

Evolution of Properties of a Thermosetting Isocyanate/Epoxy/Glass Fiber Model Composite System with Increasing Cure

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ABSTRACT: A methodology is reported for monitoring the evolution of isothermal physical properties of thermosetting systems with increasing conversion (cure). For this report, measurements of modulus vs. temperature of a single composite specimen were obtained on repetitive cooling and subsequent heating to successively higher temperatures: Cooling and subsequent heating data often displayed thermohysteresis. Crossplotting provided plots of isothermal modulus vs. conversion (as measured in the same experiment by T_g) for a wide range of temperatures (i.e., from -180 to $+380^\circ\text{C}$) from both the cooling and the heating data. Comparison of isothermal cooling and heating data provided a measure of toughness of the matrix vs. conversion through the extent of hysteresis of the data. The basis of the approach depended on five factors: (a) use of a composite specimen, (b) the ability to obtain data both on cooling and on heating, (c) the effect of microcracking (which is presumably responsible for the observed hysteresis) could be removed by heating ("healing") near the glass transition temperature, (d) the use of a single specimen provided an internal reference for comparing data, and (e) the assumption that T_g is a direct measure of conversion. The methodology is demonstrated using a complex thermosetting isocyanate/epoxy/glass fiber composite system using the TBA torsion pendulum technique. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 27–38, 1997

Key words: isocyanate/epoxy thermosetting system; isothermal modulus vs. conversion; microcracking; toughness; torsional braid analysis (TBA)

INTRODUCTION

This article deals with a complex thermosetting system with competing cure and thermal degradation reactions using the TBA torsion pendulum technique which employs a composite resin-impregnated glass braid as the specimen.¹ The unreacted formulation is a mixture of stoichiometrically excess diisocyanate, a diepoxide, and a cata-

lyst. The structures of the reactants, and the two principal and consecutive cure reactions of isocyanate trimerization to yield isocyanurate and isocyanate-epoxide cycloaddition to yield 2-oxazolidone, respectively, are shown in Figure 1.^{2,3} The catalyst promotes both reactions. Both reactions lead to crosslinking.

The overall aim of the project, of which this report is a part, was to develop a methodology for investigating the evolution of properties of complex thermosetting systems with increasing conversion (T_g).^{4,5} This was done for the present report by measuring properties of a single specimen

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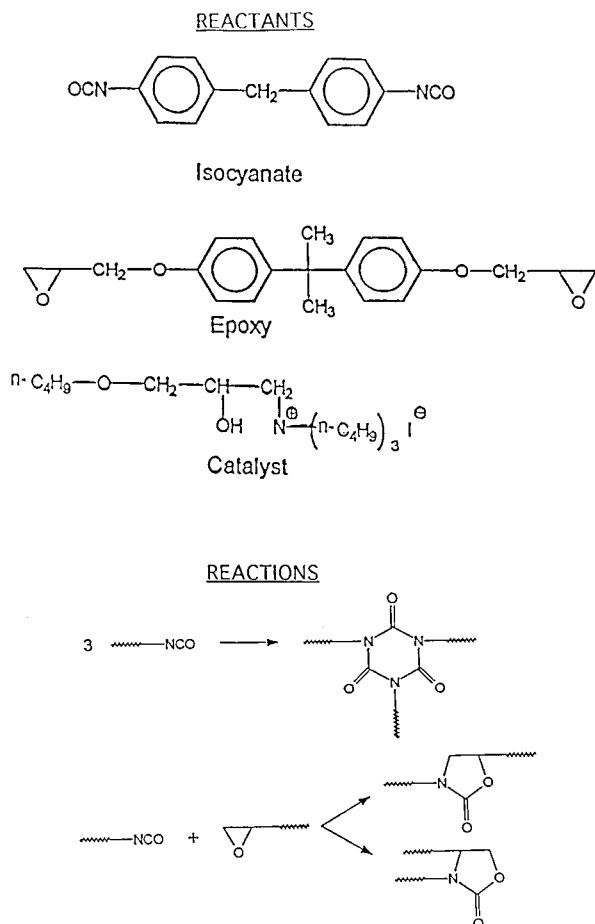


Figure 1 Chemical reactants, catalyst, and reactions.

during controlled cooling from successively increasing maximum temperatures (T_{\max}) to -180°C and on subsequent controlled heating to the next higher temperature: Crossplotting of the data provides isothermal properties vs. conversion from both cooling and heating data. Heating to successively higher temperatures increases chemical conversion (T_g). In particular, the present work deals with changes in the isothermal modulus with increasing conversion from both cooling and heating data in an inert atmosphere (He) for temperatures ranging from -180 to 380°C . The isothermal data at lower temperatures (below approximately 250°C) reflect the evolution of properties due to cure. The data at higher temperatures (in the approximate temperature range 250 – 380°C) reflect the competition between cure and high-temperature reactions (i.e., chemical rearrangement and degradation) which are designated thermal degradation. The current investigation involves the evolution (1) of the modulus with increasing conversion and (2) of toughness with increasing conversion. The latter was moni-

tored by the effect of presumed microcracking on the rigidity (modulus) of the composite specimen which gives rise to hysteresis between cooling and subsequent heating data; the microcracking presumably arises from the inability of the matrix to withstand the stresses developed from the different coefficients of thermal contraction and expansion of the matrix and glass filaments of the composite specimen. Five key factors formed the basis of the experiment: (a) use of a composite specimen, (b) the ability to collect data both on cooling and on subsequent heating, (c) the effect of microcracking that could be removed by heating (“healing”) near the glass transition temperature, (d) use of a single specimen that acted as an internal reference for comparing hysteresis data (conventional methodology employs multiple specimens which results in much scatter of data), and (e) the assumption that T_g is a direct measure of conversion. A preliminary report has been published.⁶

Previous reports^{4,5} on the particular thermosetting system examined the progress of cure through (1) temperature scanning experiments at different heating rates using a series of initially unreacted specimens and (2) isothermal experiments using a series of initially unreacted specimens, leading to a continuous heating time–temperature–transformation (CHT) diagram (Fig. 2) and an isothermal time–temperature–transformation (TTT) cure diagram (Fig. 3), respectively. In Figure 2, T_{g0} , $T_{g\text{gel}}$, and $T_{g\infty}$ are the glass transition temperatures of the initial formulation, of the reactive system at its gel point composition, and of the fully cured state, respectively. These diagrams relate the phenomena of gelation, vitrification, and devitrification to the time and temperature path of the cure. Two reaction regions for the cure, which are consecutive and separable, were inferred. This follows from the extensive interval between gelation ($T_{g\text{gel}}$) and vitrification (T_{vit}) in the temperature-scanning experiments of Figure 2. It is also consistent with the two S-shaped isothermal time-to-vitrification contours in Figure 3 which correspond to the first reaction region, giving a material with a maximum glass transition temperature $T_{g1\infty} \equiv 120^{\circ}\text{C}$, and to the second reaction region, giving a material with a maximum glass transition temperature of $T_{g2\infty} \approx 315^{\circ}\text{C}$ (1 Hz), respectively. (Note that $T_{g2\infty}$ of Fig. 3 $\equiv T_{g\infty}$ of Fig. 2.)

Other work on other thermosetting systems has been concerned with the non monotonic changes of isothermal glassy state properties with increasing conversion such as the decrease in iso-

thermal modulus with increasing conversion (“anomaly”). This eventually led to a conversion–temperature–property diagram,^{1,7,8} the self-evident essence of which is that properties depend on the relationship between the temperature of measurement and the temperature of transitions (which rise with increasing conversion). Transitions (e.g., sub- T_g transitions and T_g) and isothermal modulus vs. conversion (T_g) data were obtained in that earlier work using the basic experimental procedure as used for the present work, i.e., using measurements on a single specimen during repetitive cooling and subsequent heating with increasing values of the maximum temperature, and then crossplotting to obtain isothermal data vs. conversion (T_g). The present report extends prior work by comparing isothermal modulus vs. conversion (T_g) data obtained during cooling and subsequent heating.

T_g is used directly as a measure of conversion based on results for other thermosetting systems which showed that a unique relation often exists

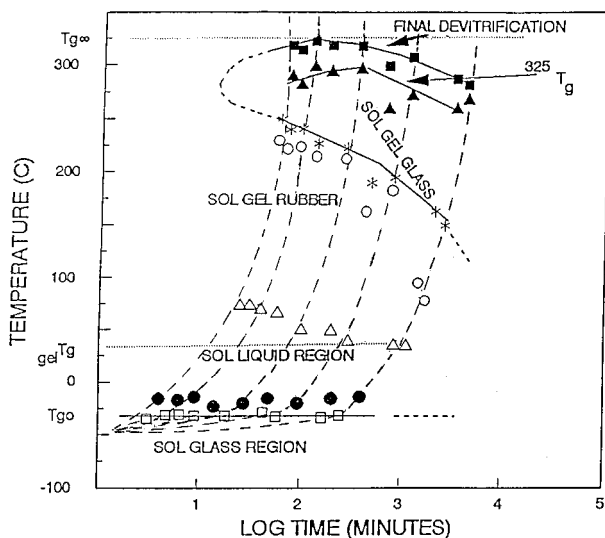


Figure 2 CHT diagram. Full lines connect (\square) initial devitrification ($\sim T_{g0}$), ($*$) vitrification (T_{vit}), and (\blacksquare) the glass transition temperature [devitrification (T_g)] on heating at different heating rates to 325°C (long-dashed lines correspond to heating rates of 5.0, 3.0, 1.0, 0.3, and 0.075°C/min). Other events identified on heating include (\bullet) the liquid–liquid transition [T_l], (\triangle) gelation (T_{gel}), and (\circ) the end of the rubbery region. (\blacktriangle) The glass transition temperature ($^{325}T_g$), measured during cooling at 2°C/min after heating to 325°C at different heating rates, is also identified. States identified are sol glass, sol liquid, sol gel rubber, and sol gel glass regions. States not identified include gel glass, degraded gel glass, gel rubber, and degraded gel rubber.

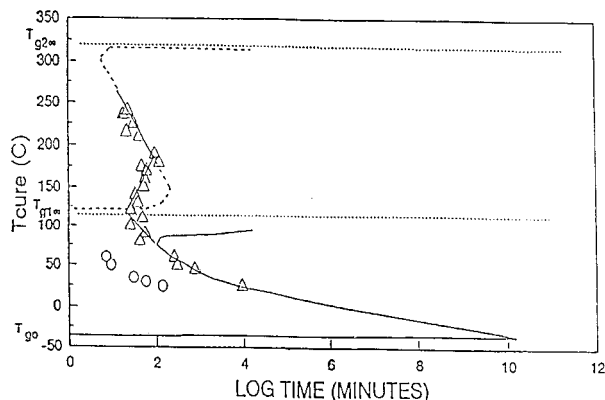


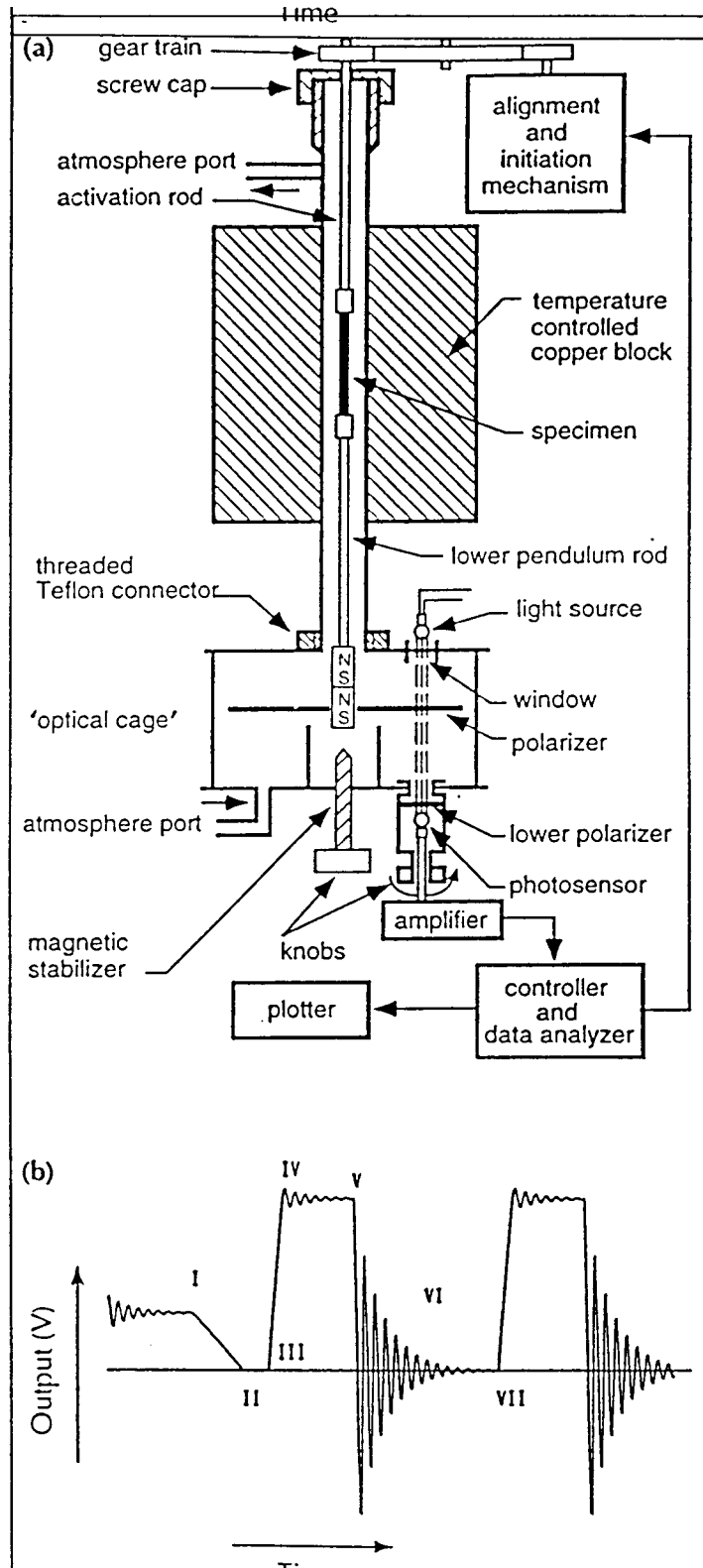
Figure 3 Isothermal TTT cure diagram: (\triangle) the time to vitrify vs. T_{cure} from T_{g0} to $T_{g2\infty}$. Also, (\circ) times to gel (experimental) for lower isothermal temperatures. Two S-shaped vitrification curves are shown by full lines corresponding to a low-temperature reaction region (as was calculated together with some experimental data) and a high-temperature reaction region (experimental).⁵

between T_g and conversion.¹ T_g is also used in the conventional sense as the glass transition temperature. For the first reaction regime of the present reactive system, conversion has also been estimated from the intensity of a cryogenic loss peak in a dynamic mechanical experiment at 1 Hz by assuming a linear relationship between conversion and the peak height of the loss peak.^{1,9}

EXPERIMENTAL

The isocyanate used in these studies is a liquid urethonimine-modified diphenylmethane diisocyanate (EniChem Co., Polyurethanes Division; 70 parts by weight) with an average isocyanate functionality of 2.15/mol and an equivalent weight of 147.9 g/eq. Its viscosity at 25°C is 50 cPs. The epoxide portion of the mixture is a diglycidyl ether of bisphenol A (Dow Chemical Co., DER 330; 29.5 parts by weight) with a theoretical epoxy functionality of 2.0 and an epoxy equivalent weight of 182.4/mol. The catalyst used was [(2-hydroxy-3-*n*-butoxy)propyl]tri-*n*-butyl ammonium iodide (0.5 parts by weight) (Fig. 1). The stoichiometry is such that an excess of isocyanate is present; moles of isocyanate groups/moles of epoxide groups = 2.8/1.0. The reactive liquid formulation was prepared by adding a homogeneous, relatively stable, mixture of the isocyanate and catalyst to the liquid epoxy at 25°C followed by thorough mixing.

Dynamic mechanical (≈ 1 Hz) data were ob-



tained on a single specimen during cooling and subsequent heating using the automated TBA torsion pendulum in which freely damped waves are induced intermittently during an experiment. A schematic diagram of the TBA apparatus and its control sequence are shown in Figure 4.¹ Transitions (e.g., T_g) were designated by the temperatures of the maxima of the logarithmic decrement ($\approx \pi \tan \delta$) during the temperature scans. The specimen was a composite of the matrix material (~ 25 mg) and heat-cleaned-in-air glass filaments (in the form of a braid) and was cylindrical in shape (about 2 in. length and 0.05 in. diameter); it was prepared simply by dipping the glass braid into the liquid formulation at 25°C. It can be considered to be an experimental element of a glass fiber/organic matrix composite. After lowering the mounted specimen into the TBA unit at 25°C, and then cooling to 15°C, the experiment involved repetitive sequences of cooling to -180°C and heating to successively higher temperatures (T_{\max}) at cooling and heating rates of 2°C/min. The higher temperatures (T_{\max}) varied from 15 to 375°C. T_g values, measured on cooling, provided estimates of conversion (see Fig. 5). Isothermal shear modulus (rigidity) data vs. conversion were obtained at different temperatures by crossplotting from the successive scans of modulus vs. temperature. Two sets of isothermal modulus vs. conversion data were obtained: one from decreasing temperature (often designated herein as “down modulus”), and the other from subsequent increasing temperature (often designated herein as “up modulus”). (Data from decreasing and increasing temperature measurements are usually plotted together as in Figs. 6–12.) All experiments were conducted in an atmosphere of flowing helium. The automated TBA torsion pendulum is available from Plastics Analysis Instruments, Inc.¹ It is noted that the proportionality between modulus and rigidity becomes invalid with changes in dimensions of the specimen, as caused, e.g., by thermal degradation of the matrix.¹⁰

RESULTS

T_g vs. T_{\max}

Figure 5 shows the relationship between T_g , obtained on cooling from T_{\max} , and T_{\max} for the single specimen. Also shown is the reference line $T_g \equiv T_{\max}$. Various regions are apparent in Figure 5:

For low values of T_{\max} , T_g is less than T_{\max} since T_g does not reach T_{\max} on heating to and cooling from T_{\max} . The reaction rate is likely to be chemically controlled in this region.

At intermediate values of T_{\max} , T_g increases to or to slightly above T_{\max} . (T_g cannot be measured on cooling if T_g is greater than T_{\max} .) For $T_g > T_{\max}$, the reactions are presumably diffusion-controlled and so T_g is close to T_{\max} .

For high values of T_{\max} , T_g is again less than T_{\max} ; however, after decreasing, T_g increases again with increasing T_{\max} (presumably, by extrapolation, increasing to above T_{\max}). The isothermal modulus at high temperatures would decrease as T_g decreases through T (i.e., isothermal devitrification) and then increase as T_g increases through T (i.e., isothermal vitrification). This region is attributed to thermal degradation.

Basis of Analysis

The evolution of the modulus and the transformation from a brittle to a tough material at isothermal temperature (T) with increasing conversion is obtained by comparing for each conversion (i.e., T_g) the rigidity (modulus) at T on cooling through T from T_{\max} with that obtained on subsequent heating from -180°C through T . The analysis involves an interpretation in terms of presumed microcracking of the matrix using (a) the assumed modulus at T after cooling to T from T_{\max} and (b) the modulus at T on cooling from T_{\max} vs. modulus at T on subsequent heating from -180°C . Microcracking can originate at the fiber/matrix interface during a temperature scan of T_{\max} to T , and T to -180°C to T . The modulus at T on cooling from T_{\max} would be decreased by microcracking;

Figure 4 (a) Schematic diagram of the automated freely oscillating torsion pendulum TBA instrument. (b) Automated torsion pendulum control sequence. Output (V, volts) vs. time. (I) Previous wave decays, offset from center of linear region (at zero volts) of pair of polarizers detected, and correction by rotation of one polarizer disc begins; (II) reference level of polarizer pair reached (at zero volts); (III) wave initiating sequence begins by stretching a spring; (IV) decay of transients at a fixed strain; (V) free oscillations begin after step-release of tension in the spring; (VI) data collected; (VII) control sequence repeated. (Plastics Analysis Instruments, Inc., Princeton, NJ.)

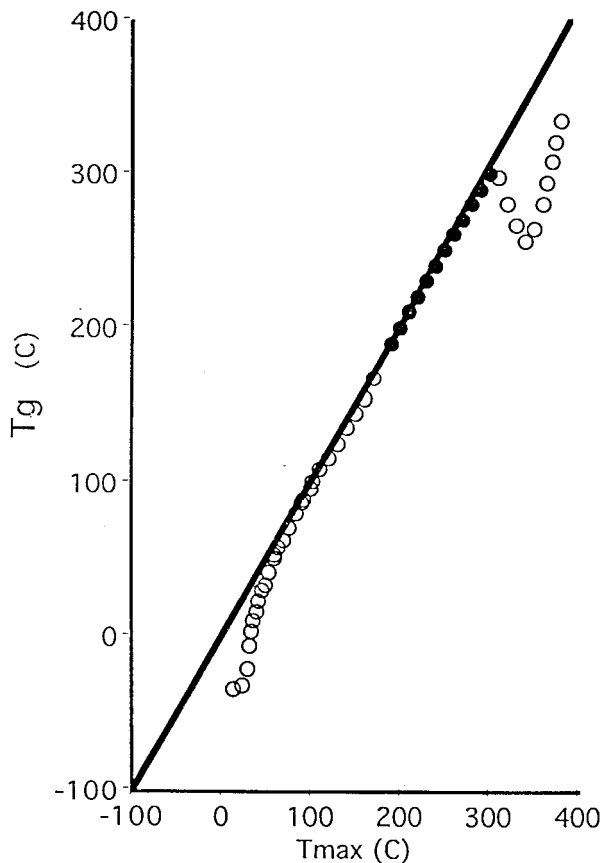


Figure 5 T_g vs. T_{max} . (O) Measured T_g values; (●) $T_g \geq T_{max}$. (see text). Data were obtained on cooling. Also shown, reference line $T_g \equiv T_{max}$.

similarly, microcracking below T would lead to the modulus being higher on cooling through temperature T than on subsequent heating through temperature T .

Assuming that reactions are quenched on cooling through T from T_{max} , and in the absence of microcracking, physical aging effects, thermal degradation, and temperature lags between cooling and heating: (1) For $T_{g0} < T < T_{g2\infty}$, isothermal modulus data vs. conversion would show an increase in modulus due to vitrification followed by a decrease in modulus due to the anomaly. Also, the down and up data for all conversions would be the same at T . (2) For $T_{g0} \gg T$, the effect of vitrification would not be applicable, and although the isothermal modulus vs. conversion curve is not known *a priori*, the down and up modulus data would be essentially the same.

In the absence of microcracking, physical aging effects, thermal degradation, and temperature lags between cooling and heating, there would be no difference in the down and up modulus data vs. temperature for a fixed conversion. For the

present system, this appears to almost occur for a conversion corresponding to $T_g \approx 120^\circ\text{C}$ (Fig. 6 shows sub- T_g data for $T_g \approx 120^\circ\text{C}$), which corresponds to the completion of the first reaction stage. (For a fixed conversion, the modulus decreases with increasing T below T_g [e.g., Fig. 6].) In practice, minor differences between down and up data arise (a) from physical aging during the experiment, which leads to the down modulus being lower than the subsequent up modulus (cf. the effect of microcracking) and (b) from thermal lags in which the specimen at the assigned " T " on cooling is actually at a higher temperature than on subsequent heating, which leads to the measured down modulus being higher than the subsequent up modulus (i.e., as for microcracking). (Helium is used rather than nitrogen in the TBA experiments as the environmental atmosphere because of its higher thermal conductivity at low temperatures.) The down and up data in Figure 6 appear to differ somewhat only in a localized region: This is probably the consequence of the modulus changing more slowly with change in temperature in this region.

A comparison of the down and up modulus (rigidity) data for $T = -20^\circ\text{C}$ (Fig. 7) shows the results of thermohysteresis. In comparison, for $T = -170^\circ\text{C}$ (Fig. 8) and for isothermal temperatures higher than 50°C (e.g., $T = 150^\circ\text{C}$, Fig. 12) in the absence of high-temperature degradation processes, the down and up data show only minor hysteresis: The reasons for the relative absence of hysteresis in the two regions are different (see later).

The following analysis is provided for the data at the isothermal temperature of -20°C (Fig. 7) before the region of thermal degradation. Similar

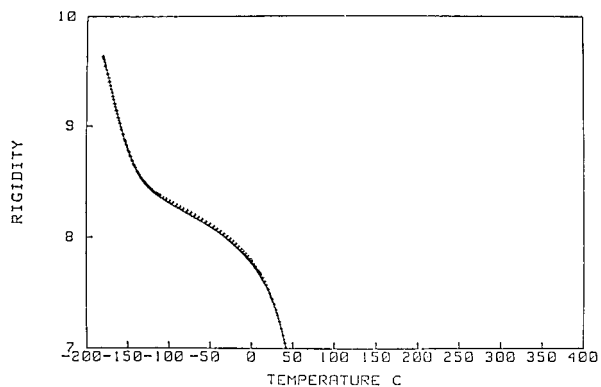


Figure 6 Modulus (rigidity) vs. temperature: sub- T_g cooling data and heating data ($T_{max} = 120^\circ\text{C}$; $T_g \approx 120^\circ\text{C}$). No distinction is made between symbols for down and up data.

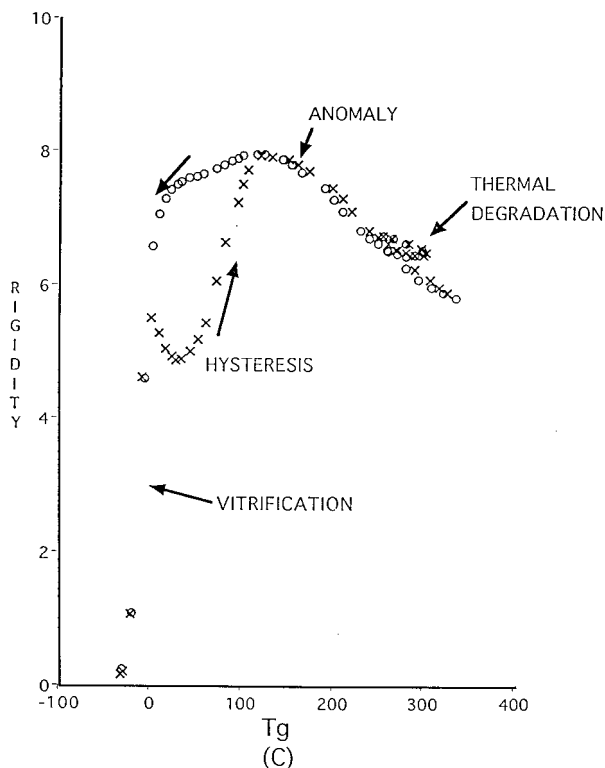


Figure 7 Isothermal (○) down and (X) up moduli (rigidity) at -20°C vs. conversion (T_g). Various regions are marked, i.e., vitrification, hysteresis, anomaly, thermal degradation.

analyses can be used for other isothermal temperatures which show hysteresis (see later). The analysis shows that for low values of conversion the extent of brittleness (hysteresis) at -20°C passes through a maximum as $T_g - T$ increases.

- When $T_g = T_{g0} = -35^{\circ}\text{C}$, the material is a liquid at -20°C . The modulus is low at -20°C and the values obtained on decreasing and increasing the temperature are the same at -20°C (although microcracking presumably occurs on cooling below T_g).
- When $T_g = -5^{\circ}\text{C}$, the material at -20°C is 15° below T_g and is in the T_g transition region. The material presumably microcracks on cooling below -5°C but heals on subsequent heating to -5°C to give the same value of the modulus at -20°C as on cooling.
- When $T_g = 5^{\circ}\text{C}$, the material at -20°C is 25°C below T_g . There is difficulty in ascertaining whether microcracking occurs on cooling from T_g to -20°C since the modulus is in the T_g transition region and the

modulus vs. temperature for a specimen at the particular T_g which has not undergone microcracking is unknown. Presumably, microcracking occurs on cooling from -20 to -180°C but healing does not occur completely on heating to -20°C (note hysteresis) since the material is deeper in the glassy state when $T_g = 5^{\circ}\text{C}$ than when $T_g = -5^{\circ}\text{C}$.

- When $T_g = 30^{\circ}\text{C}$, the material at -20°C is 50°C below T_g . The down modulus is a microcracked value (see later). Upon cooling from -20 to -180°C and heating through -20°C , the material microcracks further and severe hysteresis is observed at -20°C since it does not heal as much on heating to -20°C as in (c) above.
- When $T_g = 80^{\circ}\text{C}$, the material at -20°C is 100°C below T_g . The difference between the modulus values on cooling and heating shows the material to be brittle with respect to cooling below -20°C and reheating through -20°C , but less so than

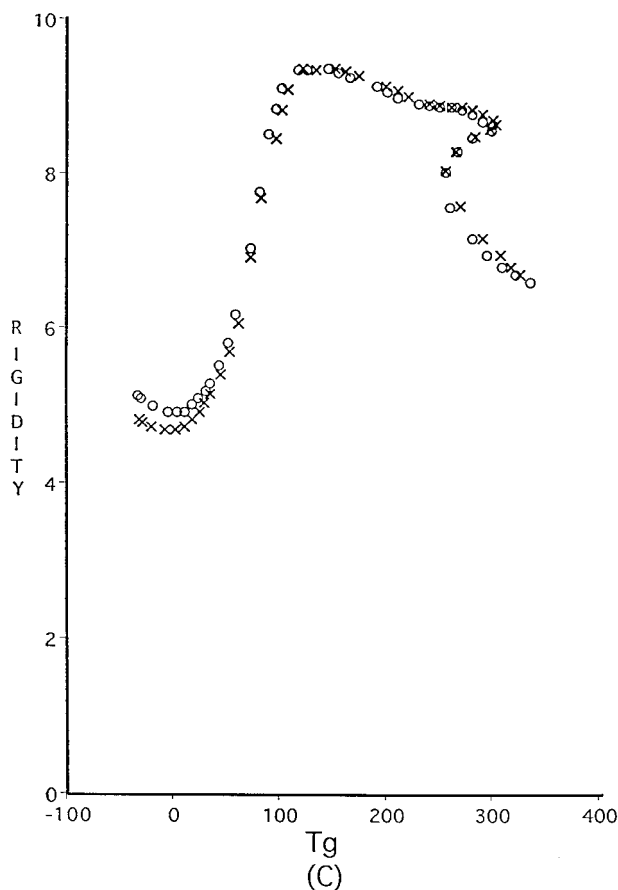


Figure 8 Isothermal (○) down and (X) up moduli (rigidity) at -170°C vs. conversion (T_g).

for a T_g value of 30°C. A question remains as to whether the material has microcracked on cooling from 80 to -20°C; further analysis shows it to be microcracked (see later).

- (f) When $T_g \geq 120^\circ\text{C}$, the material at -20°C is $\geq 140^\circ\text{C}$ below the T_g . For these T_g values, the first reaction region is complete with $T_{g1\infty} = 120^\circ\text{C}$.⁵ The material presumably does not crack below -20°C , i.e., it is tough, since the modulus is the same at -20°C (after cooling to -20°C) and after subsequent heating from -180 to -20°C . It follows also that it presumably does not microcrack on cooling from T_{max} to -20°C . The isothermal modulus decreases as T_g increases above approximately 110°C (anomaly, as before). The maximum in both the down and up modulus values at -20°C with increasing conversion arises from the competition between the onset of microcracking (on cooling) or the end of healing (on heating) and the decrease in isothermal modulus with conversion associated with the anomaly.

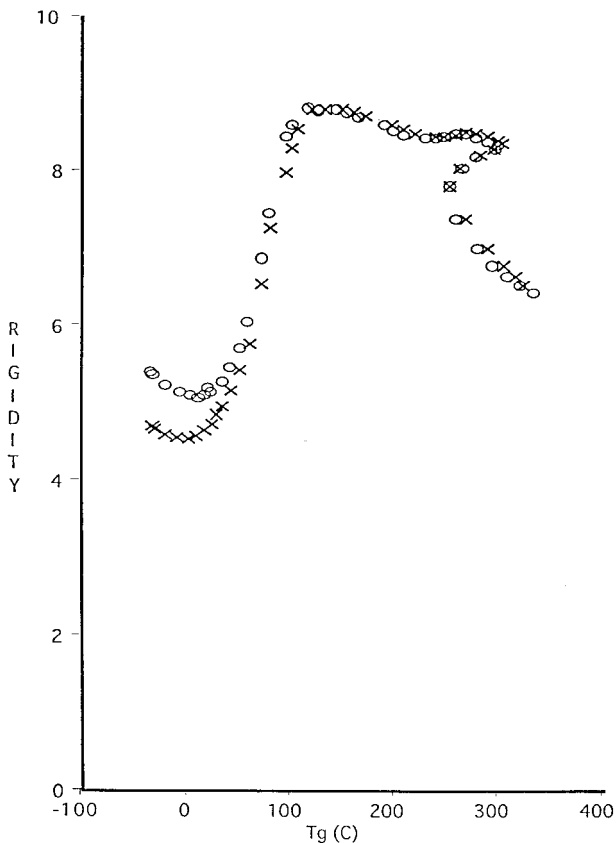


Figure 9 Isothermal (O) down and (X) up moduli (rigidity) at -150°C vs. conversion (T_g).

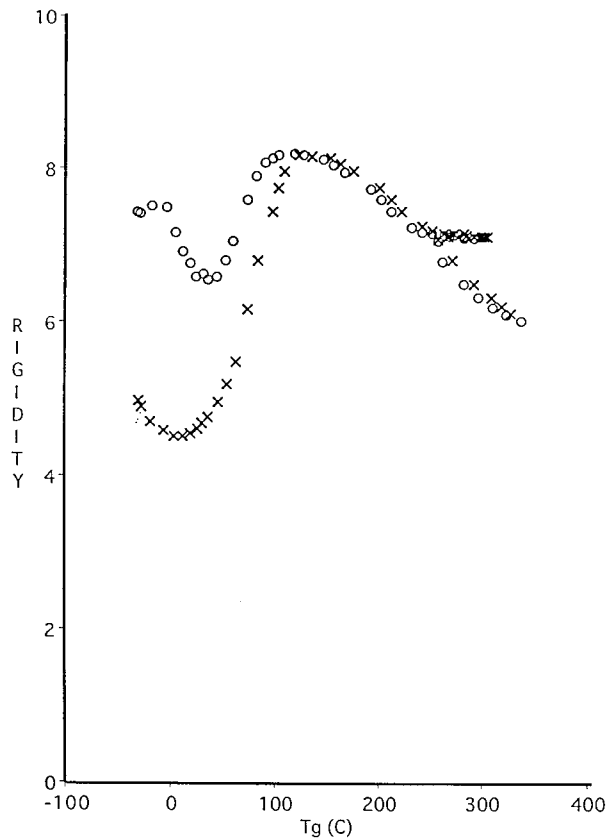


Figure 10 Isothermal (O) down and (X) up moduli (rigidity) at -70°C vs. conversion (T_g).

Regions of Temperature Behavior

Analysis of the data shows that there are distinct regions of isothermal behavior:

Region 1: $T \ll T_{g0}$ (e.g., Figs. 8 and 9: -170 and -150°C). The material at T is very deep in the glassy state.

On cooling from T_{max} , for material of low conversion up to the end of the first reaction (which corresponds to $T_g \approx 120^\circ\text{C}$), microcracking occurs on cooling to T to give a low modulus value at T . On further cooling to -180°C and subsequent heating from -180°C to T , a lower modulus is observed because the extent of microcracking is increased. For low values of T_g , the down brittleness in terms of loss of modulus on cooling increases as T decreases, e.g., modulus at $-170^\circ\text{C} <$ modulus at -150°C (cf. -170 and -150°C down data).

For material of conversion involving the second reaction (i.e., $T_g \geq 120^\circ\text{C}$, until thermal degradation which occurs in the vicinity of $T_{g2\infty} = 315^\circ\text{C}$), no hysteresis between the cooling and heating data is observed; the material is uncracked both on cooling from T_{max} to T and on subsequent treat-

ment T to -180°C to T , i.e., the material is not brittle for $T_g > 120^{\circ}\text{C}$. At a fixed T_g (conversion), the modulus decreases (as expected) with increasing temperature (Fig. 6). At a given isothermal temperature for conversions for which microcracking has not occurred (i.e., $T_g > 120^{\circ}\text{C}$), the modulus decreases with increasing conversion (-170°C [Fig. 8]; -150°C [Fig. 9]): This is the isothermal anomaly referred to above (which appears to occur for all temperatures).

Region II: $T < T_{g0}$, but properties at T affected by T_g for low T_g 's (Figs. 10 and 11: -70 and -50°C data).

The material at T for low conversions is not far below T_g . On cooling from above T_g , for material of low conversion up to the end of the first reaction which corresponds to $T_g \approx 120^{\circ}\text{C}$, the isothermal modulus pattern for down data consists of two maxima, the lower conversion one moving to higher T_g 's with increasing T (cf. $T = -70$ and -50°C). The higher conversion maximum does not appear to change with increasing T . Each maximum obtained on cooling is the result of two competing factors:

Lower conversion maximum: At very low con-

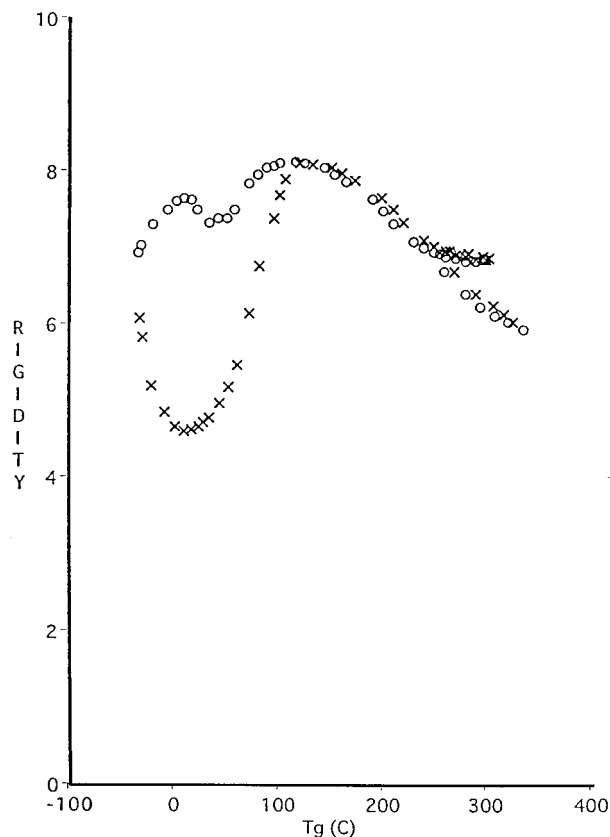


Figure 11 Isothermal (O) down and (X) up moduli (rigidity) at -50°C vs. conversion (T_g).

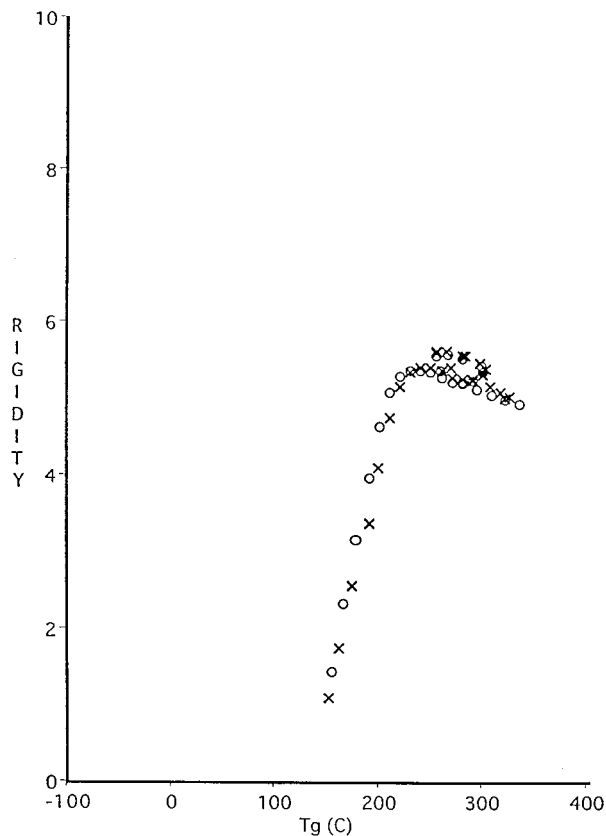


Figure 12 Isothermal (O) down and (X) up moduli (rigidity) at 150°C vs. conversion (T_g).

versions, the down modulus at T increases with conversion as a consequence of T being in the T_g region and of the interval $T_g - T$ increasing. For the same reason, the modulus of the initial material at -70°C is higher than at -50°C . With further conversion, the material at T is deeper in the glassy state which eventually leads to microcracking lowering the modulus more than the increase in modulus due to $T_g - T$ increasing. As T increases, the material at the same conversion is less brittle and so the magnitude of the minimum in the modulus after the maximum decreases.

Higher conversion maximum: As conversion increases, the material is tougher; therefore, the down isothermal modulus increases with conversion because of less microcracking on cooling. At a conversion of $T_g \approx 120^{\circ}\text{C}$ (end of first reaction), the material shows no hysteresis between the cooling and heating data (Figs. 6, 10, and 11). The subsequent decrease in the isothermal modulus with increasing conversion is due to the anomaly.

Region III: $T > T_{g0}$ (e.g., -20°C , Fig. 7; see detailed analysis of -20°C data above).

The material at T is initially in the liquid state

and shows identical values of the modulus on cooling and heating through T . As T_g increases through T , the modulus at T increases because of vitrification. In the middle of the transition region, there is no hysteresis. As T_g increases further, the material becomes brittle at T for $T \ll T_{g1\infty}$ to give hysteresis between the cooling and heating data at T : With further increase of T_g (toward completion of the first reaction), the material becomes tougher at T , which results in less hysteresis between the cooling and heating data. As T_g reaches the value corresponding to the end of the first reaction, the material is tough and shows no hysteresis between the cooling and heating data. The subsequent decrease in the modulus reflects the anomalous decrease of the isothermal modulus with increasing conversion. For $T \geq T_{g1\infty}$ (e.g., 150°C for Fig. 12), no hysteresis is observed in the absence of thermal degradation because $T_g > T$ for only high conversion.

Competition Between Vitrification and Anomalous Decrease in Modulus vs. Isothermal Temperature ($T > T_{g0}$)

In previous work⁷ with a diepoxide/tetrafunctional aromatic diamine, a normalized plot of rigidity vs. $T_g - T$ showed a single peak for all isothermal temperatures which corresponded to $\approx 50^\circ\text{C}$ for $T_g - T$. This led to the maximum representing approximately the glass transition relaxation having passed completely through the temperature of measurement with increasing conversion. Further work⁸ showed that $T_g - T$ at the maximum decreased monotonically with increasing temperature, which was attributed to the width of the glass transition region decreasing with increasing conversion. It is noted that the maximum in either case was considered to represent the competition between the modulus increasing as T_g passes through the isothermal temperature (vitrification) and decreasing isothermally with increasing conversion (anomaly).¹ The position of the maximum depends, therefore, on the rate of change of the competing processes with increased conversion and may not represent precisely the glass transition having passed through the temperature of measurement.

Figure 13 shows isothermal modulus (rigidity) data obtained on cooling vs. $T_g - T$. The latter parameter normalizes conversion as measured by T_g to the isothermal temperature of measurement.

For the present work, the following facts are understood: (1) At full conversion (first reaction),

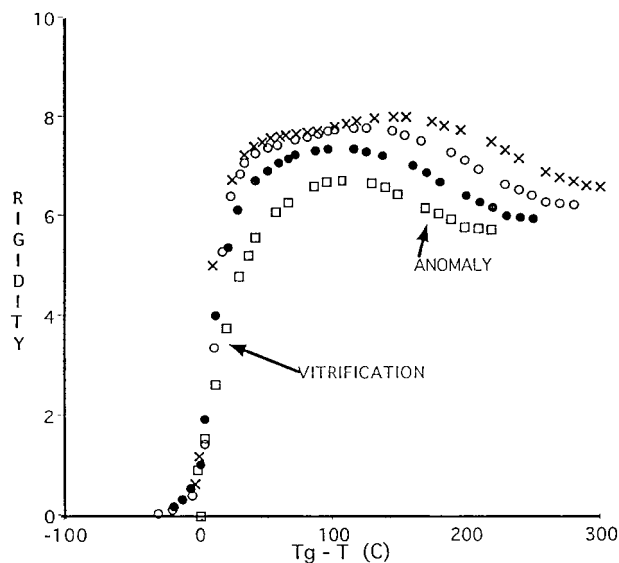


Figure 13 Modulus (rigidity) vs. $T_g - T$ showing the competition between the process of vitrification and the decrease in isothermal modulus (anomaly). Data were obtained on cooling. Symbols: (X) -30°C ; (O) 0°C ; (●) 30°C ; (□) 60°C .

the isothermal modulus decreases with increasing temperature (Fig. 6), and (2) if the maximum in isothermal modulus does represent T_g having passed through the temperature of measurement, then, since the conversion at the maximum increases with increasing isothermal temperature (Fig. 13), the modulus at the maximum would decrease with increasing temperature (Fig. 13) on account of increasing conversion (anomaly), but there is also a temperature effect which decreases it further. It should be noted that for the present system the half-width at T_g of $T_g - T$ at the maximum is 100°C or greater (Fig. 13). This is to be compared with a value of 50°C and less from previous work^{7,8} and also the modulus vs. temperature curves for a fixed conversion for the present system which show that the half-width of $T_g \approx 40^\circ\text{C}$.⁵

A reason for the double maximum at -30 and 0°C (Fig. 13) is related to the brittleness of the low molecular weight material. When $T_g = 50^\circ\text{C}$, the material at -30°C is 80°C below T_g is of relatively low conversion and could microcrack on cooling from its T_g of 50 to -30°C , whereas for higher conversions ($T_g \geq 120^\circ\text{C}$), the material is tough. Similar analysis applies for the 0°C data. In contrast, at an isothermal temperature of 60°C , the maximum in modulus corresponds to $T_g = 160^\circ\text{C}$ and the material is tough: a similar analysis applies for data at 30°C .

Degradation

As shown in the CHT diagram in Figure 2, on heating to 325°C, the glass transition temperature (T_g) passes through a maximum value in the vicinity of 325°C. This is the consequence of the competition between cure reactions which increase T_g and thermal degradation reactions which (initially) lower T_g . T_g decreases with decrease in heating rates in the CHT diagram as a consequence of the longer times at the higher temperatures on thermal degradation. Figure 2 also shows that the glass transition temperature ($^{325}T_g$) obtained on cooling (at 2°C/min) from $T_{\max} = 325^\circ\text{C}$ is less than the T_g obtained on prior heating to 325°C at successively lower heating rates. Thermal degradation in the vicinity of 300°C therefore initially decreases the T_g .

Similar results are shown in Figure 5 which displays T_g on cooling, after heating to T_{\max} , vs. T_{\max} ; it also shows that T_g increases again after heating to higher temperatures ($>325^\circ\text{C}$). The decrease and subsequent increase of T_g with increasing T_{\max} is clearly apparent in the isothermal modulus data for $T = -170^\circ\text{C}$ (Fig. 8) and $T = -150^\circ\text{C}$ (Fig. 9). It is less apparent, but discernible (on expanded scales, see below), in the corresponding data displayed for $T = -20^\circ\text{C}$ (Fig. 7), $T = -70^\circ\text{C}$ (Fig. 10), $T = -50^\circ\text{C}$ (Fig. 11), and $T = 150^\circ\text{C}$ (Fig. 12).

The data (on cooling) for $T = -70, -50, -20,$ and 150°C , in the region for T_{\max} increasing beyond approximately 300°C, are shown on an expanded scale in Figure 14 to clarify the behavior on degradation (see Fig. 5 for the relationship between T_{\max} and T_g). The corresponding data for $T = -170$ and -150°C are clear in Figures 8 and 9. As T_g decreases due to degradation, the isothermal "modulus" decreases for lower temperatures ($-170, -150,$ and -70°C) but increases for higher temperatures ($-50, -20,$ and 150°C). As T_g subsequently increases, the isothermal "modulus" decreases for all temperatures. Degradation is accompanied by loss of weight; e.g., a thermogravimetric analysis (TGA) thermogram at 1°C/min shows that the weight loss in an atmosphere of helium is 5% at 325°C (data not shown in this report). Since the modulus is directly related to rigidity only in the absence of dimensional changes, a decrease in rigidity can be the consequence of loss of mass rather than a decrease of modulus.¹⁰ Therefore, in the presence of degradation, transition values are correct; however, attributed trends in "modulus" may not be correct. It is further noted, since T_g decreases and later

increases with increase of T_{\max} , that T_g cannot be used as a measure of conversion with the occurrence of degradation.

CONCLUSIONS

A methodology for investigating the evolution of properties of thermosetting systems during cure is being developed. Previous publications, mostly on other systems, have reported the time-temperature-transformation (TTT) isothermal cure diagram, the continuous heating (CHT) cure diagram, and the conversion (T_g)-temperature-property (T_g TP) diagram.¹ It is noted that the key T_g vs. conversion relationship is part of the latter. The present report includes another approach: the analysis of thermohysteresis between cooling and heating data for the isothermal modulus vs. conversion of a composite specimen at different temperatures. Systematic changes in the isothermal modulus with increasing extent of cure (conversion) are interpreted in terms of the evolving toughness of the system, i.e., the decreasing thermohysteresis with increased conversion (cure). Modulus (rigidity) values were obtained during temperature scans both on cooling and on subsequent heating for different conversions (T_g values) via the TBA torsion pendulum technique using a single composite specimen fabricated from liquid resin and glass fibers. Isothermal modulus vs. conversion data at different temperatures

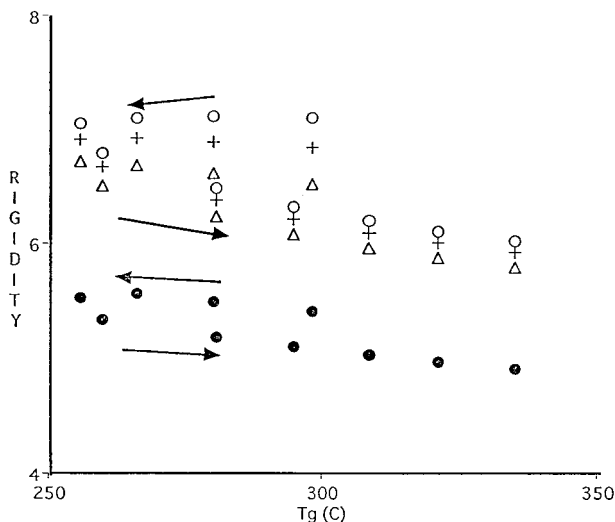


Figure 14 Isothermal down modulus (rigidity) at (○) -70°C , (+) -50°C , (Δ) -20°C , and (●) 150°C vs. T_g in the region of thermal degradation. As T_{\max} increases above 300°C (see Fig. 5), T_g decreases and subsequently increases.

were obtained by crossplotting from the consecutive series of cooling and heating temperature scans with successively higher temperatures (T_{\max}).

Results for the cure of a complex thermosetting isocyanate/epoxy system (in the absence of thermal degradation) are summarized as follows:

At low conversions, for $T < T_g < T_{g1\infty} \approx 120^\circ\text{C}$, the material is brittle and hysteresis at T is observed as judged by the modulus on cooling (from T_{\max}) being higher than the modulus on subsequent heating (from -180°C). At higher conversions for which $T_g \approx T_{g1\infty}$ (corresponding to the completion of the first of two consecutive and separable cure reaction regions), the material at T is tough for $T < T_g$ and no hysteresis is displayed.

The down and up modulus data at T can be the same if (1) $T_g \leq T$ (i.e., the material is liquid or is in the T_g region at T) or (2) for all values of T when $T_g \geq T_{g1\infty}$. The down and up modulus data at T can be similar for all conversions also for $T \ll T_{g0}$ (see next paragraph).

Isothermal modulus vs. conversion data can be described by the following regions of behavior: (a) $T_{g0} \gg T$. The material at T is in the glassy state for all T_g values. At low conversions, the material microcracks on cooling to T and also from T to -180°C and does not heal on subsequent heating to T ; this results in the down and up modulus data at T being similar. At high conversions, there is no microcracking on cooling and the subsequent heating. (b) $T_{g0} < T < T_{g1\infty}$. (Note that T_g increases through T with increasing conversion.) For $T_g \leq T$, microcracking occurs on cooling below T and healing occurs on heating to T , resulting in unchanged data at T . For $T_g > T$, microcracking may occur on cooling to T , microcracking may occur on cooling below T , and healing may not occur on subsequent heating to T : A higher modulus value may then be obtained at T on cooling than on subsequent heating. For any value of T with $T_g \geq T_{g1\infty}$, microcracking does not occur on cooling to T or in cooling to -180°C or on subsequent heating to T ; the same modulus is then obtained at T on cooling and subsequent heating.

This implies that the material is tough. (c) $T > T_{g1\infty} \ll T_{g2\infty} \approx 315^\circ\text{C}$. ($T_{g2\infty}$ corresponds to the completion of the second reaction region.) No hysteresis is observed at T between the cooling and heating data.

Further, for $T_{g0} < T$, as in previous work, the competition between vitrification and the anomalous decrease in isothermal modulus leads to the isothermal modulus passing through a maximum with increasing conversion. The position of this maximum may not correspond exactly to the end of the glass transition temperature region (as discussed earlier).

Thermal degradation complicates the results at the highest T_{\max} temperatures ($\geq T_{g2\infty}$). As thermal degradation proceeds, the value of T_g first decreases from about 325 to about 250°C and then increases to above 350°C .

REFERENCES

1. J. K. Gillham and J. B. Enns, *Trends Polym. Sci.*, **2**(12), 406–419 (1994).
2. Y. S. K. Lee, K. Hodd, W. W. Wright, and J. M. Barton, *Br. Polym. J.*, **22**, 97 (1990).
3. T. I. Kadurina, V. A. Prokopenko, and S. I. Omelchenko, *Polym. J.*, **33**, 3858 (1992).
4. M. T. DeMeuse, J. K. Gillham, and F. Parodi, in *SAMPE Conference Proceedings, Anaheim, 1994*, pp. 272–285. Also, *J. Appl. Polym. Sci.*, **64**, 15 (1997).
5. M. T. DeMeuse, J. K. Gillham, and F. Parodi, in *SAMPE Conference Proceedings, Anaheim, 1994*, pp. 286–296. Also, *J. Appl. Polym. Sci.*, **64**, 15 (1997).
6. M. T. DeMeuse, J. K. Gillham, and F. Parodi, *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.*, **36**, 781–782 (1995).
7. X. Wang and J. K. Gillham, *J. Appl. Polym. Sci.*, **47**, 425 (1993).
8. R. A. Venditti and J. K. Gillham, *J. Appl. Polym. Sci.*, **56**, 1687 (1995).
9. M. T. DeMeuse, J. K. Gillham, J. Fech, and F. Parodi, unpublished results, 1994.
10. K. P. Pang and J. K. Gillham, *J. Appl. Polym. Sci.*, **38**, 2115 (1989).