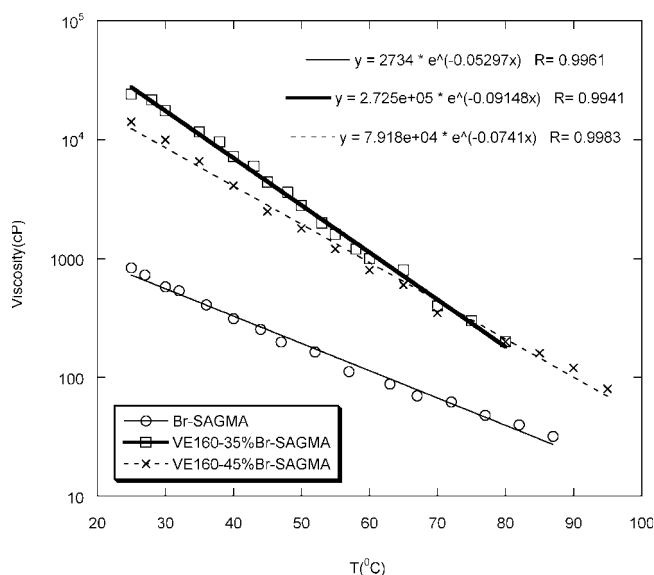| Precursor or monomer	Viscosity at 25°C (cP)
Oleic Acid	24
OAGMA	64
Di-BrOA	463
Di-BrSAGMA	834

TABLE II
Viscosities of Di-BrSAGMA Monomer with OAGMA and Styrene

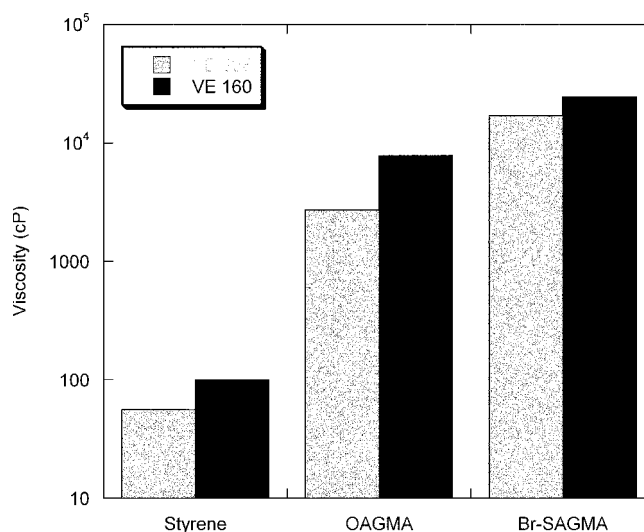| Di-BrSAGMA (wt %)	OAGMA (wt %)	Styrene (wt %)	Viscosity (cP) (25°C)
44.4	55.6	–	164 ± 4
44.4	–	55.6	8 ± 4
22.3	33.3	44.4	8 ± 4

along the fatty acid chains and increase the intermolecular spacing.

The viscosity of the Di-BrSAGMA monomer is significantly higher than the viscosity of the common reactive diluents used in VE and UPE resins (e.g., styrene (0.7cP)). Thus, this monomer has to be used in the presence of the lower viscosity styrene or the OAGMA analogue to keep the resin viscosities in a processable range at RT. As can be seen, blends of the Di-BrSAGMA with the OAGMA and styrene have viscosities suitable for use as a reactive diluent (Table II).

Alternatively, VE formulations containing Di-BrSAGMA monomer as the main comonomer can be used at higher temperatures to achieve a processable low viscosity. Figure 5 shows the viscosities of the Di-BrSAGMA monomer and the VE 160- Di-BrSAGMA resins (35 and 45 wt % comonomer) as a function of temperature. The regressed equations of viscosities versus temperature are also shown in the Figure. As can be seen, the viscosity decreased exponentially as the temperature increased. The viscosity of the VE 160 with 35 wt % and 45 wt % Di-BrSAGMA decreased to below 1000 cP at temperatures above 60°C.


Figure 6 Resin viscosity of VE 828 and VE 160 resins with a single reactive diluent in the amount of 35 wt %.

VE-Di-BrSAGMA-OAGMA-styrene liquid resin properties

The viscosities of the VE 828 and VE 160 blends with a single reactive diluent are shown in Figure 6. Styrene blends have the lowest viscosity, while Di-BrSAGMA blends have the highest viscosity. Figure 6 shows that the viscosity of VE 160 blends with a single reactive diluent were always slightly higher than the same VE 828-based blend. This is a result of the higher molecular weight and functionality of the VE 160. However, as shown in Figure 5, the viscosities of these mixtures decreased rapidly with increasing temperatures. The VE 160- Di-BrSAGMA systems reached a processable viscosity (< 1000 cP) at temperatures above 60°C.

Figure 5 The viscosities of the Br-SAGMA monomer and VE 160-Br-SAGMA resins as a function of temperature.
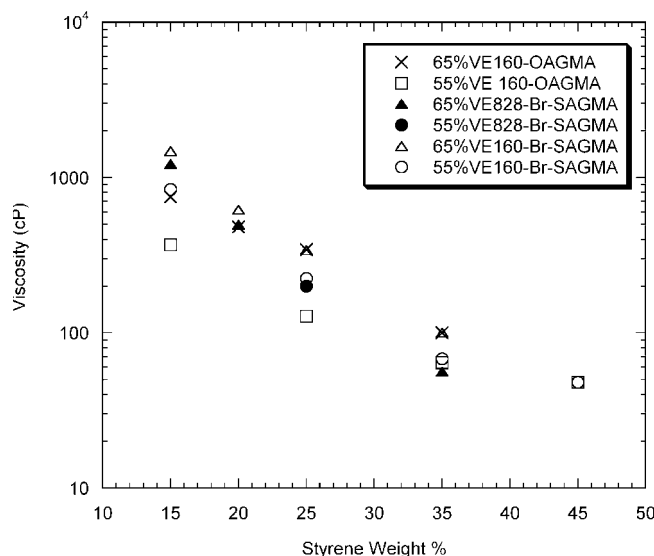

Figure 7 The resin viscosity as a function of styrene content for ternary blends of VE, styrene and either OAGMA or Br-SAGMA.

Regardless, the RT viscosities of the VE/Di-BrSAGMA and VE/OAGMA resins are much too high for liquid molding operations. In fact, even if 55 wt % vinyl ester monomer is used instead of 65 wt %, the resin viscosity is still far higher than 1000 cP at RT, which is a limit for most liquid molding operations. As a result, styrene monomer was blended into the OAGMA and Di-BrSAGMA resins to reduce the viscosity. Figure 7 shows that only 20 wt % styrene is necessary to reduce the viscosity below 1000 cP at RT. The viscosity of VE 160 ternary blends with fatty acid monomer and styrene were again slightly higher than that of VE 828 ternary blends. It is interesting to note that the effect of different fatty acid monomer type on the resin viscosity becomes fairly small. In fact, the viscosities of Di-BrSAGMA resins were only slightly higher than that of OAGMA resins for most of these ternary blends of VE, fatty acid, and styrene. This was expected because the polarity of the bromine groups and the higher molecular weight of the Di-BrSAGMA should result in a higher viscosity. The differences in the viscosities of the Di-BrSAGMA and the OAGMA resins decreased with increasing styrene content of the resins.

Polymer properties

Some of the fatty-acid-based vinyl ester samples did not have distinct loss modulus peaks. For this reason, the temperature at which the tan δ maximum occurs was used as a measure of the T_g. This value overestimates the loss modulus maximum/T_g by 10–20°C, but will be used for comparison purposes in this paper. The postcured samples exhibited significantly higher modulus and T_g values than the RT cured samples. T_g and modulus were plotted as a function of styrene
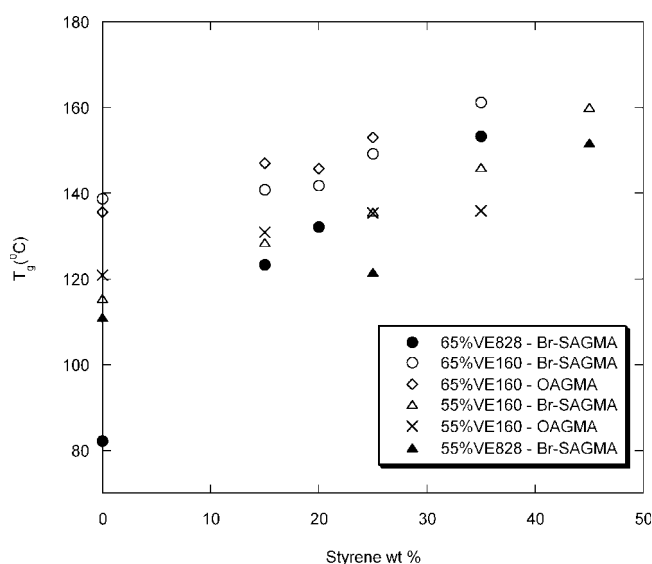
Figure 8 Comparison of the T_g (tan δ max) of the postcured OAGMA, Br-SAGMA, Styrene-VE 160 and VE 828 resins.
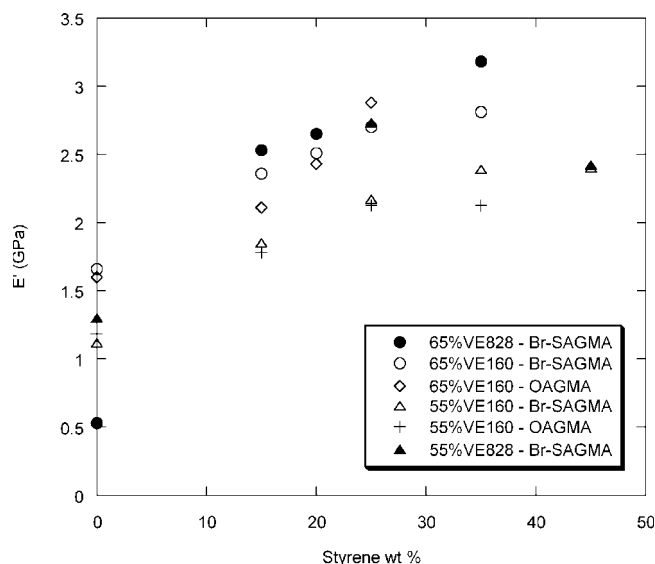
Figure 9 Comparison of the storage modulus at 30°C of the postcured OAGMA, Br-SAGMA, Styrene-VE 160 and VE 828 resins.

content for VE/fatty acid/styrene blends in Figures 8 and 9, respectively. The modulus and T_g of the polymers decreased as styrene was replaced with the fatty acid monomers. This result was expected since the replacement of the rigid aromatic structure of styrene by the flexible long alkyl chains of the fatty acid based monomers has a plasticizing effect that reduces both the modulus and T_g of the network.[9] This effect was much more pronounced for the T_g of VE 828 samples versus the VE 160 samples. The VE 160 samples also have a higher T_g for the same diluent composition and contents. This is expected because VE 160 has an average functionality of 2.5 (Fig. 4) as opposed to a functionality of 2 for VE 828 (Fig. 3). Thus the replacement of the VE 828 with VE 160 should increase the crosslink density and T_g of the resulting polymers. In addition, the backbone of the VE 160 polymers is composed of phenyl and —CH$_2$— groups, whereas the backbone of the VE 828 polymers is composed of the mixed ether of propyl and phenyl groups. The ether bonds in the latter structure should give more flexibility to this network than the VE 160 polymers which should in turn decrease the T_g of the network. This fact is confirmed by that the VE 160–35% Di-BrSAGMA polymer at 0% styrene had the largest T_g differential with the VE 828–35% Di-BrSAGMA polymer as shown in Figure 8. The glassy modulus, on the other hand, is dominated by molecular make-up, rather than the crosslink density effect. In fact, the modulus of VE 828/styrene was higher than that of VE 160/styrene. This is likely due to the less rigid bisphenol F core of VE 160 compared to the bisphenol A core of VE 828. T_g was higher for samples as the VE fraction was increased. This again was expected

because pure VE polymers have a T_g over 160°C, which is considerably higher than that of polystyrene (~ 100°C) and the fatty acid monomers.

It is possible to calculate the crosslink density, v, and the effective molecular weight between cross-links, M_c, of a thermoset polymer from experimental data using rubber elasticity theory. At higher temperatures (20–30°C above T_g), thermoset polymers behave as rubbers and the rubber elasticity theory can be applied. At small deformations, the rubber elasticity theory predicts that the modulus, E, of an ideal elastomer with a network structure is proportional to the crosslink density, the average number of crosslinks per unit volume, according to the following equation,[10]

$$E = 3vRT = \frac{3dRT}{M_c}$$

where R is the gas constant, T is the temperature, d is the density of the polymer and M_c is the effective molecular weight between crosslinks. Using this equation and the value of E in the rubbery region as determined by the DMA analysis, the crosslink densities of the VE 828 and VE160 polymers were determined. The effective molecular weights were then calculated using the experimentally determined polymer density values. M_c of VE 828 samples ranged from 225 to 453 g/mol, while M_c of VE 160 samples ranged from 180 to 440 g/mol. Overall, M_c was approximately 20–50 g/mol lower for the VE 160 samples. For example, VE 160 sample with 45 wt % OAGMA had an M_c of ~ 300 g/mol, while VE 828 with 45 wt % OAGMA had an M_c of 340 g/mol. This was expected because of the higher functionality of VE 160 versus VE 828. The OAGMA samples had M_c values on the order of 100 g/mol lower than Di-BrSAGMA samples of the same VE type, VE content and styrene content. Therefore, the crosslink density of Di-BrSAGMA samples was lower than that of OAGMA samples. For example, VE 160 sample with 45 wt % Di-BrSAGMA had an M_c of ~ 450 g/mol, while the same formulation using OAGMA had an M_c of ~ 300 g/mol. This M_c difference is on the correct order of magnitude for replacing two protons with bromine atoms (~ 160 g/mol).

Interestingly, the OAGMA and Di-BrSAGMA-based samples had similar T_g for the same styrene and VE contents. A number of effects should be considered in terms of the comparison of the glass transition temperatures of the VE polymers with the OAGMA and Di-BrSAGMA comonomers. The introduction of the polar bromine groups into the network by the Di-BrSAGMA comonomers should have an increasing effect on the T_g as compared to the OAGMA polymers, due to polar interactions between the fatty acid chains.[11] On the other hand, bromine increases the bulkiness of the pendant fatty acid chain and also decreases the crosslink density of the network. It appears that these

factors offset, thereby similar resin formulations of OAGMA and Di-BrSAGMA have similar T_g.

Commercial fire resistant VE resin formulations containing brominated DGEBA generally contain around 5–10 wt % bromine based on total resin weight for 35–45 wt % styrene contents. The resins containing 20 wt % Di-BrSAGMA, which contain about 5.5 wt % bromine based on total resin weight, show promise as an alternative to commercially available brominated vinyl ester resins. In fact, a number of formulations had a viscosity in the processable range and polymer properties that were comparable to those of standard VE resins. The results show that various formulations, including a number using significant amounts of fatty acid monomer, have T_g over 100°C and modulus over 2 GPa. VE 160 is preferred over VE 828 vinyl ester monomers because it allows use of lower styrene contents to obtain the same T_g. These formulations seem promising as an alternative to present fire resistant VE resins. If desired, the bromine content of resins with lower Di-BrSAGMA content can be increased by using partially brominated VE 828 in the formulation.

Thermal gravimetric analysis of VE 828 and VE 160 polymers

The weight loss profiles of the VE 160 resins containing various Di-BrSAGMA and styrene contents are shown in Figure 10. The total comonomer content of the resins was kept constant at 35 wt %. The weight loss profiles of the VE 828 resins with 35 wt % Di-BrSAGMA and 35 wt % styrene are shown in Figure 11. The TGA trace of the VE 160 resin with 35 wt % Di-
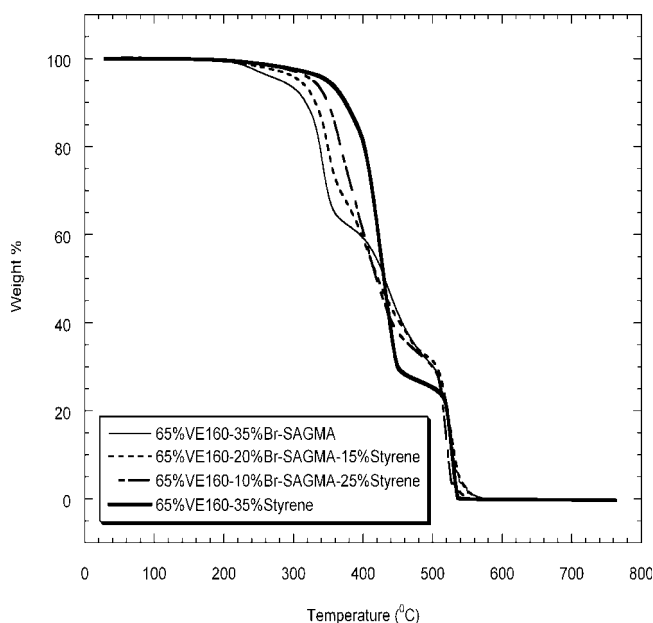
Figure 10 The TGA traces of the VE160-Br-SAGMA-styrene resins with 35 wt % comonomer content.
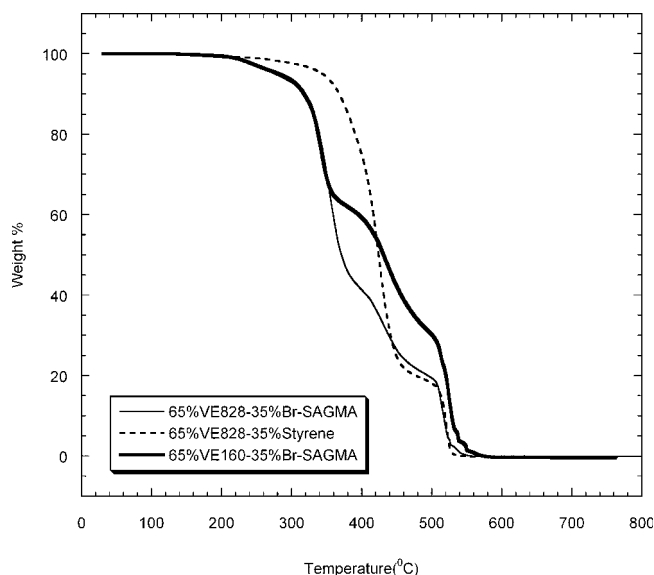
Figure 11 The TGA traces of the VE828 with 35 wt % styrene and Br-SAGMA, and VE160 with 35 wt % Br-SAGMA.

BrSAGMA is also shown in Figure 11 for a direct comparison of the thermal degradation behaviors of the VE 160 versus VE 828 polymers. For all of the resins, two decomposition temperatures were observed. The first decomposition temperature is around 400°C for the styrene polymers and shift to lower temperatures as the Di-BrSAGMA content of the resins were increased (~ 300°C). A second decomposition occurred at around 500°C for all of the resins. The 35 wt % Di-BrSAGMA-65 wt % VE resins had the lowest remaining char mass in the 250–400°C temperature range. For the Di-BrSAGMA-styrene -VE 160 resins, the remaining char content decreased with increasing Di-BrSAGMA content in this temperature range as shown in Figure 10. In the 450–500°C range, the VE-Di-BrSAGMA polymers exhibited higher char contents than the VE -styrene polymers. Figure 11 also shows that, although both VE 828 and VE 160 polymers with 35 wt % Di-BrSAGMA had similar decomposition temperatures, the char content of the VE 160 sample was considerably higher than that of the VE 828 sample after the first decomposition. This trend should be a result of the higher crosslink density of the VE 160 polymers as compared to that of the VE 828 polymers.

A comparison of the Di-BrSAGMA and OAGMA-VE 160 polymers with 35 wt % comonomer content is shown in Figure 12. The Di-BrSAGMA polymer again showed a lower first decomposition temperature and a lower remaining char yield in the 250–400°C range than the OAGMA polymer. Again the Di-BrSAGMA polymer showed a higher char yield in the 450–500°C range than the OAGMA polymer. A shift to higher

second decomposition temperature for the Di-BrSAGMA polymer was also observed. At temperatures above 600°C, these polymers did not have any remaining char.

These results can be explained by considering the mechanism of the action of halogen based fire retardants. Halogen-based flame retardants function in the vapor phase. On heating they decompose to form halogen radicals. These halogen radicals interfere with the oxidation of volatile fuels. They react with the oxygen and hydrogen radicals in the gas phase, reducing the oxygen and hydrogen concentration and extinguishing the fire.[4,12]

Table III shows the bond energies of C—halogen, C—C and C—H bonds.[4] As can be seen, the bond energies of the C—Br are much lower than those of the C—C and C—H bonds. When a halogen containing polymer is heated, the C—X (X = halogen) bond will be first to break producing a halogen radical and an organic radical. Thus, as seen in Figures 10–12, the first degradation temperature for the Di-BrSAGMA polymers is around 300°C corresponding to the temperature at which C-Br bond decomposition commences to produce the halogen radicals which prevent the oxidation reactions in the flame. For the nonbrominated polymers (OAGMA and styrene polymers) on the other hand, the first degradation starts at around 400°C, which corresponds to C—C bond breakage. Thus, the first degradation temperature shifts to lower temperatures as the Di-BrSAGMA content of the polymers was increased. The remaining char content of the Di-BrSAGMA-Styrene-VE polymer in the 250–400°C range decreased with the increasing Di-BrSAGMA
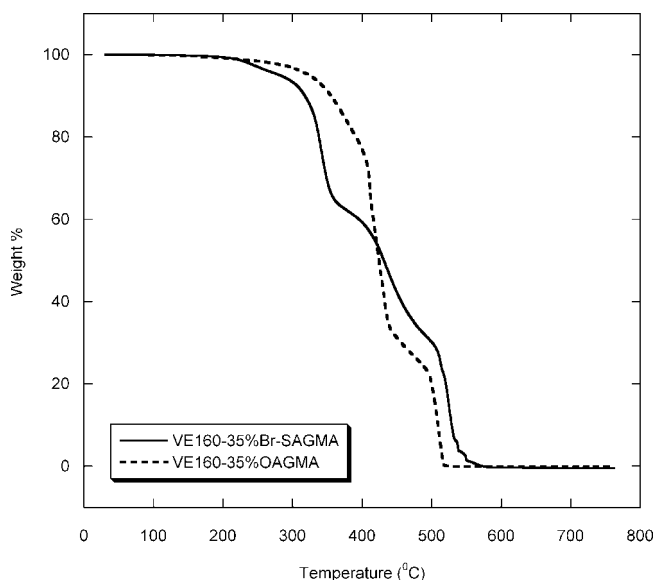
Figure 12 The weight loss profiles of the Br-SAGMA and OAGMA-VE 160 resins with 35 wt % comonomer content.

Bond	Bond energy (kJ/mol)	Temperature (°C) at which degradation commences
C_{aliph}—F	443–450	>500
C_{arom}—Cl	419	>500
C_{aliph}—Cl	339–352	370–380
C_{aliph}—Br	285–293	290
C_{arom}—Br	335	360
C_{aliph}—I	222–235	180
C_{aliph}—C_{aliph}	330–370	400
C_{aliph}—H	390–436	>500
C_{arom}—H	469	>500

concentration because the amount of volatiles produced during burning increased with increasing Di-BrSAGMA content of the resins. The second degradation that commences at around 500°C for all the polymers, on the other hand, should represent the C—H bond breakage (Table III).

Although the brominated fatty acids did not increase overall char yield in the TGA experiments, based on these results, we would expect considerable fire extinguishing power of these resins. The TGA experiments prove that the C—Br bonds break first, producing the bromine radicals that should quench a fire.

CONCLUSIONS

A novel brominated fatty acid based monomer, dibromo stearic acid glycidyl methacrylate, Di-BrSAGMA was synthesized and used in commercial VE resins as replacements for styrene in an effort to introduce fire resistance to these systems and decrease their VOC emissions. The non brominated analogue, oleic acid glycidyl methacrylate, OAGMA was also used in a similar way in the formulations for a comparison of the properties. The use of the fatty acid based monomers instead of styrene increased the viscosity of the liquid resins and decreased the modulus and T_g of the resulting polymers, as expected. However, blends of the fatty acid based monomers with styrene, at styrene contents as low as 15–20 wt % at 35–45 wt % total comonomer content in VE formulations were shown to have processable viscosities and modulus and T_g values that are comparable to those of the VE-styrene systems. In an effort to improve the T_g of the VE polymers, a Novalac type VE resin, VE 160 (average functionality = 2.5) was used instead of the bisphenol A type VE resin, VE 828 (average func-

tionality = 2). The Novalac type VE 160 resins exhibited improved T_g (+5–10°C) values with slightly decreased modulus values compared to those of the VE 828 resins, while still having processable viscosities in liquid form. The Di-BrSAGMA-VE polymers exhibited lower crosslink densities than those of the OAGMA polymers at the same comonomer concentrations, but had similar T_g and modulus values because of bromine's polarity effects, causing increased polymer segment-segment interactions. TGA analysis showed that Di-BrSAGMA polymers exhibited the lowest decomposition temperature and exhibited higher decomposition temperatures as the Di-BrSAGMA content of the resins decreased. Upon heating, the Di-BrSAGMA polymers decompose first to form bromine radicals that react with the oxygen and hydrogen radicals in the gas phase, thereby reducing their concentration to extinguish the fire.

Overall, various fire-retardant resin formulations were developed that contain brominated fatty acids. To obtain formulations that have similar liquid viscosities and polymer mechanical properties relative to styrene-based vinyl esters, the use of a novolac vinyl ester (VE 160) was required. At the same time, these partly brominated resins showed an ability to be fire-retardant while the nonbrominated resins did not.

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