Characterization of the Cure-State of DGEBA-DDS Epoxy Using Ultrasonic, Dynamic Mechanical, and Thermal Probes

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Three experimental techniques were used to characterize the cure state of an epoxy resin system of DGEBA epoxide and DDS diamine curing agent. Samples were prepared from non-stoichiometric monomer mixtures designed so as to simulate various stages of cure of a stoichiometrically prepared epoxy. Such an approach allows for variable temperature characterization of specimens without concern for ongoing chemical reactions that would cloud interpretation of results. Additional experiments were performed on stoichiometric samples that were isothermally cured. Differential scanning calorimetry (DSC) was used to measure the heat of reaction and glass transition temperature. Dynamic mechanical analysis (DMA) was used to measure complex modulus, while ultrasonic cure monitoring (UCM) was used to measure longitudinal velocity throughout cure. DSC analysis was found to be insensitive to changes occurring at the latter stage of polymer network development, especially after vitrification. DMA characterization, however, was found to be quite sensitive to the rubbery modulus (and as such, the cure state), but is limited to cure states above gelation. Only the UCM technique was robust enough to accommodate all cure states while providing highly sensitive measurements of mechanical property development.

1 INTRODUCTION

Many analytical techniques for cure characterization in thermosetting polymers or polymer composites derive their sensitivity from changes in the material’s glass transition temperature, \( T_g \). The glass transition is a complex phenomenon that is influenced by many factors including free volume, molecular mobility, and crosslink density. As polymers above \( T_g \) are characterized by rubbery or fluid-like behavior, while polymers below \( T_g \) exhibit glassy (elastic) behavior, techniques that are sensitive to such a physical transition enable sensitive characterization of thermoset cure.

Among the many cure characterization techniques that probe changes in glass transition and cure state of thermosetting polymers, the most common employs differential scanning calorimetry (DSC), a thermal analysis technique (1). In DSC analysis the internal energy liberated or absorbed by a material is measured while the material is heated, cooled, or held isothermally at a fixed temperature. If the experiments are conducted using a constant temperature ramp in the absence of chemical reaction, then the rate of heat consumption (specific heat) can be measured directly. A second-order transition (such as the glass transition) is manifest as a discontinuity in the DSC trace. More important, measurement of the heat of reaction of a sample gives useful information regarding the reaction kinetics and can be interpreted to yield an “extent of cure.”

Exploiting the large change in modulus encountered in polymers traversing the glass-rubber transition and for polymers undergoing cure (and thereby encountering a liquid-gel transition), dynamic mechanical
analysis (DMA) has provided significant insight into these processes (2). In particular, the DMA technique involves the measurement of storage and loss moduli in shear, tension, compression, or a combination thereof for a range of environmental (temperature) and loading (frequency, amplitude) conditions. The loss modulus, measured as a function of temperature or frequency, is found to exhibit a maximum (of variable width, $\Delta T$) as a mechanical relaxation is passed through (such as $T_g$ and sub-$T_g$ transitions). Thus, measurement of the loss modulus provides a convenient, yet quantitative, method for the identification of mechanical relaxation temperatures. In addition, examination of the frequency-dependence of the relaxation temperatures allows for the determination of the activation energies of the associated transitions. While DMA has been used extensively to characterize the thermal and mechanical properties of cured thermosets and cured thermoset-based composites (3–4), the characterization of the cure process itself has been conducted mainly using the related technique of rotational rheometry, given the large range of viscosity and modulus transpired by a material polymerizing from a liquid of small molecules to a glassy solid of infinite molecular weight.

Though underutilized, ultrasonic techniques have been used to characterize the behavior of polymers and to study changes in their mechanical properties during cure, beginning with Dietz and co-workers in 1956 (5–24). In this approach, high frequency (MHz-range) sound waves are launched into a material in order to measure the ultrasonic velocity and the attenuation/absorption of sonic intensity. Importantly, the velocity of sound in a material can be related to the storage modulus ($\varepsilon' \sim \rho v^2$, $\rho =$ density, $v =$ sonic velocity), while ultrasonic absorption is related to energy dissipation in the material; i.e. the loss modulus. Arridge and Speake (6) and Speake et al. (7) investigated the effect of cure state on low-temperature secondary mechanical relaxation in amine-cured epoxy resins. They also examined the effects of non-stoichiometric quantities of the resin mixture on the shear modulus, proposing that this measurement above and below the glass transition could be used to monitor, or characterize, the cure state of the material. Lindrose (8) monitored changes in ultrasonic velocity and attenuation for room temperature-cured epoxy resins using both shear and longitudinal waves. He showed that the ultrasonic shear and longitudinal velocities and attenuations can be used to measure the development of the shear and longitudinal moduli, with particular sensitivity seen for the shear mode at the point of gelation. Rokhlin et al. (13) measured the frequency dependence (2–20 MHz) of phase velocity and attenuation during epoxy cure. They found that the attenuation coefficient increases linearly with frequency for all stages of the cure reaction, and that the rate of increase is highly dependent on the cure state. They also found that the phase velocity is only moderately dependent on the frequency. In a later paper by Rokhlin (18), the temperature dependence of the velocity and attenuation for an epoxy resin at different stages of cure was examined.

While there is a wealth of information about polymer property measurement and cure monitoring in room temperature cure of neat resin samples, relatively little reliable data exists for polymers cured at elevated temperature.

In this paper, the curing of an epoxy resin at elevated temperature is investigated using three separate experimental techniques: differential scanning calorimetry (DSC), ultrasonic curing monitoring (UCM), and dynamic mechanical analysis (DMA), our goal being to compare the methods while interrogating material responses from several angles. Indeed, each of these techniques is used to probe different aspects of material behavior during cure. For instance, DSC probes the polymerization exotherm and evolving heat capacity, while DMA and UCM probe evolving elastic and viscoelastic mechanical characteristics. Moreover, the wide separation in oscillation frequency between UCM ($0.5 < f < 50$ MHz) and DMA ($0.01 < f < 50$ Hz) provide sensitivity to local (monomer, bond rotations) and longer range (polymer coils, entanglements, etc.) dynamics, respectively, given the characteristic time scales for motion of these groups. Here, sensitivity is maximized for $f \cdot \tau \sim 1$, where $\tau$ is the characteristic time. Summary accounts of both ultrasonic and dynamic mechanical characterizations of polymers provide the interested reader helpful background information (25, 26).

In this paper we present results for each of the experimental techniques separately in Section 3 for the DSC experiments, in Section 4 for the DMA experiments, and in Section 5 for the UCM experiments. In all cases, the characterization techniques were applied to a range of non-stoichiometric monomer mixtures designed in principle to simulate various stages of cure of a stoichiometrically-prepared epoxy. Such an approach has been used by others to investigate the cure kinetics and mechanical properties of epoxies (27–29). The practical motivation for this approach is that it allows for variable temperature characterization with multiple techniques without concern for ongoing chemical reaction that would cloud interpretation of results. Additional characterization was carried out on isothermally cured, stoichiometric samples using both the DSC and UCM techniques. In the final section of the paper, a comparison is made between these three techniques and the significance of the results for the processing of thermosetting polymers and thermoset-based composites is addressed.

2 MATERIALS

Diglycidyl ether of bisphenol A (DGEBA) and 4,4’-diaminodiphenyl sulfone (DDS), supplied by Aldrich Chemical Company, were chosen as the material system for this study due to its common use as a matrix material in composites and relative simplicity. Testing
was performed on specimens made from both stoichiometric (2 mol DGEBA: 1 mol DDS) and non-stoichiometric (excess DGEBA) mixtures of DGEBA and DDS in order to compare the fully cured epoxy with simulates of partially cured DGEBA-DDS. The chemical structures for each of the components are shown in Fig. 1.

During cure, each primary amine of DDS reacts with an epoxy group of DGEBA, via ring opening, to form a CH2-NH bond and a pendant hydroxyl group, the presence of which is known to accelerate subsequent ring opening reactions (30). The resulting secondary amines react in a similar manner with remaining epoxy rings to crosslink the polymer chains, though at a slower rate. Reactivity of the hydroxyl-groups, resulting from the amine-epoxide addition reaction, is safely neglected for the curing conditions employed. Knowing the functionalities and molecular weights of the epoxide and amine, the fully reacted cure state (i.e., all primary and secondary amines reacted) can then be characterized using the quantity,

\[ \alpha_s = \frac{[\text{mol}_e]}{[\text{mol}_a]} \frac{f_a}{f_e} \]  

where \( \alpha_s \) is a maximum achievable cure state, \( f \) is the functionality of each monomer, and the subscripts \( a \) and \( e \) refer to the amine and epoxide respectively. The parameter \( \alpha_s \) is defined so that for stoichiometric quantities a value of unity is achieved, while for excess epoxide \( \alpha_s < 1 \). Table I lists the functionality, molecular weight, density and melting point for both of the resin components. The presence of excess epoxide for nonstoichiometric samples is speculated to act as a diluent phase in the epoxy network, likely in the form of dangling polymer chains.

Test specimens of cure states ranging from \( \alpha_s = 0.1 \) to 1.0 were prepared for temperature scanning experiments. For each value of \( \alpha_s \), the weight ratio for the components was calculated using Eq 1. Approximately six grams of the epoxy were weighed using an analytical balance. The epoxide was then heated on a hot plate to 177°C, the melting point of the amine. The appropriate amount of amine was then added to the heated epoxide and held at that temperature just long enough to allow complete mixing, after which the specimen was quickly cooled to the cure temperature. The mixture was then stirred rapidly for an additional ten minutes. The homogeneous solution was then injected into a heated mold and the specimens were cured for one hour at 125°C followed by two hours at 200°C.

Samples for DMA experiments were prepared using slight modifications to the above procedure. In these cases, prescribed quantities of DDS were dissolved in DGEBA at 120°C until a clear liquid resulted (15 min) and the resulting liquid was refrigerated for 12 hours. Subsequently, the samples were reheated to 120°C and poured into custom molds made of aluminum and DuPont Teflon and cured for 1 hour at 120°C followed by heating at 4 °C/min to 200°C and isothermal curing at 200°C for an additional 2 hours. Samples prepared in this way yielded solid beams with dimensions of 52 mm × 10.5 mm × 5.4 mm.

3 DSC EXPERIMENTS

3.1 Experimental Procedure

A Polymer Laboratories DSC was used to perform thermal analysis of the DGEBA-DDS resin system. Both isothermal and dynamic scanning modes were used. Stoichiometric quantities of the resin system were prepared and samples of approximately 20–30 mg were prepared for the DSC. Dry N2 gas was circulated within the test cell at a flow rate of 10 cc/min.

Five isothermal cures at 150, 170, 190, 210, and 230°C were performed in the DSC for stoichiometric DGEBA-DDS resin mixtures. The specimens were placed into the DSC test cell and were ramped to a preset load temperature. For the 150°C isotherm, the load temperature was fixed at 100°C.

Approximately six grams of the epoxy were weighed using
cases the load temperature was 120°C. The rate at which the samples were heated to the cure temperature was adjusted so that the cure temperature would be obtained in one minute, except for the 230°C isothermal cure case in which the maximum heat up rate of 100°C/min was used. This technique kept the overshoot to a minimum and improved control of the system.

Unfortunately, in isothermal curing, initiation of some exothermic reaction is unavoidable during the initial heating of the cell to the cure temperature. As a result, it is difficult to determine the point in time when the baseline has been reached, since the initial response of the system is not reproducible during this heat-up period. However, the reaction rate of this system is relatively slow, especially for the lower cure temperatures. Therefore, valuable information about the reaction kinetics is still obtained. The baseline was estimated by extrapolating the baseline of the fully cured state (long times) to early times and then setting the zero time as the intersection between this baseline and the heat flow curve.

Once the baseline was defined, the degree of cure as a function of time could be determined through analysis of the DSC data. The degree of cure is found from,

$$\alpha(t) = \frac{H(t)}{H_u}$$

(2)

where $H$ is the heat of reaction at time $t$, and $H_u$ is the ultimate heat of reaction. The heat of reaction was determined by integrating the area under the heat flow curve so that,

$$H(t) = \int_0^t \frac{dH(t)}{dt} \, dt$$

(3)

The ultimate heat of reaction used in this study was the total area under the heat flow curve for the 230°C.

<table>
<thead>
<tr>
<th>Component</th>
<th>$f$</th>
<th>$\rho$ (g/cm³)</th>
<th>MW</th>
<th>$T_m$ or $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>2</td>
<td>1.17</td>
<td>348</td>
<td>41–44</td>
</tr>
<tr>
<td>DDS</td>
<td>4</td>
<td>1.43</td>
<td>248</td>
<td>175–177</td>
</tr>
</tbody>
</table>

Table 1. Material Properties of Resin System Components.

Fig. 2. Degree of cure histories from DSC analysis during isothermal cures of stoichiometric mixtures of DGEBA-DDS epoxy. [Data taken at 1 min intervals, symbols used to designate different isothermal temperature].
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isothermal cure case [328 J/g ± 3.0 J/g]. The degree of cure histories for each isothermal cure were then obtained using Eq 2 and 3.

### 3.2 DSC Results

Figure 2 shows the degree of cure histories for each of the isothermal cures. The degree of cure increases rapidly in the early stages of cure until it asymptotically approaches a maximum value, \( \alpha_{\text{max}} \). The maximum degree of cure is generally less than unity owing to vitrification effects. As the isothermal cure temperature increases, vitrification is delayed further until \( T_{\text{cure}} = 230^\circ \text{C} \), at which point \( \alpha_{\text{max}} \) reaches unity, as this condition was used to define \( H_u \), in Eq 2.

In addition to isothermal cure monitoring, DSC analysis was used to measure the \( T_g \) of each of the nonstoichiometric test specimens (\( \alpha_s < 1 \)). Prior to the \( T_g \) measurements, the specimens were completely cured in the DSC by heating at a rate of 10°C/min to 250 °C (assuring complete cure), followed by cooling to room temperature. The \( T_g \) was taken as the temperature corresponding to the midpoint of the heat capacity change (\( \Delta C_p \)) before and after the transition. As anticipated, we observe a strong increase in the glass transition temperature with increasing value of \( \alpha_s \). The results of the \( T_g \) analysis for all of the non-stoichiometric specimens are summarized in Table 2.

### 4 DMA EXPERIMENTS

#### 4.1 Experimental Procedure

Small beam specimens were examined using a Perkin-Elmer DMA-7 in three-point-bend mode. Once the sample dimensions were determined, the specimen was loaded into the DMA and the storage and loss moduli were then measured as functions of temperature under computer control. In all cases an oscillation frequency of 1 Hz was used while heating at 4.0°C/min in a gaseous helium environment. Here, we report the tensile modulus rather than shear modulus to avoid any inaccuracies which may derive from use of a particular value for the Poisson’s ratio, which we have not measured. From the tensile loss tangent versus temperature plots, the \( \alpha \)-relaxation temperature (\( T_{\alpha} \)) is determined and compared to the DSC-measured \( T_g \). Due to the increase in brittleness of specimens with a simulated cure state \( \alpha_s < 0.5 \), only samples for which \( \alpha_s \times 0.5 \) were tested with DMA. The temperature corresponding to the primary peak in the tensile loss tangent trace was used to determine \( T_{\alpha} \).

#### 4.2 DMA Results

Shown in Fig. 3 are the storage modulus versus temperature traces for the epoxy samples ranging in cure extent from \( \alpha_s = 0.5 \) to \( \alpha_s = 1.0 \). Several features of these trends and their dependence on \( \alpha_s \) are worth noting. First, there is a significant increase in the softening temperature (\( \alpha \)-transition temperature) with increasing \( \alpha_s \), with \( T_g \) spanning from 75°C for \( \alpha_s = 0.5 \) to 190°C for \( \alpha_s = 1.0 \). Another feature apparent in Fig. 3 is the strong dependence of the rubbery modulus (\( E_{\text{rubbery}} \)) on \( \alpha_s \) such that low values of \( \alpha_s \) yield tensile rubber moduli comparable to entangled polymer melts (low degree of crosslinking) while \( \alpha_s = 1 \) leads to a rubbery modulus one order of magnitude larger. Considering that \( E_{\text{rubbery}} \sim \nu RT \), where \( \nu \) is the number of crosslink sites per unit volume, \( R \) is the universal gas constant, and \( T \) is the temperature, it is apparent that the parameter \( \alpha_s \) and the actual crosslink density are strongly correlated, as anticipated. A final and somewhat surprising feature of Fig. 3 worth consideration is the slight decrease in room temperature modulus with increasing \( \alpha_s \). In particular, the tensile modulus measured at \( T = 20^\circ \text{C} \) is observed to decrease from 3.1 GPa for \( \alpha_s = 0.5 \) to ~2.3 GPa for \( \alpha_s = 1.0 \). Some explanation for this modulus decrease comes from the loss tangent data described below. The trends in modulus with degree of cure described above are summarized in Fig. 4 where tensile modulus at room temperature and for \( T = T_g + 20^\circ \text{C} \) are plotted as functions of cure extent.

Examination of the tensile loss tangent data, shown in Fig. 5, reveals more clearly the dependence of the glass transition phenomenon on the extent of cure. In particular, it is observed that an increase in the cure extent translates the peak temperature of the loss tangent to higher temperatures by approximately 30°C for each increment of 0.1 in cure extent. Interestingly, we also observe a systematic decrease in the peak magnitude of the tensile loss tangent with increasing cure extent from a value greater than 1.8 for \( \alpha_s = 0.5 \) to a value less than 0.8 for \( \alpha_s = 1.0 \). This inverse dependence of the loss tangent peak value on the cure extent is due to the fact that the rubber modulus is more sensitive to the change in cure extent than the glassy modulus, with the rubber modulus increasing dramatically with cure extent while the glassy modulus actually decreases, as described previously. The resulting manifestation of a decreasing loss tangent peak arises from the consideration that the peak value is expected to be correlated with the relaxation strength \( \Sigma \) measured as the step-lowering of storage modulus (26).

### Table 2. Transition Temperatures for DGEBA-DDS Measured by DSC, DMA, and UCM Experimental Techniques.

<table>
<thead>
<tr>
<th>( \alpha_s )</th>
<th>DSC ( T_g )</th>
<th>DMA ( T_g )</th>
<th>UCM ( T_g )</th>
<th>UCM ( T_u' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>&lt;25</td>
<td>25</td>
<td>44.3</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>&lt;25</td>
<td>25</td>
<td>72.9</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>40.5</td>
<td>27.8</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>63.0</td>
<td>38.7</td>
<td>142</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>82.5</td>
<td>−80.7</td>
<td>61.9</td>
<td>148</td>
</tr>
<tr>
<td>0.6</td>
<td>109</td>
<td>−72.3</td>
<td>76.9</td>
<td>161</td>
</tr>
<tr>
<td>0.7</td>
<td>131</td>
<td>−68.6</td>
<td>114</td>
<td>&gt;195</td>
</tr>
<tr>
<td>0.8</td>
<td>160</td>
<td>−66.5</td>
<td>139</td>
<td>205</td>
</tr>
<tr>
<td>0.9</td>
<td>188</td>
<td>−61.4</td>
<td>188</td>
<td>&gt;235</td>
</tr>
<tr>
<td>1.0</td>
<td>207</td>
<td>−58.6</td>
<td>209</td>
<td>&gt;235</td>
</tr>
</tbody>
</table>
Fig. 3. Tensile storage modulus as a function of temperature at various cure states. [Data taken at 0.35°C intervals, symbols are used to differentiate the curves].

Fig. 4. Tensile storage modulus at room temperature and 20°C above \( T_g \) as a function of degree of cure. [Curves are drawn to show general trend].
where $\Delta E'$ is the modulus lowering across the transition and $E'_o$ is the glassy storage modulus.

In addition to the strong $\alpha$-transition peaks observed in Fig. 5, each epoxy sample was also observed to exhibit a broad low temperature $\beta$-transition in a temperature range spanning $-100 < T < -10^\circ C$. Figure 5 shows an expanded inset of the loss tangent trace highlighting the $\beta$-transition peaks. It can be observed that both the peak temperature and the magnitude of the $\beta$-transition increase with $\alpha_s$. Because low temperature transitions, such as this $\beta$-transition, are sensitive to local segmental motion, and considering our observation of increasing magnitude of the $\beta$ loss tangent peak with $\alpha_s$, we suggest that this transition is directly related to the incorporation of the diphenyl sulfone moiety in the epoxy network. Moreover, the increase in magnitude of the $\beta$-transition with $\alpha_s$ is strongly correlated with the observed decrease in room temperature modulus, suggesting that the reason for the decrease is the existence of strong segmental motion related to incorporation of the diphenyl sulphone moiety in the epoxy network.

The trends in the glass transition and $\beta$-transition temperatures with degree of cure are summarized in Fig. 6. This plot shows the strong dependence of the glass transition temperature on cure extent, with significant linearity for $\alpha_s \leq 0.8$. It should be noted that this behavior is distinct from the parabolic dependence ($T_g \sim \alpha^2$) observed previously in another system where the monomer mixture feature balanced stoichiometry and different cure states were achieved by interrupting the cure process (31). The dependence of the $\alpha$-transition temperature on $\Delta E'$ is somewhat weaker and shows the approach toward an asymptote. Figure 7 summarizes the contrasting trends in magnitude of the glass transition and $\beta$ transition loss tangent peaks with increasing cure extent. As discussed above, the strong decrease in magnitude of the glass transition peak is ascribed to the increasing rubber modulus, while the strong, linear increase in $\beta$ transition peak is attributed to specific molecular motion of the diphenyl sulfone group present in increasing concentration with increasing $\alpha_s$. This hypothesis is supported by the significant linearity of the peak magnitude versus $\alpha_s$ plot ($R^2 = 0.984$).

### 5 Ultrasonic Cure Monitoring (UCM) Experiments

#### 5.1 UCM test cell

A specially built test cell was used in the UCM experiments as shown in Fig. 8a. The test cell was designed to assure a uniform temperature distribution...
throughout the cell, allowing test specimens to be cured uniformly and enabling accurate cure monitoring studies. The diameter of the cylindrical test cell’s internal cavity was chosen such that spurious echoes from the sidewalls and corners are prevented. In addition, the thickness was chosen (t = 4.8 mm) so that adequate spacing existed between subsequent reflections at the material interfaces (avoiding reflection coupling) while minimizing signal attenuation caused by sonic absorption of the material.

The test cell was made of 2026-T6 aluminum. The delay lines were constructed from Vespel SP-21, a

Fig. 6. Glass transition and β transition temperatures as a function of degree of cure. [Curves are drawn to show general trend].

Fig. 7. Loss tangent magnitudes of the glass transition and β transition peaks as a function of degree of cure. [Curves are drawn to show general trend].
polyimide manufactured by DuPont, and were bonded to the aluminum top and bottom platens of the test cell with a high temperature adhesive (EPON 828/curing agent W).

5.2 UCM Experimental Procedure

A 2.25 MHz narrow band, high temperature, ultrasonic transducer manufactured by Ultran Laboratories was used for this study. A Panametrics model 5052PR pulser/receiver was used to generate an electric pulse which was sent to the ultrasonic transducer. The pulser/receiver also received the return signal with a broad band (1 kHz – 35 MHz) receiver. The settings on the pulser/receiver were adjusted for an optimal signal trace, which was displayed on a Hewlett Packard model 54602B digital oscilloscope. LabVIEW application software was used to acquire and transfer the signal to a Macintosh Quadra 840AV personal computer for processing at a later time. A Watlow series 942 temperature controller combined with a Watlow mineral insulated band heater and thermocouple probe were used to provide accurate control (±1°C) of the test cell temperature. A schematic of the experimental set-up is shown in Fig. 8b.

Once the specimens were manufactured (as described in Section 2), the thickness of each was measured with a micrometer and recorded. A thin layer of
coupling grease (Panametrics) was applied to the face of the transducer, tip of the delay line, and the inner aluminum platen surface. The specimen was loaded in the test cell, and once a good signal trace was obtained, the cell was carefully assembled. After assembly, the cell was heated at a slow rate of 1°C/min in order to minimize the extent of temperature lag between the material and test cell. The range of temperatures scanned was variable, depending on the specimen being tested, but was within the range 25 to 235°C in all cases. Data was acquired at 10°C intervals except near the specimen’s glass transition temperature, as determined by a DSC thermal analysis. From approximately 15°C below to 15°C above the expected T_g, the interval was reduced to 1°C. The experiment was terminated when the temperature was well above T_g.

Ultrasonic data were also acquired for the epoxide and amine, anticipating use of the data in assessing epoxy cure state. Since each of the constituents was in liquid form, the thickness could not be accurately measured by standard measurement techniques. With the top platen removed the epoxide was loaded in the cell and filled just above the cell cavity. The top platen was then placed in position, and the excess material was forced out. The cell was heated at a rate of 1°C/min from 25 to 235°C and ultrasonic measurements were taken at one-minute intervals. It was much more difficult to obtain accurate measurements of the amine. Because the material is in powder form at room temperature, it was not possible to take ultrasonic measurements at low temperatures. Instead, the amine was first heated above the melting point (175°C) and then poured into the heated test cell. The cell was then heated at a rate of 1°C/min from 180 to 235°C and data was acquired at one-minute intervals. To estimate values at lower temperatures, the slope of the acquired data was measured by a linear least squares curve fit, and the curve was extrapolated back to room temperature, assuming a linear temperature dependence throughout the range of interest. Although this assumption is simplistic, the contribution to the longitudinal modulus from the amine component is very small.

For ultrasonic isothermal cure monitoring experiments, stoichiometric quantities of the DGEBA-DDS resin system were prepared and the mixture was injected into the test cell preheated to the cure temperature. A thin layer of transducer couplant was applied to the tip of the delay line and aluminum platen surface prior to assembly of the test cell which was determined to be filled when contact with the aluminum was observed ultrasonically. Data acquisition began immediately upon filling of the cell. Typically, the amount of time that transpired between mixing of the resin and data acquisition was less than one minute and subsequent data were acquired at one-minute intervals for the first 60 minutes followed by five-minute intervals until the reaction was complete.

The ultrasonic reflections and transmissions, shown schematically in Fig. 9, result from three interfaces encountered by a launched ultrasonic wave in our experimental geometry. The delay line material was acoustically matched, using intermediate acoustic impedance, to both the transducer and test material in order to maximize the energy transmission across the transducer/delay line and delay line/test material interfaces. Figure 10a shows a typical signal trace from one of the test specimens at room temperature.

Table 3 (32) shows the acoustic impedances of the materials used in this study. Since the impedance of the delay line is greater than the epoxy, a phase reversal occurs at that reflection. Note that a second phase reversal occurs at the 3–4 (aluminum/air) interface since air has a lower impedance compared to aluminum.

For this study only the first two waveforms were of interest: (i) the signal corresponding to the first reflection at the delay line/material interface, and (ii) the signal resulting from reflection at the material/test cell (aluminum) interface. These two waveforms are digitally gated by imposing an artificial window so that each waveform can be analyzed individually. Figure 10b shows the first two waveforms from Fig. 10a, superimposed after gating. It is noted that the second reflection was both time-shifted and inverted in the overlay.

5.3 Signal Processing and Analysis

Once the waveforms are separated for each oscilloscope trace, the data can then be processed by first transforming into the frequency domain for facile
interpretation. Performing a Fourier Transform on the waveform, the voltage \( v(t) \) can be written in the form,

\[ V(\omega) = A(\omega) \exp[i \phi(\omega)] \]  

(5)

where \( A \) is the amplitude and \( \phi \) is the phase, both functions of the angular frequency, \( \omega = 2\pi f \). A LabVIEW program was written to perform a Fast Fourier Transform (FFT) of the time domain signals. Once the signals are transformed and represented by their Fourier components (Eq 5), the amplitude and phase can be examined for the spectral content of both waveforms. Figure 11a shows the amplitude of the signals at room temperature as a function of frequency for the data in Fig. 10. The limited frequency range of the transducer is evident in this plot, revealing a peak frequency of approximately 1.85 MHz and a spectrum width of about 1.6 MHz at half height. Relationships developed below are subsequently applied using the resonant frequency of the transducer.

The phase velocity is an ultrasonic parameter found to be quite sensitive to the cure state of thermosetting polymers. To compute the ultrasonic phase velocity, the phase information from the FFT of each pulse is used, and the velocity computed from the phase difference using (13, 20),

\[ v_L = \frac{\omega L}{\phi_{12} - \phi_{23}} \]  

(6)
where $\phi_{12}(\omega, T)$ is the phase spectrum of the pulse reflected from the 1–2 interface ($\Psi_{12}$) and $\phi_{23}(\omega, T)$ is that from the 2–3 pulse; i.e. the epoxy-traversed wave. $
abla_{23}$. In our data processing, $\Psi_{23}$ is shifted by $\omega \tau_s$ to be superposed on $\Psi_{12}$ prior to computing the FFT. Once the FFT for each pulse has been computed, $\phi_{23}$ for Eq 6 is calculated from $\phi'_{23}$, the raw FFT phase data from the shifted $\Psi_{23}$ as.

$$\phi_{23} = \phi'_{23} - \omega \tau_s$$

(7)
to compensate for the pulse shift. Figure 11b shows the phase spectra of both pulses after applying Eq 7 and after both spectra have been adjusted so that $\phi_{12}(\omega, T) = 0$. The difference in phase between $\Psi_{12}$ and $\Psi_{23}$ is captured primarily from the manual pulse shift $\omega \tau_s$ with phase data from the FFT of the shifted pulse providing minor corrections. The magnitude of the phase shift is dependent on the cure state and

<table>
<thead>
<tr>
<th>Material</th>
<th>Acoustic Impedance, $Z$ (106 kg/m2s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vespel delay line</td>
<td>3.86</td>
</tr>
<tr>
<td>DGEBA/DDS</td>
<td>3.17</td>
</tr>
<tr>
<td>2026-T6 Aluminum</td>
<td>17.7</td>
</tr>
<tr>
<td>Air</td>
<td>0.0004*</td>
</tr>
</tbody>
</table>

*From Krautkrämer and Krautkrämer (32).
temperature, being larger for low crosslink densities and smaller for high crosslink densities, such as that of fully cured epoxy.

5.4 Ultrasonic Results for the Epoxy System

Specimens with $\alpha_s$ between 0.1 and 1.0 were heated while acquiring ultrasonic data and the phase velocity was calculated for each of the specimens as a function of temperature. A typical result is shown in Fig. 12. The change in slope of the phase velocity curve indicates where a transition in material behavior occurs; two such transitions are observed in the plot. The low temperature transition correlates reasonably well with the glass transition as measured by DSC and DMA. Interestingly, there is a high temperature transition that is revealed in the UCM data, here labeled the $\alpha'$ transition. The existence of this secondary transition was unexpected and its relaxation mechanism is the subject of further study. One possible explanation is the existence of dispersed regions (or phases) of high molecular weight which have reached the diffusion limit (vitrification). A second possibility is that the breadth of the glass transition is magnified when examined at ultrasonic frequencies, such that the higher slope region of $v = f(T)$ (spanning 62 to 148°C for $\alpha_s = 0.5$) is the glass transition itself, bridging the glassy ultrasonic velocity at low temperatures with the rubbery/liquid velocity at high temperatures. Table 2 lists the transition temperatures measured by UCM for all of the specimens and the correlation with DSC and DMA data.

Figure 13 shows the combined phase velocity data for several of the simulated cure states examined. Interestingly, all of the partial cure data falls within the upper limit (full cure $\alpha_s = 1.0$) and lower limit (pure epoxide $\alpha_s = 0.0$) curves. The data suggest that the predominant effect of an increasing crosslink density is a shift of the $v = f(T)$ curves to higher temperatures with only minor influences existing for either the glassy or rubbery ultrasonic velocities. In comparison with Fig. 3 (storage modulus versus temperature) we see very analogous behavior between the two measurements; however, the ultrasonic data show evidence of a much broader glass transition region. Additionally, it appears that low frequency (DMA) data allow for enhanced sensitivity to cure state for the rubbery modulus when compared to ultrasonic data. More $v = f(T)$ data for elevated temperatures are needed for a quantitative comparison of the two observations, however.

5.5 UCM of Isothermal Cure Experiments

We have used the ultrasonic method to characterize the change in mechanical properties of this epoxy system during isothermal curing. For these UCM isothermal experiments the cure state was characterized using the longitudinal velocity. We define a longitudinal velocity fraction, $\phi$, as,

$$\phi = \frac{v(t) - v_1}{v_f - v_1}$$

Figure 12. Typical ultrasonic result for DGERA-DDS epoxy ($\alpha_s = 0.5$) at 1.85 MHz. [DSC analysis $T_g = 82.5$°C, DMA analysis $T_g = 76.1$°C].
Fig. 13. Phase velocity versus temperature over the entire range of cure state.

Fig. 14. Velocity fraction histories from UCM analysis during isothermal cures of DGEBA-DDS epoxy.
where \( v_i \) is the initial velocity (uncured) and \( v_f \) is the final velocity (full cure), each being functions of temperature (Fig. 13). Figure 14 shows the evolution of velocity fraction during cure for each of the isothermal cure temperatures, indicating excellent sensitivity to the state of cure in all cases. We observe that as curing progresses, velocity fraction increases in magnitude until approaching unity. The data also show that as the cure temperature increases, the rate of increase in velocity fraction, and thus the rate of cure, increases. Additionally, UCM experiments for \( T_{\text{cure}} \leq 190^\circ \text{C} \) reveal a sigmoidal shape to \( \phi(t) \) where a change in curvature occurs at an early stage of the cure reaction. We speculate, based on adsorption measurements, that the point of curvature change is the point of gelation. Interestingly, referring to the isothermal DSC traces in Fig. 2, it appears that the DSC is insensitive to this phenomenon.

### 6 COMPARISON OF UCM, DMA AND DSC TECHNIQUES

Each of the experimental techniques presented in this paper provide important information about the state of cure of DGEBA-DDS. All three techniques are capable of tracking the change in glass transition as cure state advances as shown in Table 2. However, both the DMA and UCM techniques show secondary transitions as well. The low temperature \( \beta \) transition observed in the DMA data and the high temperature \( \alpha' \) transition measured by UCM are sensitive to changes at much different length scales due to vastly different time scales. That is, the DMA probes material response at frequencies of about 1 Hz compared to 1.85 MHz for the UCM. It is not surprising that these secondary transitions are exhibited only when probed by the appropriate technique and length scale.

In Fig. 15, both the thermal degree of cure history (from DSC analysis) and the velocity fraction history (from UCM analysis) are overlaid for a representative case of the isothermal curing. There is a rapid increase in thermal degree of cure at early cure times: within 30 minutes. DSC analysis shows that the material is almost fully cured (at 210°C). In contrast, the velocity fraction increases more slowly at the beginning of curing and has only reached a value of 0.75 at 30 minutes. Full cure, indicated by \( \phi = 1 \), is only reached after 90 minutes of curing.

Each of the isothermal cures shows the same behavior; during the latter stages of cure when the degree of cure is fully developed (as measured by DSC), the mechanical properties are still increasing. This same trend was observed by White and Mather (22) for an EPON 815/V140 epoxy resin system. Thus, if processing parameters are based on thermal cure kinetics modeling from DSC analysis, materials cured...
under such conditions could have underdeveloped mechanical properties. These results are especially significant for strength- or stiffness-critical applications of materials.

Since the DSC shows apparent insensitivity to changes in the mechanical properties of a developing polymer network, it is a poor choice for characterizing cure state for applications where structural properties are important. DMA, however, is quite sensitive to the rubbery modulus (and as such, the cure state), but is limited practically to cure states above gelation. We suggest, then, that among these three techniques, only UCM can be applied to all cure states and is therefore suitable for on-line process monitoring. In fact, Frigione et al. (24) recently demonstrated real time assessment of the cure state in an epoxy adhesive used in the bonding of concrete repairs.

7 CONCLUSIONS

Three experimental techniques were used to characterize the cure state and its development during cure of an epoxy resin (DGEBA-DDS). Samples of non-stoichiometric monomer mixtures were used to simulate various stages of cure of a stoichiometrically prepared epoxy, with the motivation that it allows for variable temperature characterization without concern for ongoing chemical reaction.

DSC was used to measure the heat of reaction of the resin and glass transition temperature. It was found that the maximum degree of cure was generally less than unity due to vitrification effects. Vitrification was reduced at higher cure temperatures until at 230°C αmax = 1. Postgelation samples (where α > 0.5) were interrogated using the DMA technique in which the complex modulus was measured over a range of temperatures. There is a strong dependence of the complex modulus on the cure state and its development during cure.

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9 REFERENCES