

# An Investigation of Vinyl-Ester—Styrene Bulk Copolymerization Cure Kinetics Using Fourier Transform Infrared Spectroscopy

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**ABSTRACT:** A Fourier transform infrared (FTIR) spectroscopy technique was developed to investigate the effects of reaction temperature and reactant composition on the isothermal curing kinetics of commercial vinyl ester resins comprised of vinyl-ester monomer (dimethacrylate of diglycidyl ether of bisphenol A DGEBA) and styrene. This technique enables a more complete evaluation of the bulk copolymerization reaction of vinyl-ester—styrene systems by monitoring the depletion of vinyl-ester and styrene double bonds independently. The results indicate that the rate of fractional conversion of styrene double bonds is initially less than that of vinyl-ester vinyl groups. However, styrene monomer continues to react after conversion of vinyl-ester double bonds has ceased. In addition, the overall extent of conversion was found to increase with increasing isothermal cure temperature, and it was observed that higher styrene concentration enhances final conversion of vinyl-ester double bonds and not styrene double bonds. Increasing styrene monomer concentration also resulted in lowering the apparent activation energy for the reaction of vinyl groups from both monomers as characterized by an empirical autocatalytic model used to fit the conversion results for styrene and vinyl-ester double bonds independently. The results of this work demonstrate that reaction temperature and resin composition significantly affect the cure behavior of vinyl-ester resins and provide insight into the development of the resulting network structure. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1572–1582, 2000

**Key words:** cure; vinyl-ester; FTIR; bulk copolymerization

## INTRODUCTION

Free-radical cured thermosetting resin systems, such as vinyl-ester and polyester resins, have been used extensively for the manufacture of low-cost composite systems. Polyester resins have dominated commercial markets compared to vinyl-ester systems. Similarly, research concern-

ing the cure behavior and properties of unsaturated polyester (UP) resin systems has outpaced research for vinyl-ester resins. The recent pressure to obtain higher performance composites at a lower cost has motivated an interest in vinyl-ester resin systems because they possess material properties that are superior to most UP systems and yet maintain the manufacturing ease of use associated with UP systems, unlike epoxies.

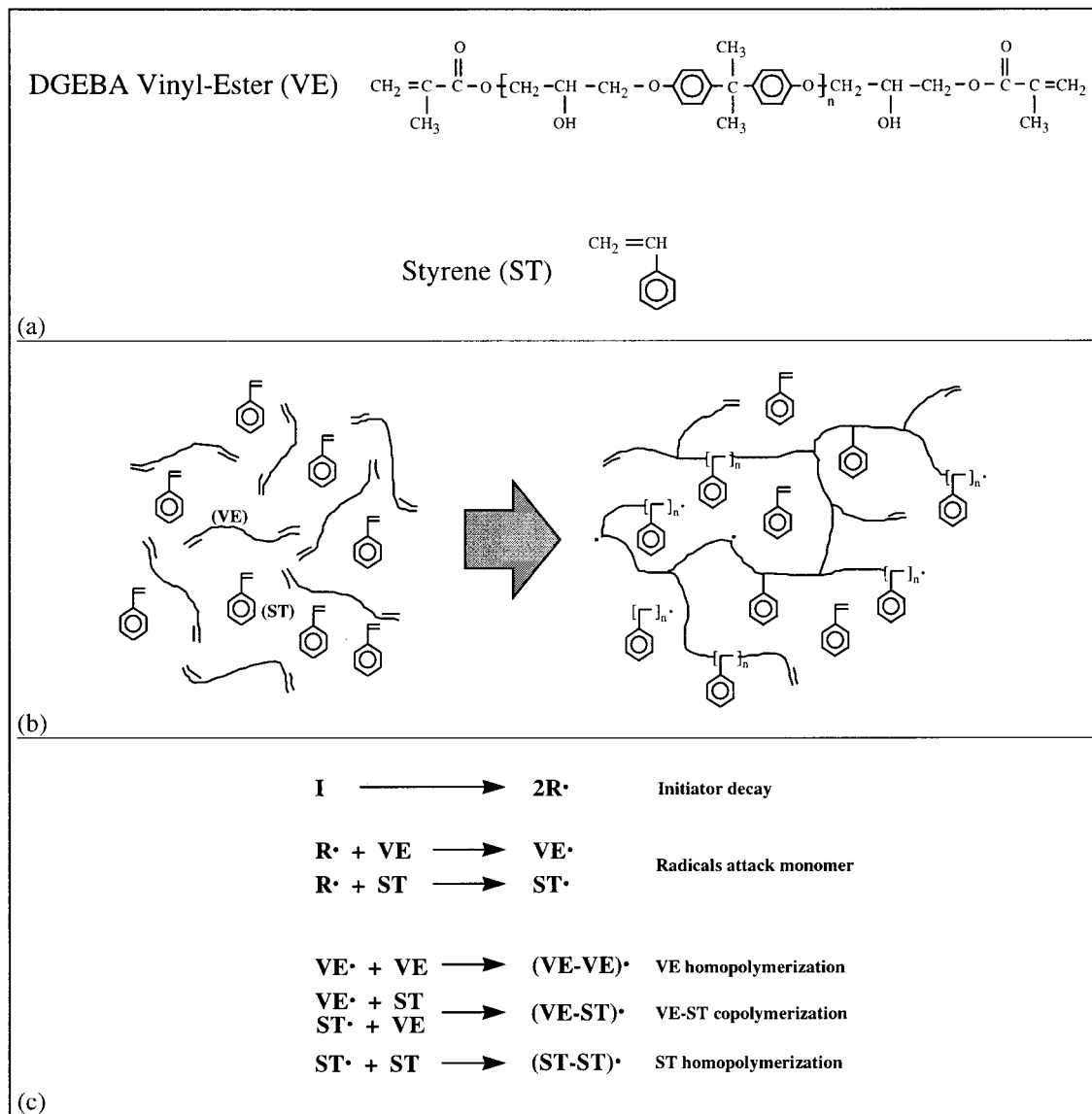
Commercial vinyl-ester resins for composite applications are comprised of difunctional vinyl-ester (VE) monomer blended with monofunctional styrene (ST) monomer. The vinyl-ester monomer is manufactured by reacting diglycidyl ether of bisphenol A (DGEBA) resins with methacrylic

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**Figure 1** (a) Chemical structure of typical DGEBA-based VE-ST resin system components, (b) a schematic representation of the VE-ST network formation showing the crosslinking capacity of the difunctional VE monomer, and (c) reactions encountered during the free radical bulk copolymerization of VE resin systems.

acid. Styrene monomer in concentrations of 30–50% by weight is typically used as a reactive diluent in such systems. As shown in Figure 1(a), the vinyl-ester monomer has two reactive vinyl end groups, while styrene has only one. Thus, the vinyl-ester monomer provides a crosslinking capacity and branch points for the formation of a network, as shown schematically in Figure 1(b), while the styrene monomer provides linear chain extension during cure. The cure of vinyl-ester resin proceeds via free-radical bulk copolymeriza-

tion initiated using appropriate peroxide initiators. Thus, as shown in Figure 1(c), reactions that contribute to the crosslinked network include homopolymerization of vinyl-ester monomer, homopolymerization of styrene, and copolymerization of vinyl-ester with styrene. A better understanding of the cure behavior of vinyl-ester resins is crucial for developing a clear understanding of vinyl-ester material performance, since it is believed that network structure development is strongly influenced by cure behavior.

Clues concerning the cure behavior of vinyl-ester resins and its relation to material properties can be gained from the more extensive literature on unsaturated polyester resins. Unsaturated polyester resins are similar to vinyl-ester resins because both systems react via a bulk free-radical chain copolymerization process, and both systems contain styrene as a reactive diluent. However, in contrast to VE monomers, which possess unsaturation only at chain termini, the reactive carbon-carbon double bonds of UP monomers are located in the backbone of the chain and are typically more than two per molecule.

The cure of UP resins has been found to result in heterogeneous morphologies characterized by the presence of spherical structures ranging in size from 10 to 200 nm.<sup>1-3</sup> Many investigators have shown that curing of UP resins results in the formation of microgels during the initial stages of reaction.<sup>1-9</sup> They define microgels as localized microregions with a higher crosslink density than the surrounding medium. It has also been suggested that the size and number of microgels depend on cure temperature and resin formulation (i.e., styrene content and degree of unsaturation), and that these factors may affect material behavior.<sup>2-7</sup>

Differential scanning calorimetry (DSC) has been used extensively for studying the cure kinetics of vinyl-ester and polyester resin systems by measuring heat evolved during reaction.<sup>10-17</sup> This technique generates cure information of a global nature, since it does not provide information concerning the rate of reaction or degree of conversion for individual species. Therefore, DSC studies yield limited insight into copolymerization reactions that lead to the final crosslinked structure. Hence, it is crucial that the depletion of the reactive double bonds in the styrene and vinyl-ester monomers be monitored separately during cure. Fourier transform infrared (FTIR) spectroscopy provides a means for measuring the depletion of reactive sites of each monomer during the cure process. The rate and extent of cure of the VE and ST reacting vinyl groups with respect to reaction temperature and monomer ratio were investigated in this work. The results indicate that these variables affect the cure behavior of vinyl-ester systems and that they, therefore, potentially affect network formation and material behavior.

## EXPERIMENTAL

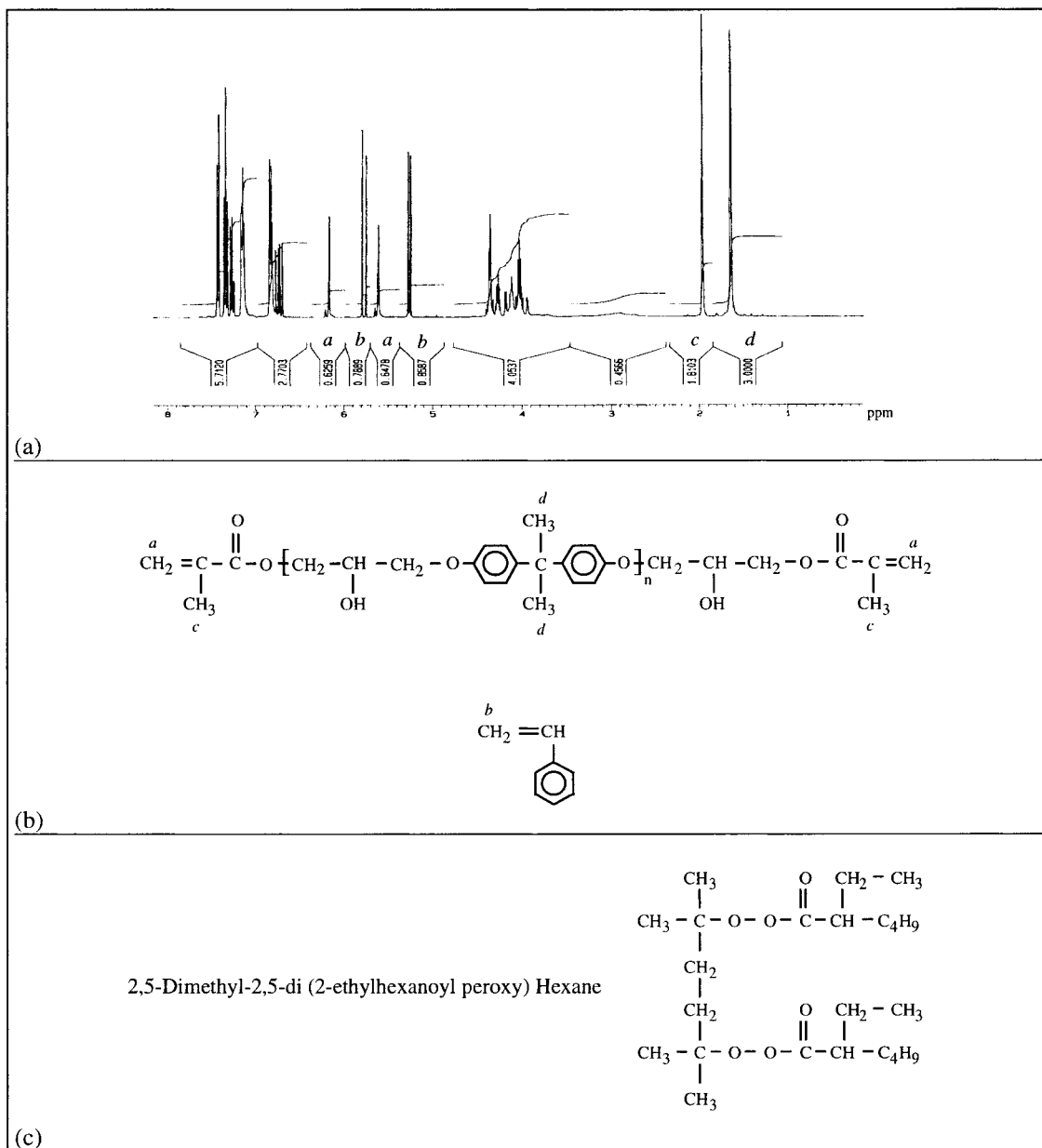
### Materials

Derakane 441-400 vinyl-ester resin was used as received from the Dow Chemical Company (Freeport, TX). Nuclear magnetic resonance (NMR) spectroscopy was used to determine styrene content of the resin and the average molecular weight of the vinyl ester monomer. The resonance peaks labeled in Figure 2(a) correspond to the protons of the methacrylate vinyl group in vinyl-ester [ $\alpha$  in Fig. 2(a), 5.60 and 6.15 ppm], of the vinyl group in styrene [ $b$  in Fig. 2(a), 5.25 and 5.75 ppm], of the methacrylate methyl endgroup in vinyl-ester [ $c$  in Fig. 2(a), 1.95 ppm], and of the methyl structopendant group of bisphenol-A [ $d$  in Fig. 2(a), 1.65 ppm]. These moieties are shown in Figure 2(b). By taking the ratio of the areas of the peak associated with the methyl group  $d$  in the repeat unit of the VE molecule to the area of the peak associated with the methyl group  $c$  at the chain ends,  $n$  was found to be 1.66, corresponding to a VE average molecular weight of 700 g/mol. In addition, by calculating the ratio of the areas of the vinyl group of each monomer and then scaling based upon the molecular weight and the number of vinyl groups per monomer, this resin was determined to contain 28% styrene by weight.

Styrene monomer, purchased from Aldrich Chemical (Milwaukee, WI), was mixed with Derakane 441-400 to achieve the desired ST-VE monomer ratios. Inhibitors and other preadditives were not removed from either the resin or the styrene. Witco USP-245 (Marshall, TX), an initiator suitable for unsaturated polyester and vinyl-ester resin systems, was added at 1.75 wt %. This difunctional peroxyester shown in Figure 2(c) was used to initiate polymerization by decomposing homolytically into free radicals. It is reported that Witco USP-245 in a 0.2M benzene solution has a half-life of 0.5 h at 90°C.<sup>18</sup>

### Apparatus

Cure monitoring experiments were performed using a Nicolet 20DXB FTIR spectrometer in the transmission mode. A small sample of resin containing initiator was compressed between two 4 × 25-mm NaCl transparent crystal plates (International Crystal Labs). A 0.025-mm Teflon® spacer was used to regulate the sample thickness and to prevent evaporation of the styrene. The



**Figure 2** (a) NMR spectra for Derakane 441-400 showing peak resonance locations and integral values, (b) protons which correspond to the NMR spectra, and (c) the chemical structure for USP-245 initiating catalyst.

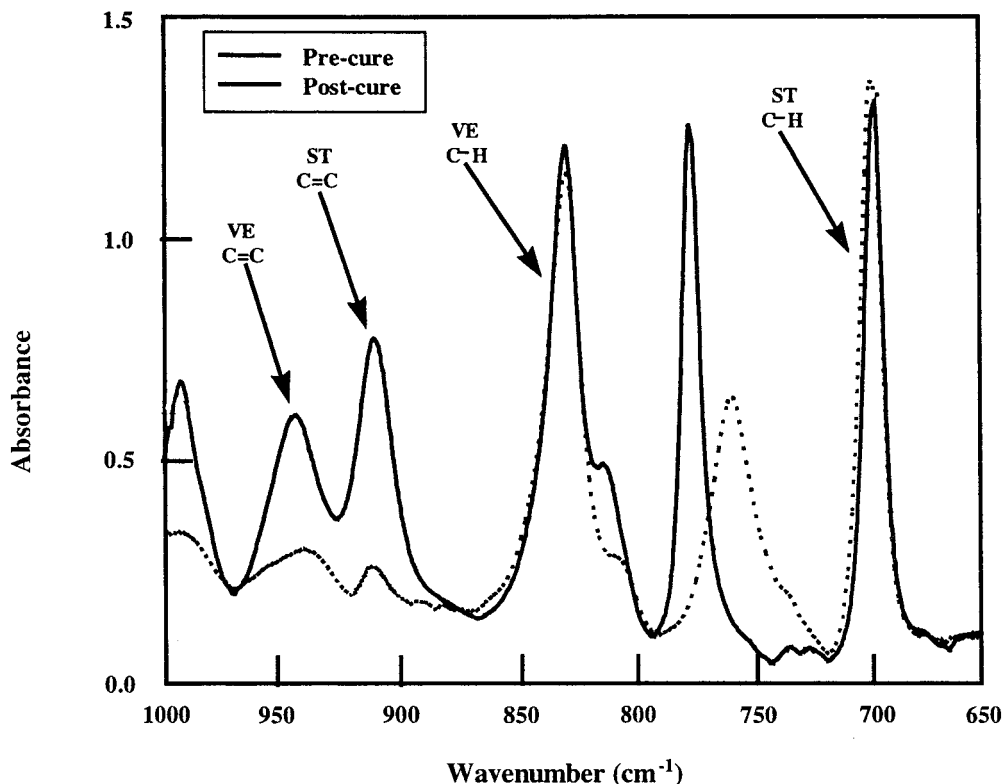
sample thickness controlled by the spacer was sufficient to provide quantitative spectral information about the bulk cure characteristics while maintaining isothermal conditions by limiting the amount of heat released by the exothermic reaction. The cell assembly was placed in an aluminum block containing two 100-W cartridge heaters designed to maintain a constant temperature through regulation by a proportional-integral-derivative (PID) controller and a thermocouple. The

cell design allowed for temperature control to within  $\pm 0.5^\circ\text{C}$  and for the cure process to be monitored in real time.

## Procedures

### Cure Monitoring by FTIR Spectroscopy

An FTIR method was developed to monitor the depletion of carbon-carbon double bonds for VE-ST systems. In FTIR spectroscopy, each vi-



**Figure 3** Deconvolution of a spectrum for a sample of Derakane 441-400 cured at 90°C showing four vibrational frequencies between 890 and 970  $\text{cm}^{-1}$ . Absorbance peaks appear at 910  $\text{cm}^{-1}$  for C=C in ST, 942  $\text{cm}^{-1}$  for C=C in VE, and 931/955  $\text{cm}^{-1}$  for VE backbone modes.

brational mode absorbs energy at a characteristic wavelength. The change in absorbance can be related to the concentration of functional groups by Beer's Law. Depletion of the reactive species in a sample can be monitored separately, provided that the absorption peaks are distinguishable from the nonreacting and product peaks. For absorbance values less than 2.0, the Deuterated Triglycine sulfate (DTGS) infrared (IR) detector response is generally linear, so a direct relationship between concentration and absorbance exists. For VE-ST systems, the depletion in double bonds of both vinyl-ester and styrene monomer indicates polymerization or cure. Figure 3 shows transmission spectra for a neat vinyl-ester-styrene system before and after cure. The absorbance at 945  $\text{cm}^{-1}$  corresponds to out-of-plane bending of carbon-hydrogen bonds in the vinyl group of the vinyl-ester monomer, while the peak at 910  $\text{cm}^{-1}$  results from wagging of  $\text{CH}_2$  in the vinyl group of the styrene monomer.<sup>19</sup> These peaks were monitored independently during cure to follow the reaction kinetics. The decrease in absorbance intensity can result from not only po-

lymerization but also physical changes, such as changes in the thickness of the sample film and/or evaporation of a component. The absorption intensities corresponding to bending of aromatic carbon-hydrogen bonds at 830  $\text{cm}^{-1}$  in VE and 700  $\text{cm}^{-1}$  in ST<sup>19</sup> were used to correct for the effects associated with evaporation and dimensional changes. Equations (1a) and (1b) were used to calculate normalized fractional conversion from FTIR absorption data of vinyl-ester and styrene double bonds respectively.

$$\alpha_{\text{VE}}(t) = 1 - \left( \frac{ABS(t)_{945 \text{ cm}^{-1}}}{ABS(t=0)_{945 \text{ cm}^{-1}}} \right) \times \left( \frac{ABS(t=0)_{830 \text{ cm}^{-1}}}{ABS(t)_{830 \text{ cm}^{-1}}} \right) \quad (1a)$$

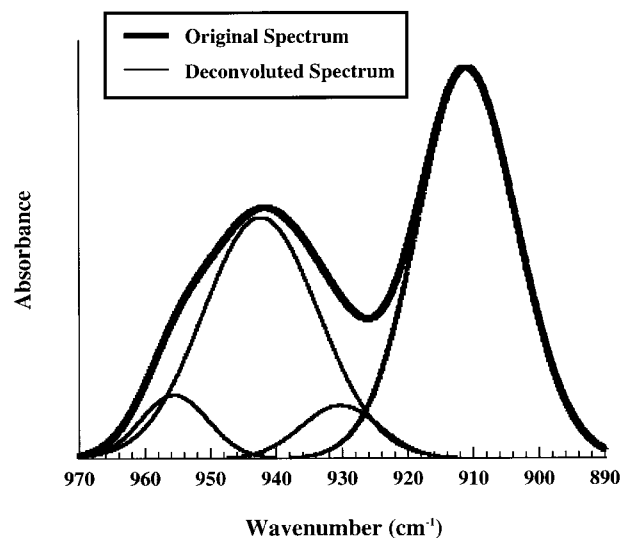
$$\alpha_{\text{ST}}(t) = 1 - \left( \frac{ABS(t)_{910 \text{ cm}^{-1}}}{ABS(t=0)_{910 \text{ cm}^{-1}}} \right) \times \left( \frac{ABS(t=0)_{700 \text{ cm}^{-1}}}{ABS(t)_{700 \text{ cm}^{-1}}} \right) \quad (1b)$$

In these equations,  $\alpha$  is the fractional conversion of double bonds associated with each monomer at time  $t$ , and  $ABS$  is the absorption intensity of the peaks at time  $t$ . For each system, the magnitudes of the relevant absorbance peaks were measured taking into consideration slight variations in the baseline.

It should be noted that the absorbance peak at  $945\text{ cm}^{-1}$  corresponding to C—H bending for the vinyl-ester monomer gradually shifts to a final value of  $941\text{ cm}^{-1}$  during cure. Since the vibrational modes in these compounds are somewhat coupled, the location of a peak can shift slightly during reaction. The conversion data for carbon-carbon double bonds of VE monomer was measured from the maximum peak height in the range of  $945$  to  $941\text{ cm}^{-1}$ .

The previous analysis of peak heights assumes that there is no contributing effect from neighboring or underlying peaks. However, it is suspected that the  $945\text{-cm}^{-1}$  peak associated with the out-of-plane bending of the C—H in the VE vinyl group might also include contributions from absorbances associated with the VE monomer and the products of the cure reaction. Indeed, the shape of the VE peak broadens at later stages of cure due to contributions from neighboring peaks. Further work including peak deconvolution and heat of reaction measurements, as described below, was necessary to quantify the uncertainty in the conversion measurement.

Deconvolution of peaks was performed using Grams/386 (Galactic Industries Corporation) and PeakFit (Jandel Scientific Software). Figure 4 shows two sets of curves for a Derakane 441-400 sample that has been cured at  $90^\circ\text{C}$ . The bold line shows the original FTIR spectrum for both VE and ST reactive groups. The thin-lined curves show the result of the deconvolution using Gaussian functions; Lorentzian and Voigt functions yield similar profiles. In addition to the peak corresponding to the styrene vinyl group at  $910\text{ cm}^{-1}$ , three separate peaks appear in the region of the VE reactive group. The most prominent of these peaks is at  $942\text{ cm}^{-1}$  and corresponds to the C—H bending frequency of the VE vinyl group. As shown in Figure 4, there is a slight difference between the fitted and unfitted peak height at  $942\text{ cm}^{-1}$ . Such differences would lead to an underestimation of the final conversion of double bonds in VE by about 5%. The smaller peaks found at  $931$  and  $955\text{ cm}^{-1}$  are believed to be from the backbone modes of VE.



**Figure 4** FTIR spectra for a vinyl-ester resin system before and after cure at  $90^\circ\text{C}$ , showing the decrease in absorbance intensities corresponding to reaction of ST ( $910\text{ cm}^{-1}$ ) and VE ( $945\text{ cm}^{-1}$ ) with reference peaks for ST ( $700\text{ cm}^{-1}$ ) and VE ( $830\text{ cm}^{-1}$ ).

DSC experiments were conducted on 441-400 resin to measure the heat released during the reaction. An average value of  $282\text{ J/g}$  was determined for the  $90^\circ\text{C}$  isothermal cure temperature. Based on published values of bond energies, the theoretical heat of reaction for full conversion of 441-400 resin is  $375\text{ J/g}$ . Thus, the overall fractional conversion of the bulk system cured at  $90^\circ\text{C}$  was calculated to be 0.76. Referring to Table I, the final fractional conversion values for 441-400 cured at  $90^\circ\text{C}$  are 0.71 and 0.80 for VE and ST, respectively. There are 1.31 ST vinyl groups per VE vinyl group; hence, the bulk fractional conversion calculated using FTIR results is about 0.75. The DSC measurement for conversion matches FTIR results closely, further supporting the accuracy of conversion measurements using the FTIR technique.

#### Experimental Conditions

FTIR was used to monitor the cure of Dow Derakane 411-400 for a number of isothermal cure temperatures and styrene concentrations. Isothermal cure temperatures ranging from  $70$  to  $110^\circ\text{C}$  in  $10^\circ$  intervals were used and thermal imaging with an AGEMA Thermovision 900 IR camera carried out to confirm the accuracy of temperature control. Derakane 441-400 vinyl-es-

**Table I Kinetic Parameters Obtained from the Autocatalytic Model for Isothermal FTIR Cure Experiments of Dow Derakane 441-400 Vinyl-Ester Resin Systems**

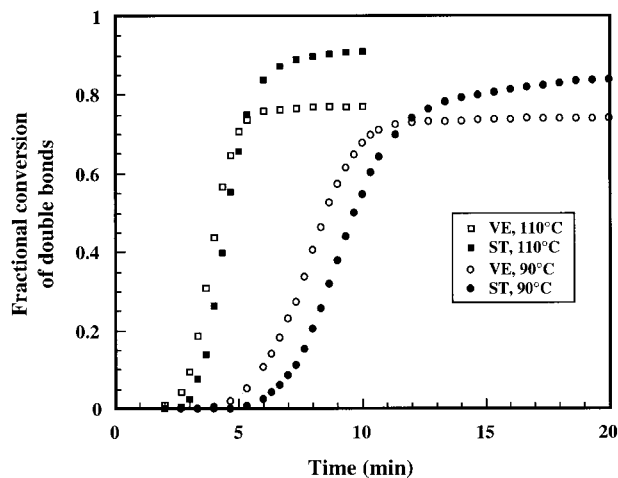
Cure Parameter	28% Styrene			37% Styrene			47% Styrene			60% Styrene		
	$\alpha_u$	k	m	$\alpha_u$	k	m	$\alpha_u$	k	m	$\alpha_u$	k	m
70°C, VE	0.65	0.09	0.85	0.68	0.40	0.93	0.73	0.26	0.88	0.72	0.31	0.88
70°C, ST	0.70	0.08	0.85	0.73	0.15	0.81	0.78	0.19	0.87	0.79	0.22	0.88
80°C, VE	0.67	0.30	0.83	0.68	0.62	0.85	0.70	0.73	0.88	0.70	0.91	0.88
80°C, ST	0.80	0.21	0.81	0.77	0.65	0.86	0.83	0.53	0.87	0.76	0.24	0.82
90°C, VE	0.71	1.13	0.85	0.74	1.36	0.90	0.75	1.63	0.89	0.78	1.17	0.84
90°C, ST	0.80	0.80	0.83	0.83	1.07	0.89	0.84	1.11	0.88	0.79	1.12	0.89
100°C, VE	0.75	2.88	0.89	0.74	3.76	0.92	0.74	3.83	0.91	0.79	2.15	0.88
100°C, ST	0.86	1.85	0.87	0.84	1.42	0.84	0.89	1.74	0.85	0.91	1.42	0.86
110°C, VE	0.74	4.81	0.92	0.76	5.51	0.91	0.77	4.27	0.92	0.80	3.77	0.89
110°C, ST	0.92	2.83	0.90	0.93	2.62	0.86	0.92	2.95	0.91	0.93	2.47	0.88

ter resin was mixed with styrene to achieve the desired VE-ST ratio. Styrene concentrations of 28 (as received), 37, 47, and 60% by weight were investigated. After the initiator was added to the resin, a small sample was placed in the curing apparatus. The time intervals for obtaining FTIR spectra varied from 30 s to 10 min, depending on the rate of cure. Twenty scans were taken per spectrum for a total acquisition time of 15 s per spectrum.

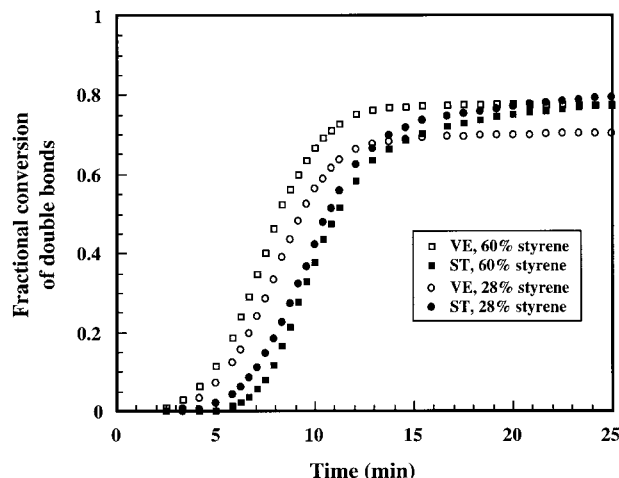
## RESULTS AND DISCUSSION

Free-radical cure of thermosetting resins generally follows three stages: initiation, propagation, and termination. Initiation occurs via the decomposition of peroxide initiator into free radicals, followed by the formation of monomer radicals. These radicals provide the active sites needed to overcome inhibition and to sustain chain reaction. During chain propagation, the polymerization rate accelerates due to diffusional limitations in the bimolecular termination reactions and, thus, results in the seemingly autocatalytic behavior known as the gel or Tromsdorff Effect. In the later stages of cure, the polymerization rate decreases rapidly due to limitations on the mobility of large molecules.<sup>20,21</sup> Thus, formation of the vitrified crosslinked network leads to entrapment of unreacted species in a crosslinked matrix and results in a final fractional conversion less than unity.<sup>22–25</sup>

Figures 5 and 6 show the fractional conversion of double bonds for both vinyl-ester and styrene monomer as a function of time. In Figure 5, the effect of temperature on conversion is shown for 47% styrene concentration. In Figure 6, the effect of styrene content on conversion is shown for a reaction temperature of 90°C. In both figures, the final conversion for VE double bonds is less than that of the styrene. It is also apparent that the reaction of VE starts before the reaction of styrene. In addition, the reaction of styrene continues after the reaction of VE terminates. As expected, an increase in temperature results in



**Figure 5** Fractional conversion of VE and ST double bonds for Derakane 441-400 with 47% styrene for isothermal cure at 90 and 110°C.



**Figure 6** Fractional conversion of VE and ST double bonds for Derakane 441-400 at 90°C for 28 and 60% styrene.

higher reaction rates and a higher final conversion for both monomers. Moreover, the addition of styrene increases VE double bond conversion but does not affect the overall ST conversion.

Empirical models have been developed to fit the cure behavior of thermosetting systems throughout the life of polymerization. Equation (2) is an expression developed by Kamal and Sourour to fit the isothermal cure behavior of resins which exhibit autocatalytic behavior.<sup>26</sup>

$$\frac{d\alpha_t}{dt} = (k_1 + k_2\alpha_t^m)(1 - \alpha_t)^{2-m} \quad (2)$$

In this expression,  $\alpha_t$  is the fractional conversion at time  $t$ ,  $k_1$  and  $k_2$  are reaction rate constants, and  $m$  is the reaction order. It should be noted that although such equations are useful for quantifying cure behavior over the entire life of the reaction, they are not intended to elucidate kinetic mechanisms of reaction.

Equation (3) is a modified form of eq. (2) that has been used extensively in the literature to fit the kinetic behavior of unsaturated polyester and vinyl ester resins.<sup>12</sup> Equation (3) neglects  $k_1$  and accounts for a final fractional conversion  $\alpha_u$ , being less than unity, as is usually the case, and thus provides more accurate replication of reaction rate data.

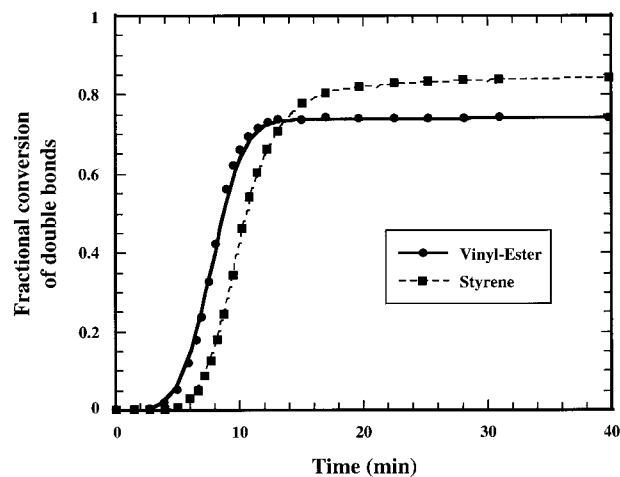
$$\frac{d\alpha_t}{dt} = k\alpha_t^m(\alpha_u - \alpha_t)^{2-m} \quad (3)$$

Equation (4) is the integrated form<sup>12</sup> of the autocatalytic eq. (3) and is particularly well suited for analysis of concentration-versus-time data obtained from FTIR spectroscopy.

$$\alpha_t = \frac{\alpha_u [kt\alpha_u(1-m)]^{1/1-m}}{1 + [kt\alpha_u(1-m)]^{1/1-m}} \quad (4)$$

Double bond concentration-versus-time data obtained from the FTIR cure experiments for both monomeric components were fit to eq. (4). Figure 7 shows cure data obtained from the FTIR spectra and the corresponding model fit to the data for 441-400 resin with 47 wt % ST cured at 90°C. The parameters for the curve-fitting process are the reaction rate constant ( $k$ ) and the reaction order ( $m$ ). These curves show that the model replicates the experimental data well. This was the case for all other conditions. Table I summarizes the resulting rate constants, reaction order, and extent of reaction for all temperature conditions and VE-ST compositions.

A number of significant conclusions can be drawn from the results in Table I. The reaction order  $m$  is 0.81–0.92, with an average value of 0.86 for both vinyl-ester and styrene monomers at all temperatures and resin compositions. Lam et al.<sup>12</sup> have also determined the reaction order of vinyl-ester resin to be relatively constant at 0.85 for isothermal cure temperatures ranging between 90 and 120°C. This result indicates that the empirical autocatalytic kinetic model adequately replicates VE-ST cure data and that the

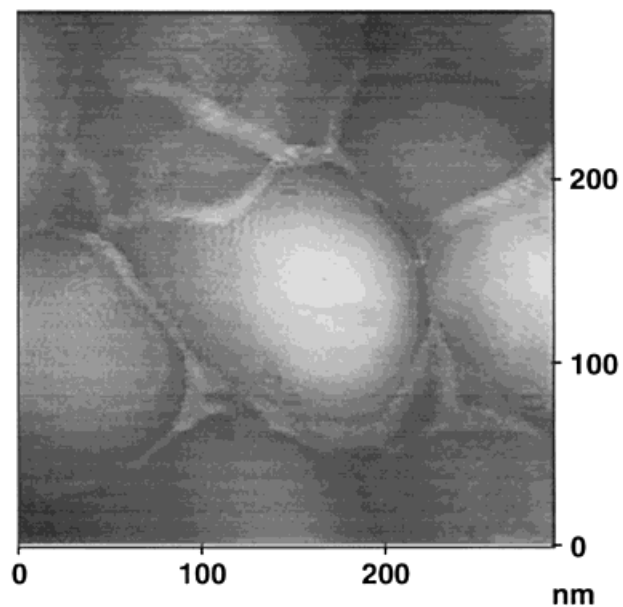


**Figure 7** Equation (4) curve fit of conversion data for 47% ST, 90°C sample.



rate constant values can be used to compare overall reaction rates.

During the initial stages of the reaction, the styrene monomer was found to react more slowly than the vinyl-ester monomer double bonds. In contrast to the methacrylate group associated with the vinyl-ester, styrene tends not to react during the early stage of cure. These observations are reflected in the generally lower overall rate constants for styrene compared to VE double bond conversion at all temperatures and compositions. It has been suggested for UP resin systems<sup>1-4</sup> that small structures known as microgels that are rich in cured UP monomer remain segregated in a medium of unreacted monomers at low conversions. As the overall degree of polymerization increases, the mobility of the larger, more encumbered UP molecules becomes limited.<sup>5,6</sup> Eventually, barriers to diffusion lead to a cessation of the UP double bond reaction, while the smaller, more mobile, styrene species may continue to react in regions surrounding the microgels.<sup>8</sup> It has been suggested<sup>7,9</sup> that this results in intermicrogel structures rich in homopolymerized styrene. A similar behavior may occur in vinyl-ester resin systems, perhaps leading to microgel structures possessing higher VE monomer content than the bulk as a result of the initial preferential reaction of VE double bonds. In fact, Figure 8 shows an atomic force microscopy (AFM) tapping mode image obtained for VE resin cured at 90°C and



**Figure 8** Tapping mode AFM micrograph of cured vinyl-ester resin showing closely packed microgels.

**Table II** Apparent Activation Energy Obtained from Arrhenius Plots of Isothermal FTIR Reaction Rate Constants for 441-400 VE Resin

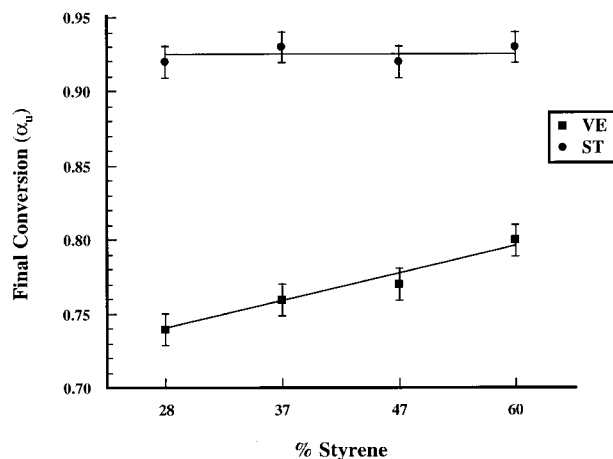
Percentage of Styrene	Activation Energy (kJ/mol)	
	VE	ST
28	112 ± 8	102 ± 8
37	77 ± 7	72 ± 12
47	80 ± 9	73 ± 6
60	64 ± 7	72 ± 12

washed with acetone, which attests to the formation of microgel structures in VE systems.<sup>27</sup> This image clearly shows closely packed microgels on the order of 100 nm in diameter.

The apparent activation energy for each monomer was determined from Arrhenius plots and is given in Table II. The values of apparent activation energy include contributions from chemical, diffusional, conformational, and other effects. As the styrene concentration increases, a significant drop in the apparent activation energy is observed. Thus, the rate constant becomes less dependent on the reaction temperature as styrene monomer is added to the system. This change in apparent activation energy with the addition of styrene is consistent with our previous assertion that higher styrene content increases molecular mobility, thus decreasing the diffusional contribution to the apparent activation energy.

Another observation is that for both the styrene and vinyl-ester components, the final extent of reaction increases with increasing cure temperature over the range of temperatures studied. As discussed previously, cessation of the reaction at less than full conversion may arise from entrapment of free radicals in the matrix. In this case, the barrier to diffusion is too great to allow the reactive species to interact during the given time period. However, an addition of thermal energy can enhance the interaction of these reactive species, resulting in further double bond conversion.<sup>22</sup>

Finally, increasing styrene concentration results in an increased ultimate conversion of VE double bonds while having little effect on the ultimate conversion of styrene, as shown in Figure 9. This effect can also be explained in terms of molecular mobility. Styrene acts as a diluent in vinyl-ester resins, facilitating crosslinking for the more encumbered vinyl-ester species. The



**Figure 9** Final conversion of monomer versus styrene content for  $T = 110^\circ\text{C}$ .

addition of styrene enables the vinyl-ester molecules to find available reactive sites after gelation occurs.

During network formation, the vinyl-ester monomer provides crosslinking capacity and branch points for the network, while the styrene monomer provides linear chain extension. Changes in the relative rates of vinyl-ester and styrene reaction could produce a significant difference in the network structure. It is expected that such differences affect the material properties, performance, and durability of the composite. Therefore, the curing kinetics provide important information about the resulting network structure, which should aid in the appropriate selection of processing conditions for such systems. This work forms the basis for ongoing research concerning the cure behavior in the region near the sized fiber and vinyl-ester resin interface.

## CONCLUSIONS

A FTIR spectroscopy technique was developed to investigate the effects of reaction temperature and composition on the curing kinetics of vinyl-ester-styrene. This technique was successfully used to obtain a more complete understanding of the bulk copolymerization of vinyl-ester-styrene systems by monitoring the depletion of vinyl-ester and styrene double bonds independently. The results indicate that the rate of conversion of styrene double bonds is initially less than that of vinyl-ester vinyl groups. However, styrene monomer

continues to react after the conversion of vinyl-ester double bonds has ceased. In addition, the overall extent of conversion was found to increase with increasing isothermal cure temperature, and it was observed that the use of higher styrene concentration results in a selectively enhanced conversion of vinyl-ester double bonds. Furthermore, AFM analysis of cured vinyl-ester specimens showed that these systems are characterized by a nodular morphology, resulting perhaps from the formation of microgels during the early stages of cure. It is clear that temperature and composition significantly affect the relative rates of vinyl group conversion, and it is expected that these differences will affect network formation and material behavior. Information solely about relative rates of reaction is not sufficient, however, to describe the connectivity of the network that forms. Thus, work is in progress to further elucidate the copolymerization behavior of this system and its relation to material behavioral characteristics.<sup>28</sup>

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