

Cure Behavior of DGEBA Vinyl Ester–Styrene Resins Near Silane-treated Interfaces

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ABSTRACT: An experimental technique using FTIR-ATR was developed for monitoring the copolymerization behavior of a DGEBA-based vinyl ester (VE) and styrene (ST) near the surface of a germanium internal reflection element. The data were compared to previously obtained bulk measurements of the cure behavior. It was found that the extent of conversion may be slightly greater for ST and slightly lower for VE near an untreated interface compared to the bulk. The cure behavior of VE–ST in the vicinity of a germanium IRE surface treated with a styryl amine silane (Dow Corning Z-6032) was also investigated. In this case the effect on the

cure was more dramatic, as exhibited by a more rapid consumption of ST compared to VE, thus resulting in a greatly reduced final conversion of VE double bonds compared to the bulk. These results suggest that, in glass fiber–reinforced composites, such sizings could significantly alter the composition of the crosslinked network in the vicinity of a fiber surface with the potential for a lower T_g interphase being formed that is rich in homopolymerized styrene. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2784–2792, 2006

Key words: interface; free radical cure; silane

INTRODUCTION

Previous work has investigated the cure of vinyl ester (VE) resins using FTIR in transmission mode.^{1–3} The results of this work provide a good understanding of the cure behavior of such systems in the bulk. However, it is well known that, as a result of fiber–resin interactions in a composite, the region near a fiber–resin interface can have dramatically different properties compared to those of the bulk matrix,⁴ thus affecting the performance of the overall composite. These differences arise from chemical and physical interactions that can locally influence cure behavior and network formation. In glass-reinforced VE composites it is believed that these changes are partly a result of sizings, or silane-containing coatings, which are applied to the fiber surface.⁵ In this investigation, experiments were conducted to examine the effect of silane coatings on the cure of VE resin using attenuated total reflectance (ATR) spectroscopy.

Several researchers have studied the effect of sized and unsized glass fibers on the cure of UP and VE resin systems.^{5–7} Ishida and Koenig⁷ noted that bare E-glass fibers inhibit the cure in unsaturated polyester (UP) resins. They described this effect as a result of a charge transfer process between free radicals in the resin and inorganic oxides on the fiber surface. Essen-

tially, polymer radicals are deactivated at the surface, leading to a decrease in free radical concentration and an increase in unreacted double bonds near the interface. Lee and Han⁶ investigated the cure of UP resin near sized and unsized glass fibers and particulates. They observed an enhanced rate and extent of cure for the resin with a silane-treated glass versus untreated glass. Palmese et al.⁵ have suggested that the adsorption of inhibitors onto sized fiber surfaces is responsible for this behavior. It is expected that such changes in cure behavior will lead to an interphase with significantly different properties to those of the bulk.

In the growing market for glass fiber–reinforced thermosetting composites, silane coupling agents are used to improve the bond strength between the glass fiber and the thermosetting matrix. These coupling agents are thought to provide a stable bond between the inorganic fiber surface and the organic resin matrix. This bond not only improves mechanical strength but also the resistance to extreme environmental conditions, such as prolonged moisture exposure and thermal cycling. Silane coupling agents form chemical bonds with inorganic surfaces, such as glass, aluminum, and other oxide-coated materials, through condensation reactions. The silane coupling agent is initially converted to a silanol by hydrolysis. The silanol groups of the coupling agents react with the hydroxyl groups of the inorganic substrate surface and release water, as shown in Figure 1. Silanol groups are then capable of hydrogen bonding or covalent bonding to adjacent silanol groups. The silane molecules also contain organofunctional groups designed to bond covalently with a reacting resin system. This en-

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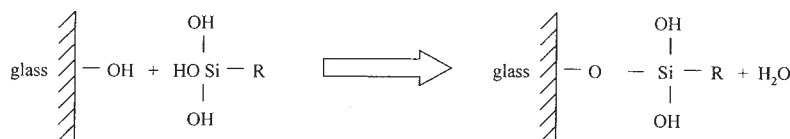


Figure 1 Schematic showing typical condensation reaction of silane coupling.

ables a silane layer to adhere to the surface and makes it capable of reacting with the resin matrix. More recently, it has been shown that the silane layer may form a crosslinked network that, in conjunction with the curing resin system, defines an interphase zone in the system.⁸

For effective coupling to occur between the resin and silane, the silane organofunctional groups must be compatible with reactions that occur during cure in the resin. For example, in the case of UP and VE resin systems that cure by a free-radical chain growth polymerization mechanism, a silane with styryl or methacrylate functional groups would participate in reaction with these resins and improve adhesion. To improve adhesion with a broad range of thermosetting resins and elastomers, coupling agents that also include amine functionality are often used.⁹

Attenuated total reflectance is a useful technique for studying molecular changes near interfaces.¹⁰ In FTIR-ATR spectroscopy, light is introduced to an internal reflection element (IRE) with a high refractive index to guide an infrared wave. When an absorbing medium, such as resin, is placed in contact with the IRE, the intensity of the infrared beam attenuates during internal reflections between crystal surfaces as a result of an evanescent wave that transmits a short distance into the resin. This wave decays exponentially as it penetrates the medium. The schematic diagram in Figure 2 shows the depth of penetration, d_p , as the distance from the IRE crystal surface where the amplitude of the evanescent wave reaches a fraction of e^{-1} of its interfacial value.¹¹ The depth of penetration, d_p , is given by eq. (1)

$$d_p = \frac{\lambda}{2\pi \left(\sin^2 \theta - \left(\frac{n_2}{n_1} \right)^2 \right)^{1/2}} \quad (1)$$

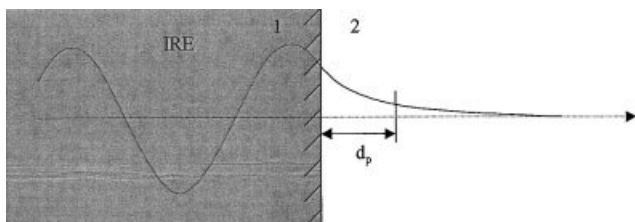


Figure 2 Schematic showing the exponential decay of the evanescent wave to the characteristic length d_p , the depth of penetration.

where λ is the infrared wavelength, θ is the angle of incidence, and n_1 and n_2 are the refractive indices of the IR crystal and resin sample, respectively.

The advantage of ATR is that it enables measurement of interfacial molecular behavior. For VE resin, the depth of penetration for ATR is only a few microns, depending on the vibrational frequency of the infrared beam and the choice of the IRE. Moreover, the evanescent wave intensity decays exponentially with distance from the interface thus giving significantly greater weight to the absorption of material closest to the interface. With transmission, the IR pathlength is controlled by the thickness of a spacer. In our previous work, a 25- μm spacer was used.¹ Although small, this makes transmission suitable for studying bulk behavior and ATR useful for examining interfacial behavior. While it is suitable for examining the cure behavior in the interphase, ATR does have drawbacks.

Unlike transmission, the effective pathlength varies with wavenumber for ATR. Therefore, care must be used when comparing molecular information generated from spectral peaks at opposite ends of the spectrum. In addition, the signal-to-noise ratio of the spectral peak measurement can be very low for ATR spectroscopy. Due to the high refractive index of the crystal, most of the infrared light never enters or leaves the crystal at the crystal-air interface. Also, elevated temperatures can lead to opacity in the IRE due to its conductivity. These factors, along with poor alignment and microscopic scratches on the IRE, result in a signal throughput much lower than that of the open beam. Therefore, steps must be taken to improve the quality of spectra. One way this can be accomplished is by increasing the number of scans during the collection of spectral data. Another way to optimize spectral quality is to increase the interaction between the sample and the evanescent wave. By using long and thin IR elements, and with greater sample contact, the number of internal reflections can be increased and sample interaction can be maximized.

In this study, the curing kinetics of VE resin obtained from FTIR-ATR will be compared to those of transmission experiments reported earlier.¹ The objective of this work is to compare the cure behavior of neat VE to that perturbed by the presence of a solid interface and to evaluate the potential influence of silane surface treatment.

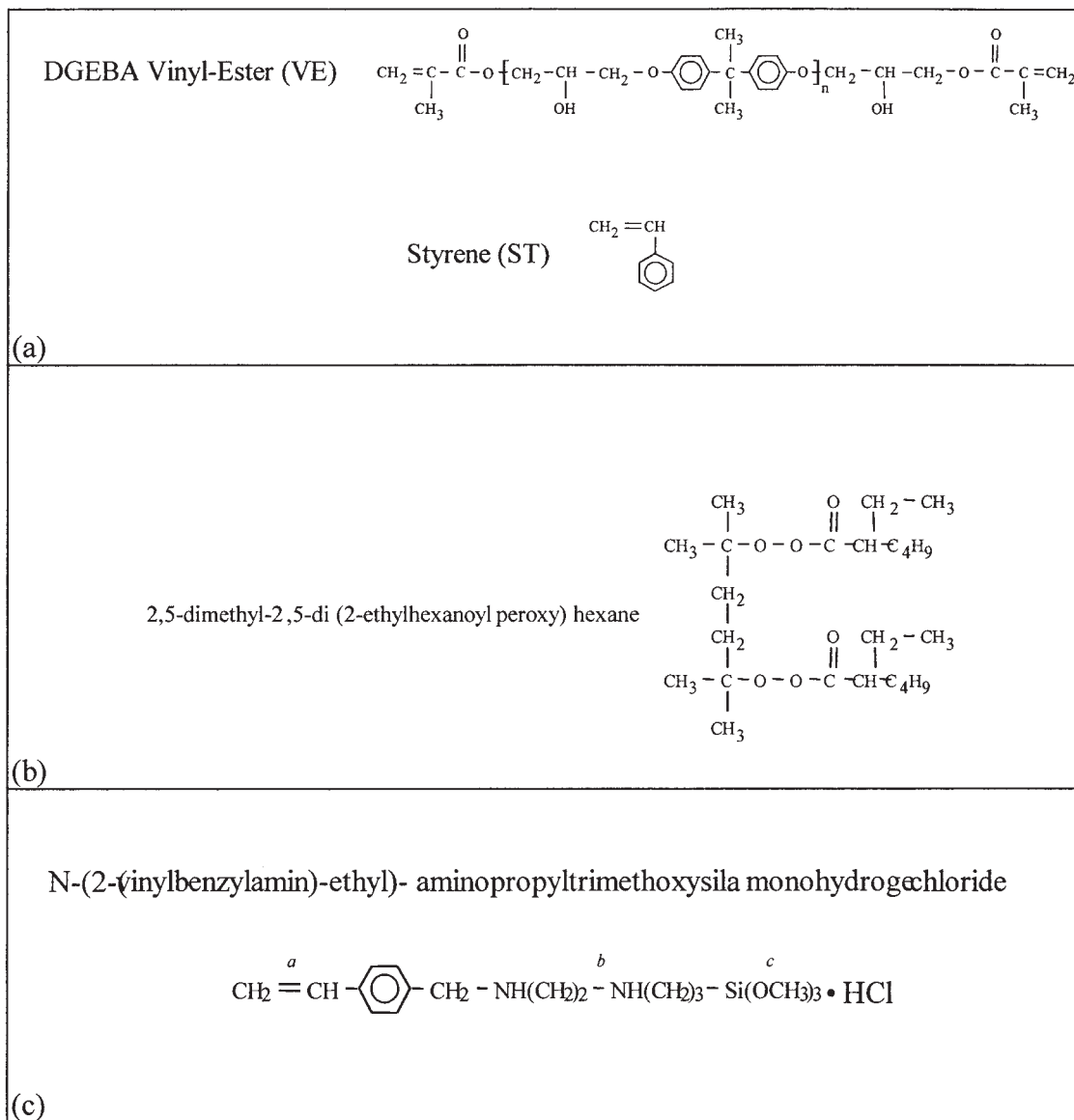


Figure 3 (a) Chemical structure of typical DGEBA-based VE-ST resin system components, (b) chemical structure for USP-245 initiating catalyst, and (c) chemical structure of Z-6032 silane showing vinylbenzyl, *a*, and amine, *b*, functional groups and trimethoxysilyl, *c*, inorganic group.

EXPERIMENTAL

Materials

Derakane 441-400 vinyl-ester resin was used as received from Dow Chemical Company. Figure 3(a) shows the chemical structure of the two reactive monomers, vinyl-ester and styrene, comprising 441-400 VE resin. NMR experiments indicate Derakane 441-400 contains 28% ST monomer by weight. Witco USP-245, an initiator suitable for initiating the polymerization reaction of UP and VE resin systems, was added at 1.75 wt %. This difunctional peroxyester is shown in Figure 3(b). Figure 3(c) shows the chemical structure for Dow Corning Z-6032, a silane coupling agent suitable for bonding inorganic surfaces to VE

and other unsaturated resins. Z-6032 silane contains two organic functional groups, vinylbenzyl (*a*) and amine (*b*), and a trimethoxysilyl (*c*) inorganic group. Because of the amine group, Z-6032 silane is soluble in water (this is necessary to sustain the hydrolysis reaction). Z-6032 sizing, as received from the manufacturer, contains 40 wt % methanol. Before use, the silane solution must be diluted with additional solvent and adjusted in pH with acetic acid. As recommended by the manufacturer, Z-6032 silane solution was mixed with distilled water at a ratio of 4 parts Z-6032 per 1 part water. Methanol was added to achieve a mixture of 3% active ingredient with the pH adjusted to 4.5 using glacial acetic acid. After stirring for 1 h, a relatively stable solution was formed, since the revers-

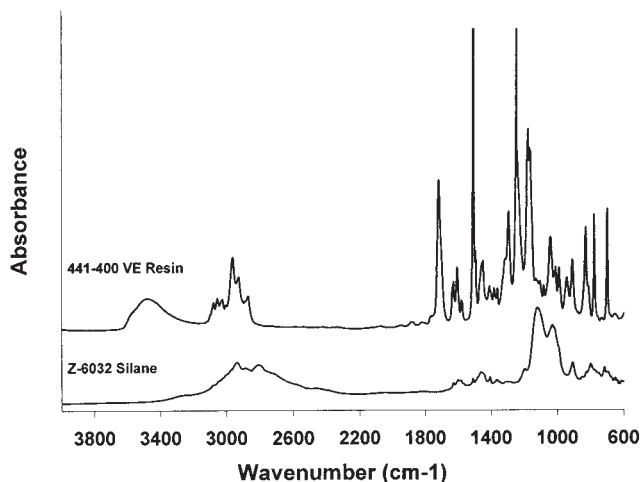


Figure 4 FTIR spectra for Derakane 441–400 VE resin system in transmission mode and condensed Z-6032 silane in ATR mode.

ibility of the reaction prevented long chain growth of silanol. Figure 4 shows the full IR spectra from 4000 to 600 cm^{-1} for Derakane 441–400 with catalyst (in transmission mode) and condensed Z-6032 silane (in ATR mode). The refractive indices¹² of 441–400 VE resin and Z-6032 silane are 1.45 and 1.40, respectively.

Apparatus

Cure monitoring experiments were performed using a Nicolet 20DXB FTIR spectrometer in ATR mode using a liquid nitrogen cooled MTC detector. The ATR cell used in these experiments was designed to provide the maximum signal-to-noise ratio while maintaining isothermal conditions by limiting the amount of heat released by the exothermic reaction. The cell consists of two Teflon® boats, each with tapped inlet and outlet ports. As shown in Figure 5, these boats were compressed on either side of an IRE, thus maximizing the contact area while limiting the effect on noise. Other factors that enhance the signal in the IRE are a high angle of incidence and a narrow thickness, since both increase the number of internal reflections in the crystal. For this experiment, a Harrick Scientific trapezoidal germanium crystal with a 60° incident angle, 50 mm \times 10 mm \times 1 mm dimensions, and a refractive index, n_1 , of 4.0 was used. In addition, a 250- μm silicone gasket was placed between the Teflon® boats and the crystal to provide a region for resin to cure in intimate contact with the crystal. The gasket provided an adequate seal and was sufficiently thin to limit heat generated by the exothermic reaction. The external compression plates were equipped with two 15-W cartridge heaters and designed to maintain a constant temperature through regulation by a PID controller and a thermocouple. The cell design enables temper-

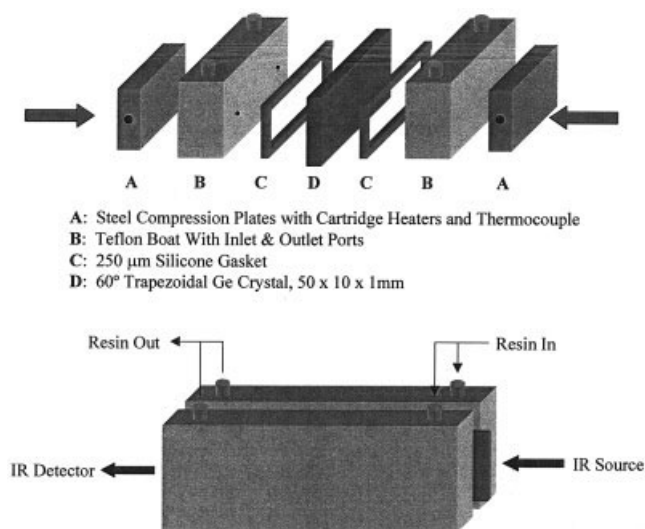


Figure 5 FTIR-ATR experimental cell used for monitoring the curing process of vinyl-ester resins near an interface.

ature control to $\pm 2^\circ\text{C}$ while allowing the cure process to be monitored in real time.

Procedures

Spin coating

For studying the effect of sizing on the cure of VE resin near the interface, ATR crystals were coated with the silane solution by spin coating. The silane solution was first applied to a clean crystal and allowed to stand for 3 min. The crystal was then spun for 25 s at 1000 RPM to remove excess solution. This procedure consistently produced a golden-colored film that adhered to the crystal. Electron microscopy indicates that a film with this color and refractive index corresponds to a thickness of about 0.15 μm .¹³ After spin coating, the crystal was dried for 10 min at 90°C. The same procedure was applied to the other side of the crystal, however, it was dried for 30 min. The FTIR-ATR spectrum in Figure 6 shows the result of spin coating the silane solution onto an IRE. The resonance

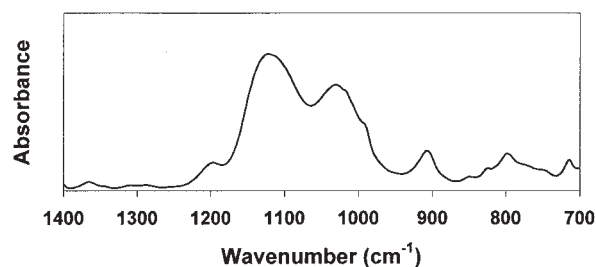


Figure 6 FTIR-ATR spectrum showing condensed Z-6032 silane, the result of spin coating onto an IRE.

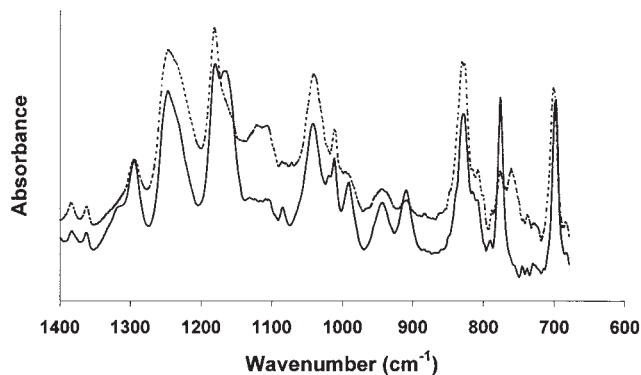


Figure 7 FTIR-ATR spectra for a VE resin system at early (—) and late (---) stages of cure at 80°C showing the decrease in absorbance intensities corresponding to reaction of ST (910 cm^{-1}) and VE (945 cm^{-1}) with reference peaks for ST (700 cm^{-1}) and VE (830 cm^{-1}).

frequency 1120 cm^{-1} corresponds to the Si-O-Si functional group, indicative of a fully condensed system.¹⁴

Cure monitoring by FTIR spectroscopy

An FTIR method for monitoring the depletion of carbon-carbon double bonds in VE-ST systems was introduced in a previous communication.¹ As with the transmission experiments, the VE resin spectra in ATR are referenced from a background of the cell at temperature. When a sized interface is used, the background spectrum is generated with the silane coating, so that the spectral data includes only the contribution from the resin system.

Figure 7 shows spectra at early and late stages of cure for VE resin using FTIR-ATR. The peak locations are similar when compared with transmission experiments, however, the quality of the spectra is significantly reduced in ATR due to low signal throughput. Nevertheless, the characteristic wavelengths of the reactive species are the same in both techniques. The absorbance at 945 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 cm^{-1} results from wagging of CH_2 in the vinyl group of the styrene monomer.¹⁵ The absorption intensities corresponding to bending of aromatic carbon-hydrogen bonds at 830 cm^{-1} in VE and 700 cm^{-1} in ST¹⁰ were used to normalize any effects associated with evaporation and dimensional changes. Equations (2a) and (2b) were used to calculate normalized fractional conversion of vinyl-ester and styrene double bonds from FTIR absorption data, respectively.

$$\alpha_{\text{VE}}(t) = 1 - \left(\frac{ABS(t)_{945 \text{ cm}^{-1}}}{ABS(t=0)_{945 \text{ cm}^{-1}}} \right) \left(\frac{ABS(t=0)_{830 \text{ cm}^{-1}}}{ABS(t)_{830 \text{ cm}^{-1}}} \right) \quad (2a)$$

$$\alpha_{\text{ST}}(t) = 1 - \left(\frac{ABS(t)_{910 \text{ cm}^{-1}}}{ABS(t=0)_{910 \text{ cm}^{-1}}} \right) \left(\frac{ABS(t=0)_{700 \text{ cm}^{-1}}}{ABS(t)_{700 \text{ cm}^{-1}}} \right) \quad (2b)$$

In these equations, α 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 absorption peaks were measured taking into consideration slight variations in the baseline.

Using FTIR-ATR in the region between 700 and 945 cm^{-1} , the depth of penetration of the evanescent wave into VE resin for a clean, 60° germanium crystal is about 2 to 2.5 μm . Moreover, the depth of penetration is about the same for VE resin using a 60° Ge crystal coated with Z-6032 silane, since the refractive indices of VE resin and Z-6032 silane are similar.

Since Z-6032 silane contains a styryl group, it is important to evaluate its contribution to the frequency at 910 cm^{-1} . Any depletion of vinyl double bonds in the silane should not be misconstrued as conversion of ST double bonds in the resin. This problem was approached by performing analytic calculations based on the absorption intensities of the evanescent wave in an effort to bound the contribution of Z-6032 to the resonant frequency at 910 cm^{-1} .

The technique for bounding the contribution of the styryl group in silane involves computing the relative intensities of the vinyl groups based on the total number of vinyl groups present in each region. The thickness of the silane film is 0.15 μm and the depth of penetration into the resin boat is 2.2 μm at 910 cm^{-1} . By integrating the exponential decay of the evanescent wave from 0 to 0.15 μm and 0.15 to 2.2 μm for the silane and resin regions, respectively, the relative intensity of the absorption measurements were determined. This computation suggests that the spectral information gained from the resin region is 5.4 times greater than that from the silane region. The number of double bonds associated with styryl groups in each region must then be determined. Since there is one vinyl group per molecule for both the silane and ST monomer, calculating the number of silane and styrene molecules in each region can be used to determine the number of double bonds. By multiplying the density by the volume of each region and dividing by the molecular weight of each species, the number of moles can be computed. The ratio of the molecules of styrene to silane is 12.4, indicating that there are 12.4 times more styryl double bonds in the resin region than in the silane film. Since the resin also has an absorption weighting factor of 5.4, the overall contribution to the resonant frequency at 910 cm^{-1} from styrene C=C double bonds would be 67 times greater than the contribution from silane C=C double bonds. Therefore, it is reasonable to assume that depletion of

TABLE I
Kinetic Parameters Obtained from the Autocatalytic Model for Isothermal Cure Experiments of Dow Derakane 441-400 Vinyl-Ester Resin Systems Comparing FTIR in Transmission,^a FTIR-ATR without Surface Treatment, and FTIR-ATR with Z-6032 Surface Treatment^b

	Transmission			ATR			Z-6032 ATR		
	α_u	k	m	α_u	k	m	α_u	k	m
70°C VE	0.65	0.09 (0.01)	0.85 (0.01)	0.58	0.07 (0.01)	0.96 (0.03)			
ST	0.70	0.08 (0.01)	0.85 (0.01)	0.77	0.05 (0.01)	0.80 (0.02)			
80°C VE	0.67	0.30 (0.02)	0.83 (0.01)	0.65	0.29 (0.03)	0.91 (0.02)	0.24	0.03 (0.01)	0.56 (0.04)
ST	0.80	0.21 (0.01)	0.81 (0.01)	0.83	0.16 (0.02)	0.87 (0.01)	0.74	0.13 (0.02)	0.94 (0.02)
90°C VE	0.71	1.13 (0.04)	0.85 (0.01)	0.69	1.22 (0.08)	0.81 (0.02)			
ST	0.80	0.80 (0.02)	0.83 (0.01)	0.84	0.91 (0.05)	0.86 (0.01)			
100°C VE	0.75	2.88 (0.13)	0.89 (0.01)						
ST	0.86	1.85 (0.14)	0.87 (0.01)						
110°C VE	0.74	4.81 (0.27)	0.92 (0.01)						
ST	0.92	2.83 (0.31)	0.90 (0.01)						

^a Results from Brill et al.¹

^b Values in parentheses are SE.

the resonance frequency at 910 cm⁻¹ is primarily due to the conversion of styrene double bonds in the resin.

Experimental conditions

The cure of Derakane 441-400 vinyl-ester resin was monitored using FTIR-ATR. For the unmodified crystal surface, constant temperatures of 70, 80, and 90°C were used, with an AGEMA Thermovision 900-IR Camera confirming the accuracy of temperature control. For the experiments with a silane-coated surface, an 80°C reaction temperature was investigated.

After the curing apparatus stabilized at the desired reaction temperature, the resin was mixed with initiator. With two syringes, a small sample was injected into the inlet port of each boat simultaneously, and the data acquisition was initiated. Each absorption spectrum was generated from 30 scans (approx. 30 s), and the time at which absorption spectra were taken varied from 1 to 10 min depending on the rate of cure.

RESULTS AND DISCUSSION

Noncoated ATR versus transmission

The isothermal cure of VE resin near an unsized interface has been examined using FTIR-ATR for 70, 80, and 90°C. In addition, the bulk curing behavior of VE resin has been investigated with FTIR in transmission for a temperature range of 70 to 110°C. A modified form¹⁶ of an empirical model, originally developed by Kamal and Sourour,¹⁷ was used to generate quantitative kinetic information for the isothermal curing experiments of thermosetting resins. Equation 3 is well suited for analysis of concentration versus time data obtained from FTIR spectroscopy,

$$\alpha_t = \frac{\alpha_u [kt\alpha_u(1-m)]^{\frac{1}{1-m}}}{1 + [kt\alpha_u(1-m)]^{\frac{1}{1-m}}} \quad (3)$$

where α_t is the fractional conversion at time t , α_u is the final conversion, k is the reaction rate constant, and m is the reaction order.

Double bond concentration versus time data obtained from the FTIR cure experiments for both monomeric components were fit to eq. (3). Table I summarizes the resulting rate constants and extent of reaction for all temperatures for both transmission and ATR experiments.

As with transmission, the final extent of conversion of VE and ST double bonds using ATR increased with increasing reaction temperature. It is thought that the final fractional conversion of double bonds in cured ST-based thermosetting systems is often less than unity due to entrapment of unreacted species in a vitrified crosslinked network.^{6,18-20} By adding thermal energy to the system, some of these barriers to diffusion may be overcome, leading to greater extent of polymerization.

Figure 8 shows representative plots of fractional conversion of VE and ST double bonds over time at 80°C for both transmission and ATR techniques. By examining the slopes of the conversion plots, it appears that the monomer near the ATR crystal reacts at a similar rate to the monomer in transmission. Since the resin mixture and reaction temperatures used in both techniques are the same, this may be anticipated. However, since the geometries of the two techniques are different, it is important to examine any differences that may exist. One such difference is that, with ATR, the reaction of VE and ST double bonds is always initiated at about the same time. In transmission, the reaction of VE monomer often precedes the reac-

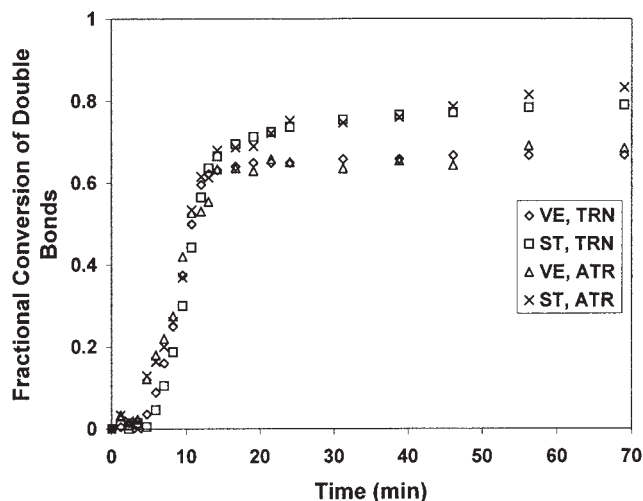


Figure 8 Fractional conversion of VE and ST double bonds for Derakane 441-400 at 80°C using FTIR in transmission and FTIR-ATR.

tion of ST monomer. If these early reactions are slightly different, the resulting network structure and morphology of the cured resin could be somewhat affected. It also appears that the final conversion of VE double bonds may be lower near the IRE interface than the VE double bond conversion obtained in transmission. In addition, ST monomer may achieve a slightly greater extent of conversion near the IRE than in the bulk. Despite these subtle differences, both techniques generate fractional conversion profiles that are quite similar as is also demonstrated by the values of reaction order and rate constants that generally fall within the fitting and experimental errors.

Silane coated versus noncoated ATR

Silane was applied to the ATR crystal surface using the spin-coating method discussed earlier. With the system assembled, resin was injected into the cell and spectral data were collected. Figure 9 shows spectra at early and late stages of VE resin cure near the Z-6032 coated interface.

First, it is important to determine whether the silane remained bound to the crystal during the experiment. It is also important to determine whether silane loss would affect monomeric conversion measurements. In Figure 9, the spectral peak associated with Si-O-Si resonance at 1120 cm^{-1} dropped before the first data acquisition, as indicated by the trough in that region. This is not surprising, since the injected resin could wash away poorly bound sizing. However, since the silane contains a styryl group, any sizing that disappears could be misinterpreted as ST conversion in the vinyl-ester resin. Fortunately, as shown earlier, the overall contribution from silane toward the styryl peak at 910 cm^{-1} is much smaller than the contribu-

tion from ST in the resin. Also, by comparing Figures 9 and 7, the initial ratio of VE to ST absorption intensities is equivalent, confirming no significant effect on the peak at 910 cm^{-1} . In addition, from running numerous experiments, it is clear that the cured resin reacts to form a strong bond with the crystal, which cannot be separated without damage to the IRE—this is not the case for uncoated crystals.

To quantify the degree of silane loss, we note from Figure 6 that the intensity of the peak at 910 cm^{-1} is roughly 20% that of the peak at 1120 cm^{-1} . Since the resin has no resonance frequency at 1120 cm^{-1} , any negative value at 1120 cm^{-1} would correspond to loss of silane. Referring to Figure 9, styryl C=C would be expected to decrease by 20% of the Si-O-Si decrease. Thus, at the first collection of spectral data, ST concentration may be about 4% less than indicated.

Silane washed into solution with the resin system may affect the bulk cure. An additional experiment in transmission mode was run with 3% Z-6032 and 97% Derakane 441-400 (plus initiator) at 80°C to investigate this possibility. The silane in this case had no distinguishable effect on the bulk cure. For all of the ATR experiments, the volume of sizing is 0.06% of the volume of the resin in the experimental cell. So, if the cure near the interface is found to be significantly different than the bulk resin cure, it would not be a result of a high silane concentration throughout the cell, but rather a very high concentration of silane at the crystal surface. This would also suggest that some of the silane is sufficiently bound to the crystal surface and that any washed-away silane that is mixed with the bulk resin in the cell does not influence the cure or the infrared spectra.

Figure 10 shows the average fractional conversion of double bonds in VE resin for three experiments

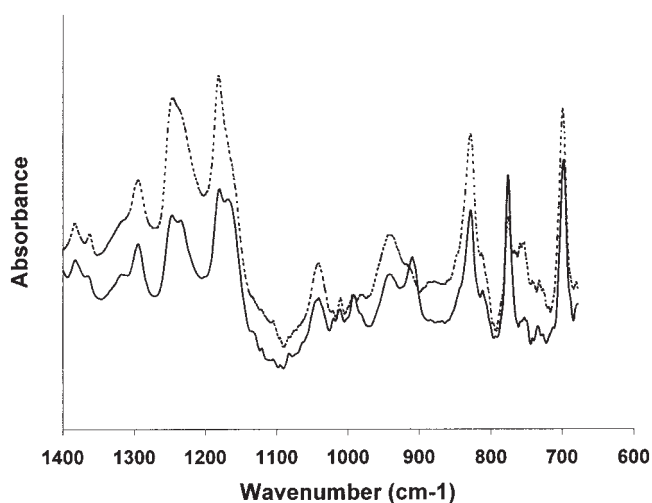


Figure 9 FTIR-ATR spectra at early (—) and late (---) stages of vinyl-ester resin cure at 80°C near a Z-6032 modified interface.

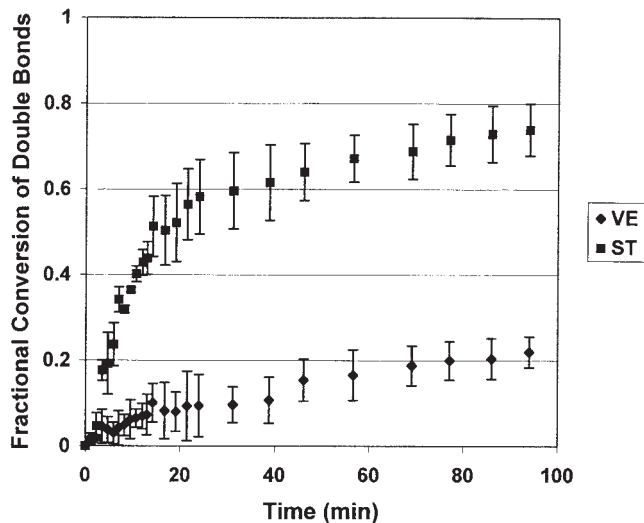


Figure 10 Fractional conversion of VE and ST double bonds for Derakane 441-400 at 80°C using FTIR-ATR with Z-6032 surface treatment. Values shown are averages of three experiments, with standard deviation given by the error bars.

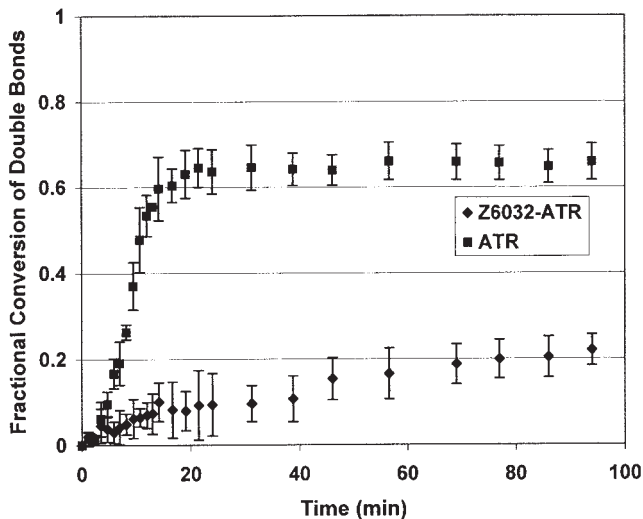


Figure 12 Fractional conversion of VE double bonds for Derakane 441-400 at 80°C using FTIR-ATR with and without Z-6032 surface treatment. Values shown are averages of three experiments, with standard deviation given by the error bars.

using FTIR-ATR near a Z-6032 interface. Figures 11 and 12 are plots of average conversion of double bonds in ST and VE, respectively. Each compares the cure near a Z-6032 silane-modified interface with that of a nonmodified interface at 80°C. Even with the large errors shown in Figure 10, it is clear that the Z-6032 interface dramatically influenced the cure behavior. Near the Z-6032 interface, the ST monomer may have a shorter inhibition period, yielding an extent of conversion in the early stages at least as great as for the

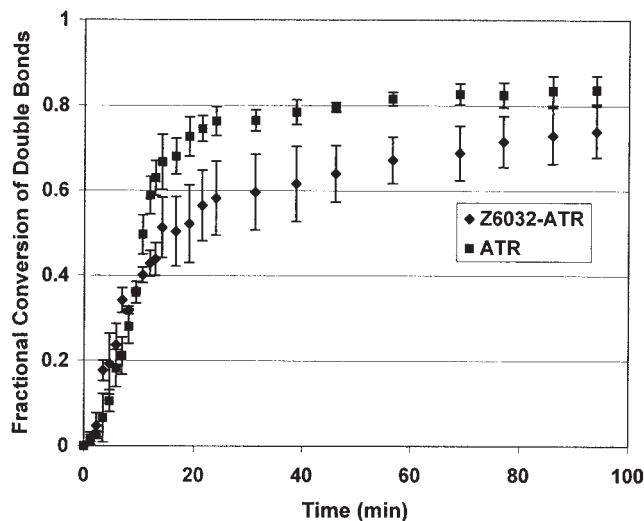


Figure 11 Fractional conversion of ST double bonds for Derakane 441-400 at 80°C using FTIR-ATR with and without Z-6032 surface treatment. Values shown are averages of three experiments, with standard deviation given by the error bars.

nontreated interface during the same time period. The most significant finding is the greatly reduced rate of cure for the VE monomer. The VE conversion rate is significantly lower than in all other cases studied and results in a network of mostly unreacted VE monomer. In fact, in all the experiments with a Z-6032 silane interface, no fewer than 70% of the VE double bonds remain in the system at latter stages of cure.

It appears that the styryl amine-based silane coating significantly alters the cure behavior of the VE resin at the interface. Particularly, the relative conversion rates and final conversions are greatly affected. This suggests that the interphase near the Z-6032 surface is rich in homopolymerized styrene. Extending this result to a fiber surface, it is plausible that a sheath of polystyrene, with significantly different properties to the bulk crosslinked resin, would envelop the fiber.

CONCLUSIONS

It has been determined that the curing behavior of VE resin near an interface can be different from the reaction of the bulk resin away from an interface. An experimental cell was made to monitor interfacial cure using FTIR-ATR while limiting exothermal behavior. For an unsized IRE crystal surface using FTIR-ATR, the cure of both VE and ST double bonds was similar when compared with results obtained using FTIR in transmission. However, the final extent of conversion may be slightly greater for ST and slightly lower for VE near the interface compared to the bulk. Also, a spin-coating technique for applying a thin and uniform layer of silane was developed. When an interface

with Z-6032 sizing was introduced, the effect on the cure was more dramatic, resulting in rapid consumption of ST double bonds in contrast to the VE double bonds. Perhaps due to a combination of altered copolymerization behavior and molecular mobility constraints, the final conversion of VE double bonds can be as low as 20% in many cases. These results suggest that a layer of homopolymerized ST is formed around the sized fibers in a composite. This work further elucidates the effect of sizings on the cure of VE resin near the interface.

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