

# Room Temperature-Curable VARTM Epoxy Resins: Promising Alternative to Vinyl Ester Resins

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**ABSTRACT:** The objective of this investigation is to characterize various room temperature (RT)-curable epoxies for vacuum-assisted resin transfer molding (VARTM) of large structure manufacturing. Six epoxy candidate resins: X-40, 780-33, 780-35, 8601/8602, 8602, 8603, and two vinyl ester resins (VE), 411-350 and 411-510A, are physically and thermochemically characterized. All the resins are cured at RT with extended period of time. The degree of cure for 24-h RT-cured samples ranges from 70 to 85% for epoxies and is comparable with the baseline VE systems (75%). After 1 year at RT, the degree of cure increases from 90 to 98%. Most of the epoxies show a single transition in dynamic mechanical analysis and differential scanning calorimetry. However, two heterogeneous transitions are observed for the VE systems. The glass transition temperature increases monotonically with expo-

sure time, except X-40, that rapidly achieves a plateau and remains constant. The degree of cure for the majority of the systems increases logarithmically with RT curing time with excellent fitting ( $R^2$  varies from 0.92 to 1). Consistent with the increase in degree of cure, the storage modulus increases and  $(\tan \delta)_{\max}$  decreases with time of exposure. A negative correlation between the curing temperature range and the total heat of reaction is observed among the epoxy systems. However, the VE systems show the reverse trend. RT curing epoxy resin (X-40) shows promising overall result to VE system and can be a viable alternative to VE for VARTM processing. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 665–673, 2010

**Key words:** room temperature epoxy; vinyl ester; cure kinetics; microgels; glass transition temperature

## INTRODUCTION

Vinyl ester (VE) resins are used to make polymer-matrix composites (PMC) in military and commercial applications because of their excellent properties such as exceptional chemical resistance, thermal stability, mechanical strength, low weight, and low cost. These resins contain high concentrations of reactive diluents, styrene (ST) that lower the viscosity, to allow these resins to be molded using resin transfer molding and other inexpensive liquid molding techniques. Because the ST is a hazardous air pollutant and a volatile organic compound, the Federal Environmental Protection Agency of the United States of America introduced legislation of limit ST emissions from composite manufacturing.<sup>1</sup> Therefore, replacements of VE resins are needed to solve the ST pollution, which is a suspected carcinogen. Carbon fiber-reinforced polymer (CFRP) composites are widely used in marine, aerospace, transportation, and infrastructure applications because of their high strength and stiffness. Next-generation US Navy

ship systems will incorporate advanced PMC superstructures. Current design approaches rely on the use of carbon reinforcement to enable lightweight top side structures. VE has been selected as the resin system because of its low-cost manufacturability. However, the experience has shown poor mechanical properties because of microcracking generated from shrinkage during resin curing, carbon-VE compatibility in the interface regions, temperature gradient properties in thick sections, poor long-term durability, and processing challenges such as filament and tow wetting due to low permeability, diameter sizes, and higher tow counts of the fibers.<sup>2–5</sup> Fire hazards of the existing VE resins are also of considerable concern.<sup>6–8</sup>

Epoxy resins are considered to be an alternative to VE systems having improved adhesion to carbon fibers, low shrinkage, and better mechanical properties. Room temperature (RT) curing of toughened epoxy and their adhesive with elevated temperature service capability has been reported.<sup>9,10</sup> It is well known that the C-epoxy compatibility is improved when compared with existing C-VE systems with existing carbon fiber sizing. However, only high-temperature-cured epoxy systems are commercially available.<sup>9–15</sup> These epoxy resins are expensive and do not allow ambient temperature processing, a

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requirement for the production of large structures. On the other hand, the various epoxy compatible-sized carbon fibers commercially exist in the market for making the CPMC.<sup>11–13</sup> This study describes the evaluation of low-cost RT-cured epoxies as possible alternatives to address the issues with C–VE. Commercially available vacuum-assisted resin transfer molding (VARTM) resins are selected for this study and cured at RT over various periods of time. Thermomechanical and processing parameters for the resins were evaluated. A methodology was established to characterize these candidate resins versus VE baseline.

## EXPERIMENTAL

### Materials

Twelve resin systems were used in this study. Of these, 10 of 12 are epoxy resins, three from RenInfusion (RenInfusion 8601/Ren 8602, RenInfusion 8603/Ren 8603, RenInfusion 8604/Ren 8604), (The Woodlands, TX), five from Applied Polymeric (SC15, SC79, 780-33, 780-35, and X-40), (Benicia, CA) and two from Center for Composite Materials, University of Delaware (CCMFCS1, CCMFCS2) (Newark, DE). Two VE resin systems from Dow Chemicals (411-350 and 510A) (Columbus, OH) were used as the baseline materials for comparison. These two resins are commonly used for manufacturing the large structures. The epoxy resins were mixed stoichiometrically with respective hardeners. The VE resins are mixed with the 0.2% Trigonox (Azo Chemicals, USA) and the 2% CoNap (Cobalt Napthenate, Witco, USA) for curing. The details of materials are described in material safety data sheets (MSDS) and product data sheets of API, RenInfusion, and Dow Chemicals.<sup>16–24</sup> All of the resins are cured at RT. The maximum  $T_g$  was determined from the resin samples after postcuring (SC79: 177°C, 2 h; SC15: 121°C, 4 h; CCMFCS1 and CCMFCS2: 93.3°C, 8 h; 8601/8602, 8603, 8604, VE411-350, and VE 510A: 121°C, 4 h).

### Sample preparation

The neat resin samples were prepared by simple mixing the resin in a mold, cure, and postcured. The time and temperatures for the curing and postcuring were described previously. The samples were surface ground, polished, and cut into DMA sample dimension of 55 mm × 13 mm × 3 mm size.

### Viscosity

RT viscosity and gelation times were measured using a Brookfield viscometer. A total of 100 g of resin was used for the measurement. The resin was

mixed, and then the viscosity was measured immediately. Periodically, the viscosity was measured till the resin reached the gel state.

### Dynamic mechanical analysis

Dynamic mechanical analysis (DMA)-2980 from TA instruments was used to thermally characterize the samples. The liquid nitrogen atmosphere with double cantilever mode, 1 Hz frequency was used to measure the temperature dependence of the viscoelastic properties  $E^*$  (storage  $E'$  and loss  $E''$  moduli) from –100 to 250°C. A heating ramp of 1–5°C/min having an amplitude of 15  $\mu$ m was used for the DMA measurement. The  $T_g$  of the polymer in its various conditions was obtained by selecting the peak of loss modulus. The values presented are the average of three samples.

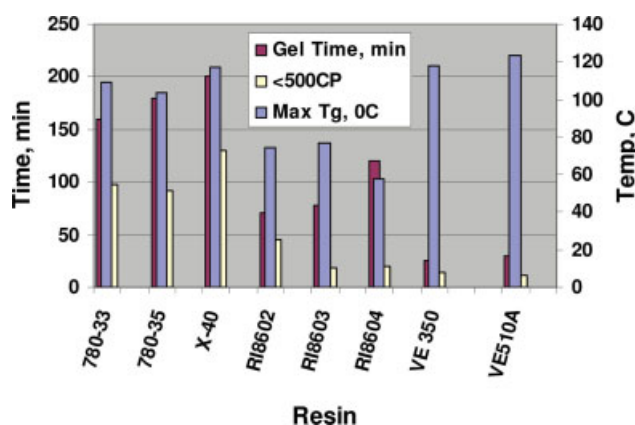
### Differential scanning calorimetry

Differential scanning calorimeter (DSC)-Q100 from TA instrument was used to characterize the total heat of reaction,  $T_g$ , and percentage of cure. For the DSC experiments, the resin and hardener samples were mixed and ~ 5 mg of sample was taken immediately into the DSC pan. The resin was typically cooled to –90°C and heated to 300°C at a constant rate (10°C/min in this study) to get the total heat of reaction for every resin. Approximately 5 mg of resin is cured at RT for different elapsed times. Samples were then heated at the same rate to get the total residual heat of reaction to calculate the degree of cure at RT. The  $T_g$  is also measured from the graphs.

## RESULTS AND DISCUSSION

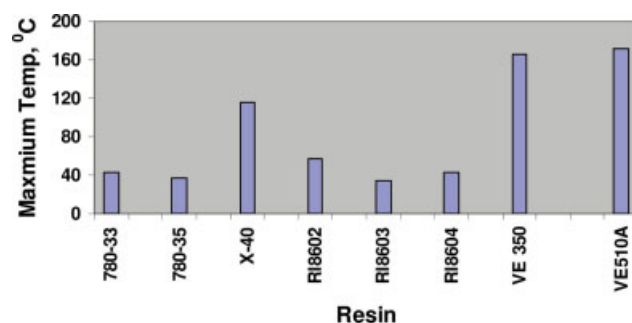
### Viscosity, gel time, and pot life

VARTM system requires resin viscosity to be below 500cp for infusion of preforms. So, the time to reach this viscosity is chosen as the maximum infusion time and provides a basis for comparing the process capability of the various VARTM resins. Figure 1 shows the correlation of viscosity with infusion and the gelation times. The API resins have higher gelation time, low viscosity, and longer pot life. The VE gel times can be increased or decreased using accelerator and inhibitors, and this is a common industrial practice. X-40 shows the overall highest infusion time at about 120 min. The API resins, 780-33, 780-35, and X-40, offer more time to process than the RenInfusion systems. A temperature measurement was done using 100 g mass of resin in a 100-mL plastic beaker. These data were useful to rank the resins in terms of exothermic reactions (relevant for thick section processing) and also to generate



**Figure 1** Variation of gel time, maximum  $T_g$ , and time to reach <500cp viscosity of the resins. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

more realistic pot life (higher thermal mass results in faster gelation in the resin reservoir). Figure 2 shows the highest temperature measured in the 100 g mass samples. The VE resins have the highest exothermic temperature and achieved  $\sim 171^\circ\text{C}$ . The X-40 achieves  $\sim 116^\circ\text{C}$  and has vitrified after 200 min followed by 8601/8602 at  $49\text{--}60^\circ\text{C}$ . The other epoxy resins had peak temperatures in the range of  $32\text{--}43^\circ\text{C}$ . All of the epoxies seem to be less exothermic than the VE baseline and should be feasible for thick section composite processing. These results are useful in interpreting the glass transition temperature achievable at RT. The DSC and DMA samples are of much smaller mass and do not exotherm to the same extent. So these results are representative. However, higher exothermic temperatures can essentially postbake the resin leading to higher apparent  $T_g$  after RT cure. Amplification of resin content eventually increases the cumulative temperature in the pot due to minimum heat loss that helps to postbake the resin. In real applications, the contribution of the exothermic reaction to postcuring will be very



**Figure 2** Maximum temperature achieved for 100 g of resin in a 100-mL beaker. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

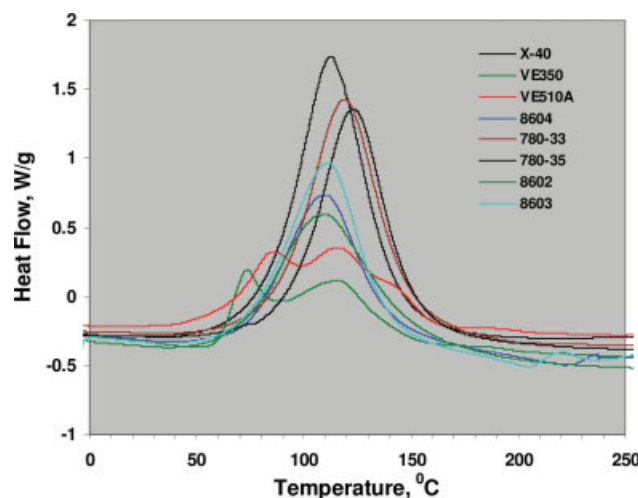
dependent on heat losses to the environment (mold and bag surfaces) and part thickness.

### Degree of cure

Degree of cure and total heat of reaction have been measured using differential scanning calorimeter. The % extent of cure was measured using eq. (1):

$$\% \text{ Conversion} = ((H_{\text{rxn}} - H_r)/H_{\text{rxn}}) \times 100 \quad (1)$$

The term,  $H_r$ , is the residual heat of cure measured during the heating ramp of a sample cured at RT for various elapsed times of interest with a given thermal history. The ultimate heat of reaction ( $H_{\text{rxn}}$ ) is taken to be the area under the cure peak observed for an uncured resin sample ramp from  $-90$  to  $300^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$  (Fig. 3). The VE 411-350 system shows two peaks, and VE 411-510A shows three peaks during ramping in the DSC (Fig. 3). This indicates the existence of different types of polymer formed during curing. The initial temperature of the curing reaction ( $T_i$ ), peak temperature during curing process ( $T_p$ ), and completed cure temperature ( $T_f$ ) were measured for all the resin systems. The VE resins generally started the reaction at lower temperature ( $20^\circ\text{C}$  for VE 411-510A) and needed longer time for completion of the cure when compared with the epoxy systems. An inverse relationship is observed between the curing temperature range and the total heat of reaction for the epoxy systems analyzed ( $Y = -0.353X + 326.6$ ; where  $Y$  = cure temperature range,  $^\circ\text{C}$ ;  $X$  = total heat of reaction,  $\text{J}/\text{g}$ ;  $R^2 = 0.908$ ). In general, for various epoxy systems, higher total heat of reaction needs lower time to cure the resin completely. The opposite trend is observed for the VE systems. However, we have only analyzed two VE



**Figure 3** Typical DSC graphs for the resins used to calculate the total heat of reaction. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

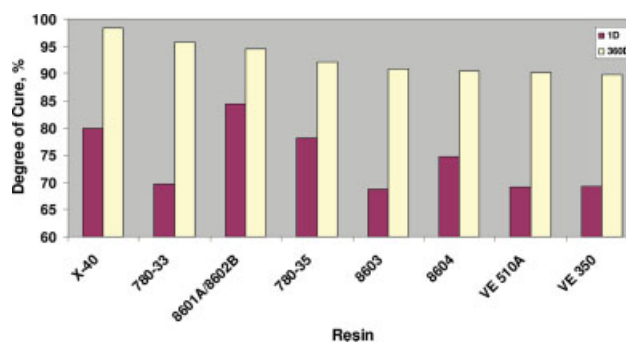
**TABLE I**  
Glass Transition Temperature and Heat of Reaction Measurement for Each Resin System

Resin	$T_g$ DMA ( $^{\circ}$ C)	Max $T_g$ DMA ( $^{\circ}$ C)	Max $T_g$ DSC ( $^{\circ}$ C)	Total heat of reaction ( $n = 3$ ) (J/g)	% $T_g$ increased
780-33	3D-60	105 $\pm$ 4	102 $\pm$ 2	465	0
	17D-66				7
	23D-68				13
	360D-76				27
780-35	3D-56	102 $\pm$ 2	98 $\pm$ 2	438	0
	23D-60				7
	360D-72				33
X-40	3D-107	114 $\pm$ 2	112 $\pm$ 2	510	0
	13D-107				0
	27D-106				0
	360D-105				-1
8601/8602	2D-51	61	60 $\pm$ 2	391	0
	12D-54				6
	360D-64				25
8603	2D-50	78	65	412	0
	4D-54				8
	10D-63				26
	360D-63				26
8604	20 hrs-50	55	52	345	0
	7D-53				6
	360D-58				16
411-350	1D-63	116 $\pm$ 2	114	235	0
	7D-75				19
	12D-80				28
	26D-82				30
	360D-87				38
510A	3D-64	121	124	266	0
	17D-78				22
	49D-92				43
	360D-104				63

systems. The fully cured materials were also ramped at the same rate from  $-90$  to  $300^{\circ}$ C to get the maximum  $T_g$  of each system. DSC data show only a single broad transition for each of the epoxy systems. Although only a single transition is apparent for each epoxy system, it cannot be immediately concluded that all the resins tested have a single component. The broad nature of the glass transitions observed in the DSC data for VE system suggests that in some cases the ST transition and the VE transition overlap. To rule out the possibility of phase separation, we have performed DMA experiments discussed later.

The total estimated heat released during curing and the maximum glass transition temperature of the fully cured material are presented in Table I. The magnitude and rate of heat release for the X-40 is the highest followed by 780-33 and 780-35 (see Table I). The ResInfusion resins have lower heat of reaction than the API resins. However, VE systems have the lowest total heat of reaction. The degree of cure is in the range of 70–85% for all the resins that are cured at RT for 24 h (5 mg sample) as shown in Figure 4. VE resins have a degree of cure of 74%,

which is comparable with the epoxy systems having the same mass analyzed. It is found that the 8604 has the highest degree of cure after 24 h of exposure, but has a relatively low dry  $T_g$  of  $71^{\circ}$ C when compared with the VE baseline. Degree of cure was also measured for the 360 days RT-cured samples of all resin systems (Fig. 4). The degree of cure for the epoxy systems changes significantly with time and



**Figure 4** Degree of conversion for 1 day and 1 year room temperature-cured samples (5 mg sample) of eight resin systems. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE II**  
Least-Square Values for Degree of Cure versus Time Plot

Resins	% $D_0$	$A$	$R^2$
780-33	70	4.377	1
780-35	78	3.0302	1
X-40	73.562	4.1836	0.9289
8601A/8602B	84.4	1.738	1
8603	70.081	3.8617	0.9303
8604	74.118	2.5971	0.961
VE 350	70.725	2.9995	0.9284
VE 510A	69.676	3.6959	0.9711

reaches to maximum value. With conditioning for longer time and exposure to sunlight, the resin will undergo additional curing that will increase the degree of cure and  $T_g$ . For all resin systems considered, the degree of cure increases with time and are logarithmic correlated with the time following the equation:

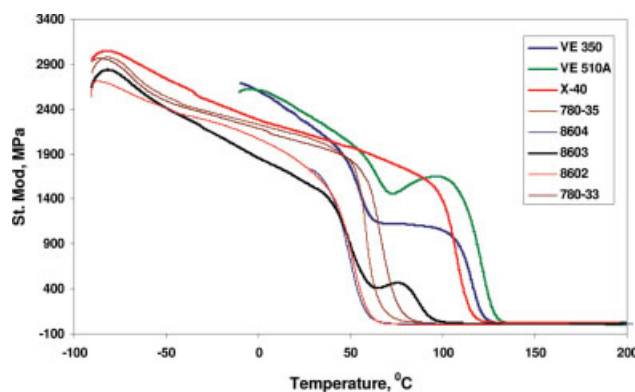
$$\text{Degree of cure (\%D)} = A \ln(\text{days}) + D_0 \quad (2)$$

where  $D_0$  is the %D in 1 day;  $A$  is the constant for a particular resin system on the degree of cure of resin, the composition of the resin, and the interaction parameter value of the component polymers. Table II represents the values of  $D_0$ ,  $A$ , and the  $R^2$  for all resins. The  $R^2$  varies from 0.92 to 1. It is found that the degree of cure after 1 year for all the resins increased to a level in the range of 90–98%; X-40 is the highest among them. The extent of curing of thermoset resin at RT is not complete because of vitrification. The epoxy and VE have different reaction chemistry. The effect of initiator promoter stoichiometry of the VE and the ST play an important role on the extent of curing. The cure of VE resin systems proceeds via the free radical bulk copolymerization of ST and difunctional VE. The structure and properties of the networks that forms will be dependent on the copolymerization behavior of these two components. In the early stage of reaction for the VE resin systems, the VE double bonds rate of reaction is faster when compared with the ST double bonds. During ramping in DSC, the VE reacted initially followed by ST. Thus, two network systems were developed at RT cure. This provides one plausible explanation for the doublet nature of the DSC curve (Fig. 3). However, during postcuring, exposure to higher temperature, modifies the extent of the reaction and the structure of the resin. An active VE prefers to react with ST monomer, whereas the active ST will prefer to react with VE double bond. Therefore, homogeneous copolymerization may take place. This may cause a single transition and one  $T_g$  after postcuring. In case of the epoxy system, the addition polymerization reaction

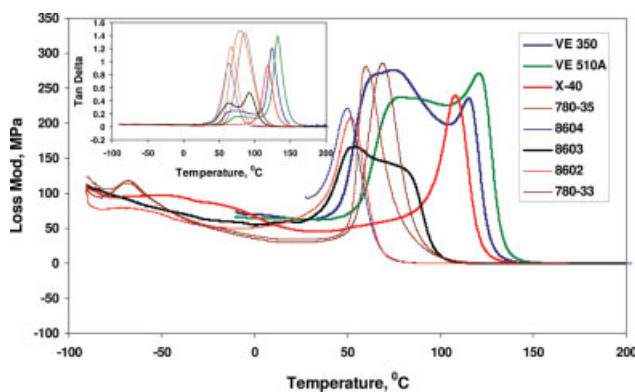
takes place. Single polymer chain is observed during curing. However, branching may occur but the rate of branching is very low when compare with free radical chain reaction polymerization of VE having two systems. So, we always observed the single peak in the DSC. When thermosetting materials remain for a long period of time below this  $T_g$ , they may also undergo physical aging that may produce an incremental value of  $T_g$  similar to the effects of increased degree of cure with time.

### Viscoelastic properties

DMA is an efficient tool to measure the viscoelastic properties of crosslinked networks. Figures 5 and 6 show the typical DMA graphs for the eight resin systems. The glassy modulus, loss factor ( $\tan \delta$ ) rubbery modulus ( $E_r'$ ),  $T_g$ , and the amplitude of the damping peak ( $\tan \delta$ )<sub>max</sub> are shown in the viscoelastic spectra. Figures 7–9 show the typical curves for modulus and  $T_g$  (loss modulus peak) of the 8603, VE411-350, and VE 510A after various times of exposure at RT. Table I summarizes the  $T_g$  values for each resin system. Upon examining the loss modulus data, we have seen a single relaxation peak corresponding to the matrix glass transition. The DMA loss modulus curves for API resin systems (except 8603) show two sharp transitions one above the RT and another below the subambient temperature. The high-temperature peak corresponds to the  $T_g$ , whereas the low-temperature peak ( $-65^\circ\text{C}$ ) corresponds to the beta-relaxation of the amine used for the curing of epoxy system. The 8603 system exhibits two peaks for the matrix  $T_g$  (Fig. 7). During sample preparation, we also found evidence of phase separation of this resin. However, other epoxy systems have single  $T_g$  and are well-mixed systems having single-phase system. A possible explanation for this is uneven mixing of the 8603 and/or it may contains

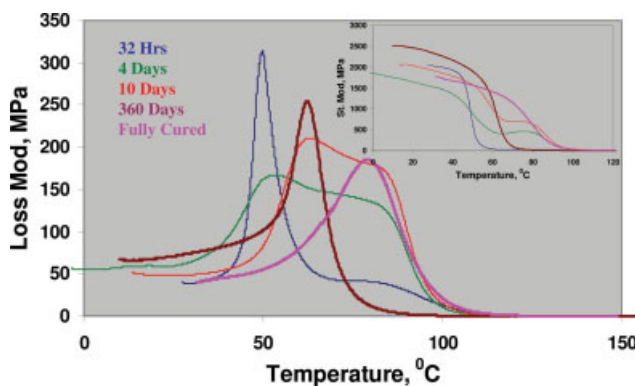


**Figure 5** Typical storage modulus curves for neat resin samples cured at room temperature. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

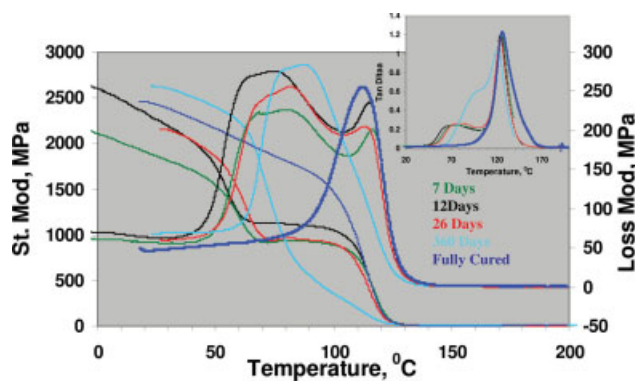


**Figure 6** Typical loss modulus and  $\tan \delta$  (inset) curves of the neat resin samples cured at room temperature. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

two phase systems having different  $T_g$ s. Additional research is required to find the exact cause and the way to prevent this problem. The VE resins show two broad peaks above RT (Figs. 8 and 9) and has two  $T_g$ s. The peak shape and the  $T_g$  change with the cure time at RT (Figs. 8 and 9). The high temperature transition ( $T_{g1}$ ) peak decreases with increasing cure time and shifted to the lower temperature, whereas the low temperature transition ( $T_{g2}$ ) peak shifted to high temperature with increasing cure time. Both the  $T_g$ s are merged at an intermediate temperature and finally formed a single peak, i.e., a single  $T_g$ . The postcured VE samples show single peak in DMA (Figs. 8 and 9). VE systems are mixtures of ST with methacrylated compounds (VE). The viscosity of the resin is controlled by adjusting the molecular weight of the VE and the ST content. The initial curing process for VE system begins with an induction period because of the presence of inhibitors and cage effects, followed by the formation of microgels.<sup>24</sup> The crosslink density of such microgels does not contribute to the global network

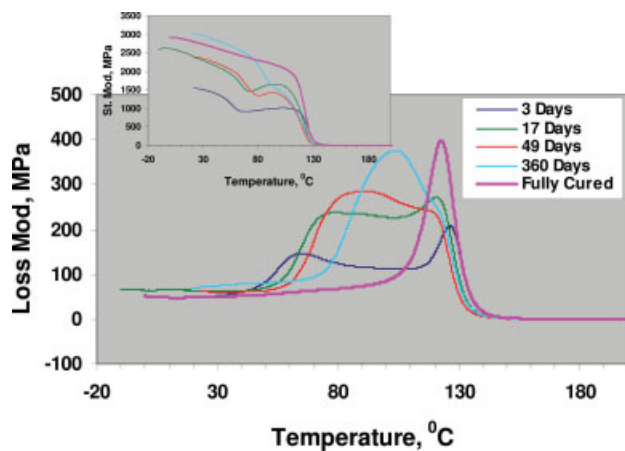


**Figure 7** DMA graph of the 8603 resin cured at room temperature in different times. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 8** DMA graph of the vinyl ester 411-350 resin cured at room temperature in different times. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

structure until they are incorporated into the gel phase. A difference in microgel composition for individual polymer with respect to matrix composition is possible. Phase separation has occurred<sup>25</sup> during curing of VE resins. The rate of reaction in the early stage of reaction for the VE and ST differs significantly. During the later stages of cure, the double bond of the VE cannot access active free radicals and are trapped as a result of the network structure. The poly-ST is being formed at the end stage of the reaction. Thus, diffusion limitations play an important role for final uniform copolymerization and that mostly depends on the curing temperature. This clearly indicates that RT curing has potential for forming multiple reacting phases during curing. It is also reported that the VE used as a crosslinking agent is not consumed homogeneously throughout the network.<sup>26</sup> This may be one of the causes to get the two distinct  $T_g$ s for RT-cured VE resins. Time and temperatures influences the microstructures and



**Figure 9** DMA graph of the vinyl ester 510A resin cured at room temperature in different times. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

$T_g$ s. The  $T_g$  increases with curing time at RT (Table I). After 360 days of RT curing, the materials reach an  $T_g$  ranging from and 85 to 104°C. The percent of  $T_g$  increased after 360 days at RT exposure for resins, and these results are given in Table I. However, for X-40, the  $T_g$  remains constant throughout the exposure time. For the VE 510A, the  $T_g$  has increased to a maximum of 63%. It is expected that the mechanical properties will also change with exposure time.

We have also measured the maximum dry  $T_g$ s for postcured resins. The resin was postcured at 121°C for 4 h, and the DMA was run for all samples. Figure 1 shows the values of each resin. The VE resins have the highest values. X-40 has comparable  $T_g$  with the VE resins (Table I). The fully cured materials have a single  $T_g$ . At higher temperature, the molecular mobility increases. Unreacted and partly reacted monomers/oligomers are mobile and rearrange themselves so that they come closer and react. The partially crosslinked molecules have better chance for further crosslinking and that ultimately increase the  $T_g$  at higher temperature as discussed previously. Table I presents the dry glass transition temperatures of the resins as a function of cure time at RT (DMA). The elapsed time to reach a target  $T_g$  will allow ranking of candidate resin systems. The X-40 and the 780-33 have achieved a  $T_g$  of 71°C and higher in less than 14 days and are superior to VE systems in this respect. The VE resins show the doublet peaks and have lower  $T_g$  than the X-40 in the same range of time. More interestingly, the X-40 is a single-phase system. The  $T_g$  increases with time of exposure for all the resin systems, except X-40 which remains almost constant. This result suggests that the crosslinking is completed in very short periods of time at RT. The crosslinking occur in an isolated second-phase system composed of microgels. The lack of sufficient global connectivity causes no significant change in  $T_g$  until the later stages of cure during postcuring at elevated points, where a tightly linked microgels network is formed. Three hundred sixty days cured VEs samples show broad loss modulus peaks and are doublet in nature (Figs. 8 and 9). It seems that the two separate peaks are moving closer with time of exposure. The 8603 after 360 days exposure has a single peak (Fig. 7). The peak maxima are in between. It can be expected that upon longer time of exposure, the systems may develop a single  $T_g$  having uniform crosslink density; we have seen for the system after postcuring where all the microgels are connected to give an uniform global microgel network.

## Modulus

The storage modulus curve for 780-33 is stable up to 50°C and decreases very sharply with temperature

(Fig. 5). The same trend is observed for the 780-35, 8602, 8604, and X-40 epoxy system. The 8603 epoxy system shows a slow decrease in storage modulus with temperature (Fig. 7). After 48°C, the modulus drop sharply and again increases with increasing temperature (additional cure is occurring above this temperature). The same trend is also observed for the VE systems (Figs. 8 and 9). This may be the multiphase systems formed during curing of the resin, as discussed earlier. This observation for the VE systems is very crucial for structural composite applications. The structure may be stable up to 50°C and there is a high probability for the malfunction of the structure after 50°C. However, for the X-40, the modulus decreases slowly with temperature and sharp drop of modulus occurred at 96°C. Any composite fabricated with the X-40 will be thermally stable up to 98°C and have better thermal stability when compared with the RT-cured VE systems.

In general, modulus is found to increase with cure time (Table I). It is interesting to note that after 360 days of RT exposure, the modulus values at 25°C are higher when compared with the fully cured materials for all the resin systems. This observation clearly indicates that the sluggish curing plays an important role for the structural performance of thermoset systems. The modulus of a material is greatly dependent on the microstructural features that develop during curing and on the property of the networks that are formed. It is expected that the cluster size are uniform during RT curing. In this time, the system undergo further curing due to the diffusion of the reactive molecule. Therefore, there is an increase in the polymer network (microgel structure) and the cluster size. However, the overall size decreases because of the collapsing of the two or more cluster to a single cluster. The overall free volume will be expected to decrease, which may ultimately increase the modulus. Postcuring of the resin samples could also lead to the build up of residual thermal stresses upon cooling associated with a higher  $T_g$  system. The phenomenon is more pronounced for the VE systems. So the lower modulus is observed for the postcured samples.

From the rubber elasticity theory,<sup>27</sup> it may be assumed that the effect of internal energy of the formed network can be neglected above  $T_g$  and by relating the changes in entropy because of the motion of segments among the network strands. Thus, the variation in the rubbery modulus ( $E_r'$ ) can be expressed as a function of crosslink density by the following relationship:

$$E_r' = 30\rho RT/M_c$$

where  $R$  is the gas constant,  $T$  is the absolute temperature,  $\rho$  is the density of the crosslink network,  $\theta$

**TABLE III**  
**Modulus Retention at 60, 71, and 82°C with Respect to 30°C for Each Resin System with Varying Time**

Resin	% of $E'$ 60°C/ $E'$ 30°C	% of $E'$ 71°C/ $E'$ 30°C	% of $E'$ 82°C/ $E'$ 30°C
780-33	3D-35	3D-5	3D-1
	17D-65	17D-15	17D-3.2
	23D-78	23D-25	23D-3.5
780-35	360D-91	360D-77	360D-7.4
	3D-18	3D-2.9	3D-1.3
	23D-37	23D-5.2	23D-1.6
X-40	3D-91	3D-87	3D-81
	13D-90	13D-86	13D-81
	27D-88	27D-83	27D-79
	360D-86	360D-77	360D-72
8601/8602	4D-8	4D-0.6	4D-0.2
	12D-2	12D-0.3	12D-0.3
	360D-59	360D-2.2	360D-0.4
8603	32Hrs-2	32Hrs-1	32 Hrs-1
	4D-30	4D-29	4D-26
	10D-52	10D-36	10D-29
	360D-50	360D-3.3	360D-0.7
8604	20 hrs-6	20 hrs-1	20 hrs-0.7
	7D-12	7D-1.7	7D-0.7
	360D-30	360D-2.3	360D-0.7
411-350	7D-56	7D-52	7D-51
	12D-66	12D-50	12D-52
	26D-69	26D-46	26D-45
	360D-86	360D-60	360D-30
510A	3D-66	3D-64	3D-61
	17D-79	17D-66	17D-64
	49D-83	49D-67	49D-58
	360D-89	60D-83	360D-70

D, days.

is the "front factor" (the value of  $\theta$  is close to unity), and  $M_c$  is the average molecular weight between the crosslinks. The equation shows that  $E_r'$  is proportional to  $1/M_c$ ; in other words, an increase in the crosslink density will cause an increase in  $E_r'$ . In most of the resin systems, the  $E_r'$  increases with the time of cure representing the increase in the crosslink density of the system. In the 360 days exposed samples, the  $E_r'$  is also higher for all of the resin systems when compared with the fully cured samples. This confirms the higher crosslink density for the 360 days exposure system.

Table III represents the modulus retention for the eight resins at 60, 71, and 82°C with respect to 30°C. X-40 shows the highest retention for all the temperatures followed by VE resins. 780-33 also shows better retention of modulus when compared with the RenInfusion resin systems. The API resins are better when compared with modulus retention to VE. Res-Infusion resins have lower values and are considered inferior based on this criteria. These results are consistent with the measurement of the  $T_g$ s. Clearly, the significant loss of modulus occurs when the reference temperature exceeds the glass transition temperature corresponding to the number of days cured

at RT. For most of the resin systems, the modulus retention at 60, 71, and 82°C is increased with the time except for the 8603, where the modulus retention at 71 and 82°C has been decreased with time. This may be due to the collapsing of the two microgel structures to form a homogenous uniform single network structure with intermediate  $T_g$  (Fig. 7). For X-40, the modulus retention is almost unchanged with increased curing. The shape of the loss spectra ( $\tan \delta$  versus temperature; Fig. 6 inset) can provide additional information about the structure of the crosslink networks. Thus, the height of the  $\alpha$ -transition (glass transition temperature),  $(\tan \delta)_{\max}$ , for a thermosetting system supplies information about the extent of cure, i.e.,  $(\tan \delta)_{\max}$  becomes lower.<sup>28-30</sup> It is observed that the  $(\tan \delta)_{\max}$  for neat resins decreases with increasing the time, which indicates that the crosslink network structure is denser with increasing cure time. The result is consistent with the degree of cure measured experimentally, i.e., lower  $(\tan \delta)_{\max}$  leads to a more densely crosslink network and more degree of cure. On the other hand, the widths at the half-height on the  $\alpha$ -relaxation peak are sensitive to the homogeneity of the networks.<sup>28-30</sup> From Figure 6, it is clear that all the epoxy system except 8603 exhibit a single peak and the widths at the half-height on the  $\alpha$ -relaxation peaks are much lower than the 8603. Fully cured 8603 resin spectrum shows the narrower width at half-height exhibiting a single peak and a single  $T_g$ . With appropriate heating, the two separate identities are compatible and give a homogenous system, as discussed earlier. VE systems exhibit same trend as the 8603, having very broad width at half-height. In fact, two distinct peaks are overlapped that produces large width at half-height. However, the width at half-height decreases with time indicating the increase in homogeneity.

## CONCLUSIONS

In this study, 12 candidate resins, including two VE systems, are characterized. Only resins from API meet the service temperature requirement of 71°C. The RT-curable VE systems show two peaks representing two phase systems. The two phase systems for VE last after 360 days of exposure. VE resins develop two distinct microphases during curing. The two phase systems collapse with curing time, and upon postcuring at high temperature, build up a uniform homogenous network. However, X-40 is a single-component system that has one peak and maintains consistent network with exposure time. The degree of cure, modulus, and  $T_g$  increases with RT exposure time for all resins except X-40, where  $T_g$  remain the same with exposure time. Global connection may be the prime cause that increases the  $T_g$



for the resins. The rubbery modulus after 360 days of RT exposure is higher for all of the resin systems when compared with the postcured samples signifying higher crosslink density of the 360 days networks. Longer RT curing time enhances the modulus than high-temperature postcured materials. The percent  $T_g$  increase for the epoxies (except X-40) after 360 days at RT exposure is lower, 14–33%, than VEs, 38–63%. So, the mechanical properties will be expected to change with time. However, for the case of X-40, the percent change in  $T_g$  is minimum.

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