

Conversion–Temperature–Property Diagram for a Liquid Dicyanate Ester/High- T_g Polycyanurate Thermosetting System

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SYNOPSIS

The effects of conversion and temperature on the dynamic mechanical properties (at ≈ 1 Hz) of a dicyanate ester/polycyanurate thermosetting system are investigated after cure using torsional braid analysis (TBA). Extent of conversion is measured by T_g . The isothermal glassy-state modulus at measurement temperatures below the glass transition temperature of the monomer (T_{g0}) decreases with increasing conversion. The isothermal modulus at temperatures above T_{g0} passes through a maximum due to competition between increase in the isothermal glassy-state modulus at the measurement temperature due to the vitrification process during cooling and the aforementioned decrease in the modulus with increasing conversion, which is considered to be due primarily to steric constraints in the developing network. The maximum in the isothermal modulus is associated with the boundary between the glass and glass transition regions. The experimental results are summarized in a conversion (T_g)-temperature-property diagram, the T_g TP diagram, which is a framework for understanding relationships between transitions and material properties for thermosetting systems. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Thermosetting polymers are versatile high-performance materials with applications in coatings, adhesives, composites, electronic component “packaging,” and circuit boards. The effects of temperature and conversion on the glassy-state properties of these materials are of importance for optimizing performance. In this work, the effects of these variables on the dynamic mechanical modulus and loss properties are studied for a new liquid dicyanate ester/high- T_g polycyanurate thermosetting system, which is a potential replacement for epoxy systems.

The dicyanate ester monomer investigated was commercially introduced in 1990. Its practical advantages include its liquid state at room temperature, low volatility, and cure via addition trimerization reaction without volatile byproducts. The

maximum glass transition temperature, $T_{g\infty}$, of the present system is 200°C. Lower molecular weight dicyanate ester monomers based on bisphenol A give rise to higher $T_{g\infty}$ values, in the range between epoxy and polyimide systems. Polycyanurate materials display toughness, low moisture absorption, and low dielectric constant and loss.¹⁻³ Dicyanate ester/polycyanurate systems have other characteristics that facilitate study, including high purity, strong characteristic infrared absorption bands for both reactant and product species, and slow polymerization rates when uncatalyzed.

The cure of a thermosetting polymeric material is accompanied by a decrease in the free volume associated with chain ends. Consequently, it might be expected that the density and modulus of the material will increase as the conversion increases, both at the cure temperature (T_c) and in the glassy state. Several researchers have made such observations for epoxy systems.⁴⁻⁶ However, many investigations on thermosetting systems have indicated that the specific volume at room temperature does not decrease monotonically with increasing conversion and/or

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cross-link density, but, rather, increases at the later stages of conversion.^{1,7-23} This behavior has been termed anomalous⁷ because it is unintuitive and not widely appreciated, although it has been shown to exist in many thermosetting systems.

In our laboratory, the behavior of various interrelated properties in the glassy state at 25°C has been observed for high- T_g epoxy/amine systems: The density is found to pass through a maximum with increasing conversion⁷; the modulus passes through a maximum with increasing conversion^{8,9}; the equilibrium moisture content increases at later stages of conversion¹⁰; and the rate of isothermal physical aging passes through a minimum with increasing T_g .^{8,9,11}

Other researchers have reported similar behavior for various isothermal properties of epoxy systems measured at temperatures below T_g .¹²⁻²⁰ Shimizaki measured the density of aromatic epoxy/acid anhydride specimens, cured for various times, and found that the specific volumes measured at temperatures below T_g increased with increasing T_g (i.e., conversion).¹² Shito similarly observed increased specific volume with increased cross-link density for aromatic epoxy/acid anhydride systems.¹³ Gupta et al. showed that for an aromatic epoxy cured with aromatic diamine the room-temperature equilibrium moisture absorption, initial water diffusion coefficient, and specific volume all increased the higher the T_g and the cross-link density, and that this trend was reversed for these properties measured at 100°C.¹⁴ Choy and Plazek similarly found that the density of an aromatic epoxy/aromatic amine system at room temperature decreased with postcure.¹⁵ Danieleley and Long found that moisture absorption at room temperature increased with cure time for a different aromatic epoxy/aromatic amine system.¹⁶ Ol'khovik reported that for epoxies cured at 150 and 160°C the strength at 20°C, a high-strain property, decreased paralleling a decrease in room-temperature density.¹⁷ Fisch et al. found that the room-temperature density decreased with increasing T_g for several aliphatic epoxies cured with acid anhydride or aromatic diamine.¹⁸ Day et al. found that the amount of water absorbed increased with increasing conversion for an epoxy system, but that the diffusion coefficients were essentially constant.¹⁹ Ogata et al. reported that as the cross-linking density increased in a series of phenol-formaldehyde novolac-cured epoxy resins the modulus increased in the rubbery region; however, in the glassy state, the coefficient of linear thermal expansion, specific volume, water absorption, diffusion coefficient, and permeability increased and the modulus decreased.²⁰

Similar results have also been reported for various dicyanate ester/polycyanurate thermosetting systems. Shimp observed that the room-temperature specific volume of various dicyanate ester/polycyanurate systems passed through a minimum with increasing conversion.¹ Snow and Armistead made similar measurements.²¹ Preliminary studies for the present work found that the isothermal modulus passed through a maximum with increasing conversion and that this maximum was associated with the boundary between the glass transition and glassy states.^{8,22,23}

The increases in isothermal specific volume and water absorption and the decrease in isothermal modulus that are observed in the glassy state at the later stages of cure are interrelated and infer an increase in the isothermal free volume. This increase in the glassy-state free volume with further cure has been considered to result from the kinetics of the glass transition and/or to nonkinetic structural molecular factors⁷: The increasing molecular weight and cross-link density, which accompany cure, may result in (1) a lesser ability to relax and dissipate excess free volume when cooling from the curing temperature through the glass transition to the glassy state and (2) structural or steric factors associated with the developing molecular structure limiting the ability of the volume to collapse. The kinetic factor (1) results in excess free volume accessible to submolecular rearrangements, whereas the nonkinetic factor (2) results in excess free volume inaccessible to submolecular rearrangements.

In this work, experimental evidence for the predominance of the structural factor is given. In a recent report, Ogata et al. appeared to reach a similar conclusion suggesting that the free volume due to steric effects increases with increasing cross-link density and causes the total free volume to increase with increasing cross-link density.²⁰ The predominance of the structural factor is also supported by measurements of the change in specific volume at the cure temperature made by other researchers.^{15,21} Snow and Armistead found that the change in specific volume at 200°C during the cure of a dicyanate ester/polycyanurate system was not linear with respect to conversion but rather that the rate of decrease of specific volume decreased at the later stages of cure with the deviation from linearity occurring prior to gelation.²¹ Choy and Plazek found that the decrease in specific volume at the cure temperature of an aromatic epoxy/aromatic amine system was linearly related to the glass transition temperature.¹⁵ Due to the one-to-one nonlinear relationship between the glass transition temperature and conver-

sion,^{7,24-32} the specific volume vs. the conversion relationship for this epoxy/amine system at the curing temperature should also be nonlinear.

The nonlinear relationship between specific volume and conversion at the cure temperature is considered to be due to structural factors since relaxation effects are not operative (as long as $T_c > T_g$). The nonlinearity is considered to arise from the increasing importance of steric constraints in the developing network which hinder densification with increasing conversion. The fact that the deviation from linearity arises prior to gelation suggests that branch points and entanglements as well as chemical cross-links act as steric constraints in the developing network.

The conversion-temperature-property (T_g TP) diagram has recently been developed in our laboratory as an intellectual framework for summarizing and predicting properties as a function of the structure (conversion) of thermosetting systems.^{8,9} The T_g TP diagram is analogous to the time-temperature-transformation (TTT) isothermal cure diagram,³³ except that it deals with properties after cure rather than during cure. The y -axis of the T_g TP diagram is the temperature of measurement (T). The x -axis is the glass transition temperature, T_g , which is used as a measure of conversion (or structure) in the T_g TP diagram rather than time as in the TTT diagram. The glass transition temperature is used since it is uniquely related to fractional conversion and since it is more sensitive than fractional conversion to changes in network structure especially at high conversions.²⁴ The glass transition temperature is also directly related to both the solidification process and to the state (and, thus, properties) of the material with respect to temperature. For example, glassy-state properties have been shown to depend on the interval between the glass transition temperature and the measurement temperature, $T_g - T$.¹¹ Furthermore, the use of T_g on the x -axis linearizes the contours for gelation, vitrification, and T_β on the diagram.¹¹ The inferred third dimension of the diagram is any property of interest, such as density, modulus, mechanical loss, or physical aging rate. Iso-value contours of the property can be projected onto the two-dimensional T_g vs. T surface. The T_g TP diagram originally was intended to demonstrate the effect of conversion or structure, as measured by T_g , on the isothermal properties of the material [e.g., contours designated maxima and minima of the selected property(ies) with respect to conversion]. However, of equal interest, is the effect of temperature on the properties of an iso-conversion (iso- T_g) material. Conse-

quently, contours designating maxima and minima of the selected property(ies) with respect to the measurement temperature can also be incorporated. Other structure-temperature-property diagrams could be constructed, e.g., for thermoplastic systems, molecular weight could be used as a measure of structure and as the x -axis variable.

The basis for the T_g TP diagram is the interrelatedness of all properties and the dependence of the properties on conversion (structure) and the dependence of properties on transitions such as gelation, vitrification, and the β -transition for thermosetting systems. The T_g TP diagram has thus far been obtained for a stoichiometric epoxy/amine system,⁸ two off-stoichiometric epoxy/amine systems,³⁴ a polyamic acid/polyimide system,³⁵ and the dicyanate ester/polycyanurate system described in this work.^{22,23} The generality of the diagram is being further investigated in our laboratory for both low and high strain properties.

Interpretation of the T_g TP diagrams will lead to an understanding of the factors that affect properties. For example, it was found that the isothermal modulus vs. conversion for an epoxy/amine system beyond gelation displays a minimum at the conversion that approximately corresponds to the β -transition temperature (T_β) rising to the measurement temperature ($T_{\text{measurement}}$).^{8,9} The decrease in the isothermal modulus for $T_\beta < T_{\text{measurement}}$ is attributed to the decrease in packing density due to network constraints and to the increased quantity of β relaxations that accompany increased conversion in that system. The subsequent increase in the isothermal modulus with increased conversion for $T_\beta > T_{\text{measurement}}$ is attributed the freezing out of the β motions at the measurement temperature over the decrease in packing density. Similarly, the maximum in the isothermal modulus that occurs for the same system at measurement temperatures above T_{g0} (Refs. 8 and 9) is considered to be due to competition between the increase in modulus that results from the freezing out of segmental motions as the glass transition temperature rises from below to above the measurement temperature and the decrease in modulus that results from the packing density decreasing with conversion.

In this work, the effects temperature and structure (i.e., extent of cure) on dynamic mechanical properties at ≈ 1 Hz of a relatively new liquid dicyanate ester/polycyanurate material are investigated using torsional braid analysis (TBA). The properties studied include the relative modulus and the relative mechanical loss. A T_g TP diagram is used to summarize the experimental results and as a

framework for interpretation of the results. Isothermal physical aging results are incorporated in another article³⁶ and some of those results are incorporated into the T_g /TP diagram presented here. Preliminary reports have been published.^{22,23}

MATERIALS

The thermosetting monomer investigated is a dicyanate ester (Hi-Tek Polymers, Inc.) derived from 4,4'-[1,3-phenylene bis(1-methylethylidene)]-bisphenol. The monomer is homopolymerized in this work without added catalyst. Chemical structures of the monomer and resulting network polymer are shown in Figure 1. The monomer is a metastable liquid at room temperature, which will crystallize on long-term storage in a freezer ($T \approx -15^\circ\text{C}$). The onset of melting of the crystalline material is found to be 41°C by differential scanning calorimetry (DSC) scans at $10^\circ\text{C}/\text{min}$. The glass transition temperature of the amorphous monomer, T_{g0} , is -18°C from the maximum in relative mechanical loss during TBA scans at $1^\circ\text{C}/\text{min}$ and approximately 1 Hz. The glass transition of the fully cured polycyanurate, $T_{g\infty}$, is approximately 201°C from the maximum in relative mechanical loss during TBA scans at $1^\circ\text{C}/\text{min}$ and approximately 1 Hz. The monomer was synthesized for this project by W. M. Craig of Hi-Tek Polymers, Inc., on the basis of our request for a pure, liquid, nonvolatile dicyanate ester monomer for research.

The cure kinetics of the uncatalyzed and catalyzed dicyanate ester/polycyanurate system inves-

tigated in this work have been analyzed in both kinetically and diffusion-controlled regimes.²⁵ The uncatalyzed system was chosen for the present work because its relatively slow rate of chemical reaction facilitated investigation of the material properties as a function of conversion. For example, since chemical reaction does not occur during a temperature scan at $1^\circ\text{C}/\text{min}$ until the material is well above T_g (e.g., $T > T_g + 30^\circ\text{C}$), the measurement of T_g is a reliable measure of conversion.

EXPERIMENTAL

Torsional braid analysis (TBA) is a dynamic mechanical technique in which a composite specimen, a resin-impregnated heat-cleaned fiberglass braid, is the active element in a freely oscillating torsion pendulum.^{37,38} The composite specimen is used in order to investigate the material properties throughout the liquid (or rubber) and glassy states upon changes of conversion and/or temperature. The specimen is intermittently torqued through a small angle and allowed to oscillate freely (the natural frequency depends on the state of the material and ranges from 0.5 to 2.5 Hz with a sensitivity of 0.0001 Hz). Low-strain dynamic mechanical properties of the composite specimen can be obtained during isothermal cure or isothermal physical aging and during temperature-scanning experiments, all of which are accomplished under a continuous helium purge. In this work, the properties reported include the relative rigidity ($1/P^2$, where P is the period in seconds of the oscillation), which is pro-

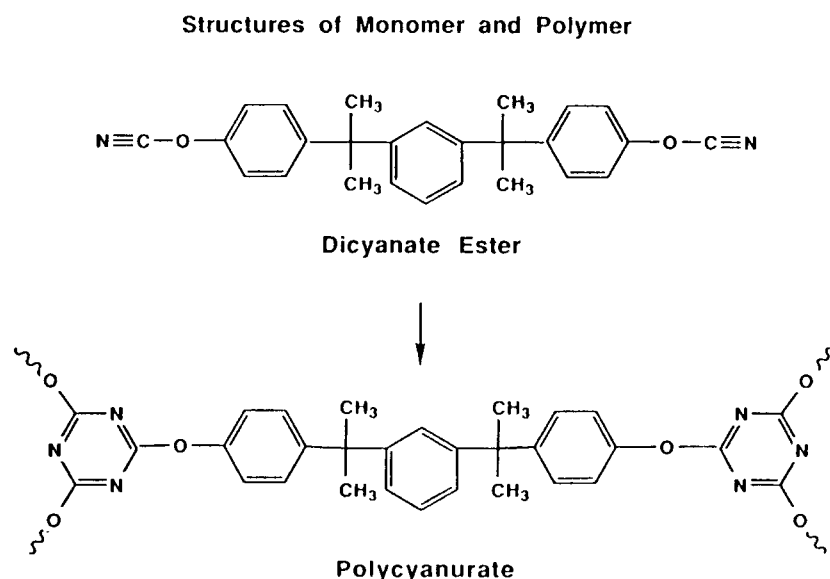


Figure 1 Chemical structures of monomer and polymer.

portional to shear modulus (G') by a constant k , and the relative mechanical loss, which is proportional to the loss modulus (G'') by the factor πk . The constant $k = (1/P^2 G') = r^4/8\pi IL$, where r and L are the radius and length of the specimen, respectively, and I is the moment of inertia of the moving part of the torsion pendulum. Thus, k increases with increasing temperature at constant conversion due to thermal expansion of the specimen. The automated TBA torsion pendulum is available from Plastics Analysis Instruments, Inc.

A TBA experiment that includes temperature ramps from low to successively higher temperatures using a single specimen provides data on the thermomechanical properties as a function of T_g . The specimen is cooled at $5^\circ\text{C}/\text{min}$ from above T_g to -180°C and then heated at $1^\circ\text{C}/\text{min}$ to obtain the thermomechanical modulus and loss properties. The temperatures at which various relaxations occur are assigned during heating: T_β , associated with localized subsegmental motions of the β -transition below T_g ; T_g , associated with cooperative or segmental motions of the glass transition; and T_{ll} , generally associated with the liquid-liquid transition of low molecular weight material above T_g .³⁹ The transition temperatures are obtained from the maxima in the relative mechanical loss (rather than the maxima in logarithmic decrement, $\approx \pi G''/G'$, because the T_{ll} peak overwhelms the T_g peak for conversions prior to gelation when it is plotted as logarithmic decrement). Further curing is accomplished, when desired, during the temperature scan up by ramping to well above T_g , and the cooling/heating cycle is repeated for the higher T_g material. Because of the slow rate of reaction of the uncatalyzed system,²⁵ chemical conversion occurs only well above T_g . Consequently, on a temperature scan up, chemical reaction does not affect the measured value of T_g .⁴⁰ Material that has not gelled is cooled to -75°C , rather than to -180°C , in order to minimize microcracking of the brittle low molecular weight material; from the reversibility of the temperature scans (in the absence of further chemical reaction), it is inferred that no microcracking occurs during scanning down to and up from -75°C . Gelled samples show no thermal hysteresis on scanning down to and up from -180°C .

RESULTS AND DISCUSSION

The Glass Transition Temperature as a Measure of Extent of Cure

The glass transition temperature is uniquely related to conversion for various thermosetting systems^{7,24-32}

and can thus be used as a measure of extent of cure. Experimental data for the present uncatalyzed system demonstrating the one-to-one relationship between T_g and fractional conversion, as measured by the step-change and the residual heat of partially cured materials in differential scanning calorimetry (DSC) temperature-scanning experiments,²⁵ are shown in Figure 2. The relationship is satisfactorily described by the following equation derived for thermosetting systems by Venditti and Gillham³² from the Couchman equation⁴¹:

$$\ln(T_g) = \frac{(1-x)\ln(T_{g0}) + \frac{\Delta c_{p\alpha}}{\Delta c_{p0}} x \ln(T_{g\alpha})}{(1-x) + \frac{\Delta c_{p\alpha}}{\Delta c_{p0}} x} \quad (1)$$

where T_{g0} and $T_{g\alpha}$ are the values of T_g for the initial uncured material and final "fully" cured material, respectively; x , the fractional conversion; and Δc_{p0} and $\Delta c_{p\alpha}$, the values of the change in the heat capacity at T_g for the initial uncured material and final "fully" cured material, respectively. The parameter $\Delta c_{p\alpha}/\Delta c_{p0}$ is found to be 0.62 by a best fit of the data³² and is in agreement with the experimental value of 0.6 ± 0.1 .⁴⁰ The applicability of eq. (1) to systems in which there are sequential or competing reactions is not proven.

The values of T_{g0} and $T_{g\alpha}$ systematically differ in the DSC and TBA experimental techniques, with

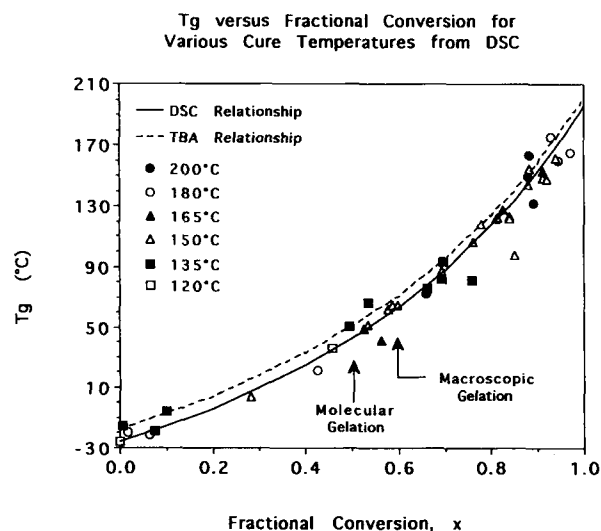


Figure 2 Relationship between T_g and fractional conversion for various cure temperatures. The solid line is the relationship using eq. (1) for the experimental DSC data (symbols).²⁵ The dashed line is the relationship for the TBA data using eq. (1). The conversions at which molecular and macroscopic gelation occur are marked.

the TBA values being 8 and 5°C higher, respectively. The dashed line in Figure 2 is the relationship between T_g and fractional conversion determined from eq. (1) for the TBA data.

It is noted that full conversion is probably not realizable in this thermosetting system due to isolation of functional groups in the cross-linked network. Thus, $T_{g\infty}$ and "full" conversion refer to the maximum T_g and conversion, respectively, which can be obtained in the absence of thermal degradation.

The conversions at which idealized molecular and macroscopic gelation occur are marked by arrows in Figure 2. Molecular gelation is calculated to occur theoretically, in the absence of intramolecular reactions prior to gelation, at a fractional conversion of 0.50 for cyanate esters (or at $_{gel}T_g = 52^\circ\text{C}$ for the present system using the TBA relationship between T_g and conversion).⁴² Macroscopic gelation, which is often considered to be an iso-viscous event,³⁷ is found to occur at a conversion of approximately 0.64, or at $_{gel}T_g = 80^\circ\text{C}$, in this work (see later for the method of its assignment). In other work on the catalyzed system of the particular monomer studied in this laboratory, macroscopic gelation was found to occur at a conversion of approximately 0.64 by using the kinetic model of the reaction to determine the conversion at which the mechanical loss peak attributed to gelation occurred in TBA isothermal cure experiments.^{25,40} The results of other researchers working on other dicyanate ester systems show gelation occurs at conversions from 0.58 to 0.65,⁴³⁻⁴⁵ although one group of researchers finds gelation occurring at 0.50.⁴⁶

Transitions During Temperature Scans vs. Extent of Cure

The thermomechanical properties, relative rigidity (modulus) and relative mechanical loss, obtained during temperature scans for materials cured to different extents, are shown in Figure 3(a) and (b), respectively. Each curve in Figure 3(a) is composed of two sets of data: the solid symbols designate the temperature scans during cooling at 5°C/min, whereas the crossed symbols are for the temperature scan during subsequent heating at 1°C/min. There is no apparent hysteresis observed between the temperature scans down and up for any particular extent of cure. Thus, it is considered that crystallization, melting, or microcracking do not occur during the experiments and that the thermal lag between cooling and heating is small.

The glass transition is the dominant relaxation peak in the mechanical loss curves shown in Figure

3(b). The glass transition increases from T_{g0} (-18°C) to $T_{g\infty}$ (201°C) as the result of cure. The intensity of the mechanical loss peak at the glass transition passes through a minimum with increas-

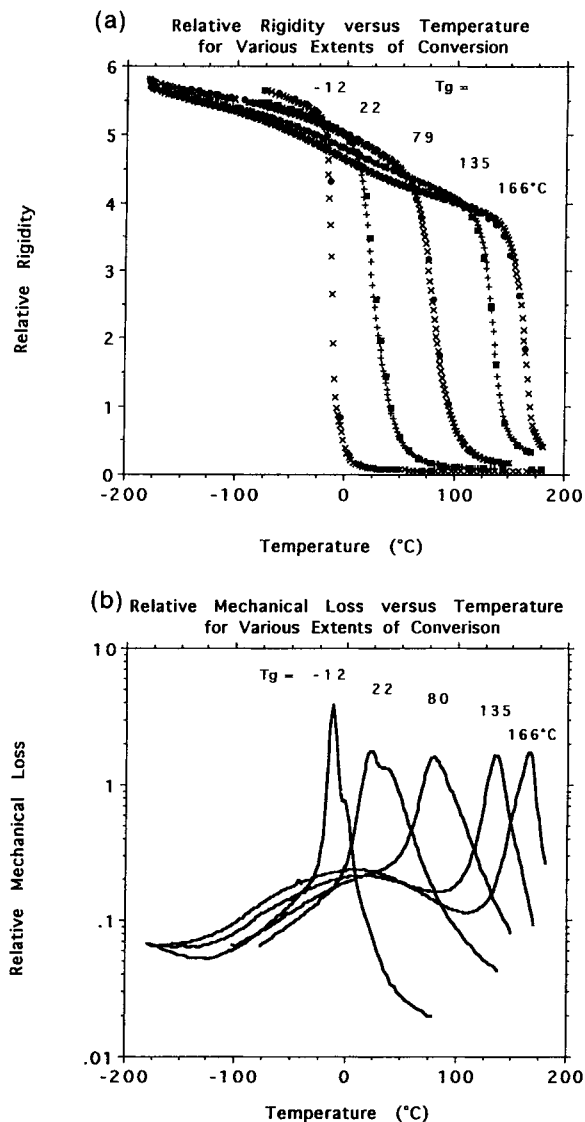


Figure 3 (a) Relative rigidity (modulus) vs. temperature for five extents of conversion (T_g). The temperature scans both on cooling and heating are shown; no hysteresis is observed. Also note that for $T < T_{g0}$ the isothermal modulus decreases with increasing T_g ; for $T_{g\infty} > T > T_{g0}$, the isothermal modulus passes through a maximum; and for $T > T_g$, the isothermal modulus is expected to increase with increasing conversion (as indicated by the limited data). (b) Relative mechanical loss vs. temperature for various extents of conversion (T_g) from data on heating. The primary transition is the glass transition. Two secondary transitions are observed: prior to gelation, the liquid-liquid relaxation above T_g ; after gelation, the β -relaxation below T_g .

ing conversion, whereas the breadth passes through a maximum. The intensity and breadth of the transition reflect the distribution of relaxation times (corresponding to the distribution of internal structure): The initial uncured material and the fully cured material have a narrower distribution of relaxation times than do materials at intermediate extents of conversion.

Prior to macroscopic gelation, which occurs at a T_g of approximately 80°C , the "liquid-liquid" relaxation³⁹ is observed in the mechanical loss curves approximately $15\text{--}20^\circ\text{C}$ above T_g . This relaxation was observed in preliminary temperature cycling experiments prior to gelation and also after the onset of thermal degradation reactions with repeated scanning to over 250°C .⁴⁷ The "liquid-liquid" transition, designated T_{ll} , has been considered to be associated with low molecular weight species.³⁹

Below T_g , the β -relaxation maximum is observed in the mechanical loss data. The intensity of the β process increases with increasing conversion, suggesting that it is associated with flexible parts of the developing network (the ether linkages of the triazine ring). The temperature of the maximum of the β process, T_β , appears to decrease from approximately 30 to 10°C with increasing conversion after gelation. However, in the vicinity of gelation, the β and glass transitions overlap substantially, so that the measured value of T_β is higher than it actually is. Prior to gelation, only the glass transition temperature is discerned.

Isothermal Relative Modulus and Relative Mechanical Loss vs. Extent of Cure

The behavior of the glassy-state modulus is apparent in Figure 3 (a), which shows that the isothermal relative rigidity (modulus) decreases with increasing conversion in the glassy state at temperatures below T_{g0} ($T < -18^\circ\text{C}$), whereas the modulus passes through a maximum with increasing conversion at temperatures above T_{g0} but below $T_{g\infty}$. However, in the liquid or rubbery state above the glass transition temperature, the isothermal relative rigidity (modulus) increases with increasing conversion due to increasing molecular weight and cross-link density, as indicated by the limited data in Figure 3 (a).

The isothermal modulus (relative rigidity) vs. extent of cure (as measured by T_g) is shown in Figure 4 for temperatures below T_{g0} (-175 to -25°C) and in Figure 5 for temperatures above T_{g0} (0 to 125°C). Recall that pregel data were not obtained for temperatures below -75°C in order to avoid microcracking of the specimen for ungelled materials.

In Figure 4, the isothermal glassy-state modulus (relative rigidity) is observed to decrease with increasing extent of conversion (T_g). A distinct but subtle change of slope in the isothermal modulus (relative rigidity) vs. T_g data at intermediate conversions (T_g 's) for temperatures from -25 to -75°C in Figure 4 occurs at a conversion corresponding to macroscopic gelation and is marked by the vertical dotted line. The change in slope is presumably due

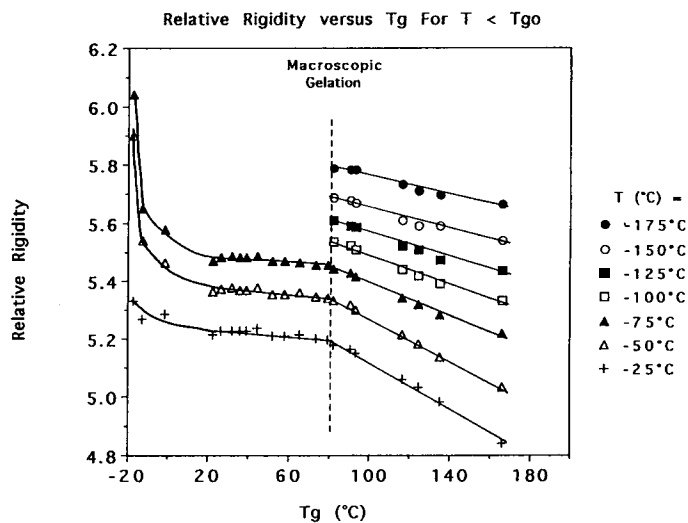


Figure 4 Isothermal relative rigidity (modulus) vs. extent of conversion (T_g) for temperatures below T_{g0} . At low T_g 's, the modulus decreases rapidly. The subtle but distinct change in slope in the modulus vs. T_g data at intermediate T_g 's is attributed to macroscopic gelation and is marked by the vertical dashed line.

to the decreased ability of the gelled network to pack effectively during cooling through the glass transition due to network constraints: The isothermal modulus decreases with increasing T_g at a higher rate after gelation. The change in slope of the curves in Figure 4 occurs at a T_g of $80 \pm 4^\circ\text{C}$ or at a fractional conversion of 0.64 ± 0.02 . This value of conversion at macroscopic gelation, x_{gel} , agrees with other results in this laboratory in which a reaction model was used to determine conversion at macroscopic gelation observed in isothermal TBA experiments on the catalyzed system ($x_{\text{gel}} = 0.64$).²⁵ Other researchers have similarly found that the gel point, as measured by solubility studies using various solvents, occurs in the vicinity of 0.58 to 0.65.^{1,43-45} One explanation for the delay in gelation from the ideal value of 0.50 is the presence of intramolecular reactions prior to gelation. Another explanation postulated by one group of researchers is that the reaction is heterogeneous (i.e., the reaction is localized at active centers) and, thus, the distribution of molecular weight would deviate from that predicted by Flory's theory.⁴⁵ However, another group of researchers found that gelation does occur at the ideal value of 0.50 and implicitly suggests that the shift in the conversion at gelation is due to impurities.⁴⁶ Another research group has recently shown that the conversion at gelation deviates from the theoretical value when moisture is present during cure.⁴⁷

At temperatures below T_{g0} (-18°C), the isothermal modulus (relative rigidity) decreases rapidly at low conversions with increasing conversion as

shown in Figure 4. Similar results are found for other experiments in which the cooling rate is $2^\circ\text{C}/\text{min}$ rather than $5^\circ\text{C}/\text{min}$.⁴⁰ The initial rapid decrease in modulus in the glassy state with increasing conversion is attributed to the decreased ability of the low molecular weight molecules to pack effectively due to branching as the molecular weight initially increases; e.g., trimers cannot pack as efficiently as monomers in the amorphous state. However, the initial decrease in the glassy-state relative rigidity with increasing conversion could be attributed to an artifact of the experiment: Flow of low molecular weight fluid above its glass transition temperature could lead to the observed behavior because of a change in specimen dimensions. However, if this were dominant, a corresponding decrease in relative rigidity would be expected in the liquid state above T_g , which is not observed. Note that in the liquid or rubbery state above T_g the isothermal relative rigidity increases with increasing conversion even at low conversions, as is indicated by the limited data above T_g in Figure 3(a).

For temperatures above T_{g0} , Figure 5 shows that the isothermal modulus (relative rigidity) passes through a maximum after vitrification ($T = T_g$) with increasing conversion. The maximum in the glassy-state modulus (relative rigidity) with increasing conversion is presumed to be directly related to a minimum in specific volume. For the system investigated, other researchers have found a minimum in the specific volume at 25°C at a conversion of approximately 0.53.¹ The corresponding maximum in

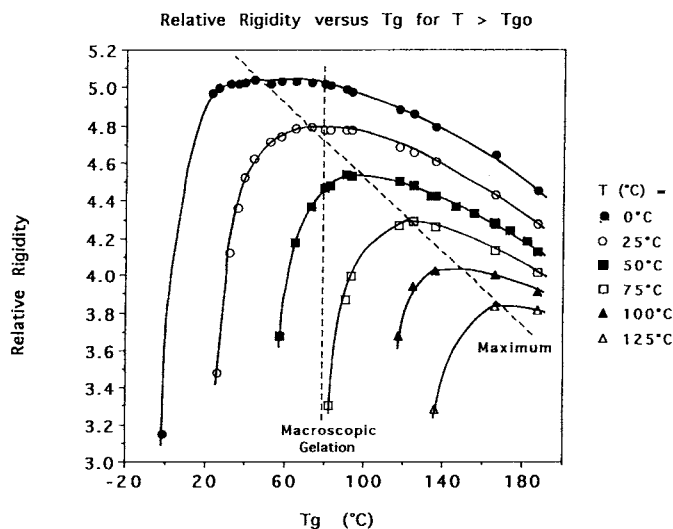


Figure 5 Isothermal relative rigidity (modulus) vs. extent of conversion (T_g) for temperatures above T_{g0} . The maximum in isothermal modulus with respect to T_g (conversion) is marked by a dashed line. Another dashed line marks macroscopic gelation.

modulus (relative rigidity) at 25°C is found in this work to occur at a conversion of approximately 0.61 ($T_g \approx 73^\circ\text{C}$). The discrepancy between the two values is considered to be due to the lack of curvature in the vicinity of the maximum in the isothermal relative rigidity data at 25°C that makes the maximum difficult to place. Differences in experimental procedure (particularly cooling rates) may also contribute to the discrepancy.

The maximum in room temperature (25°C) density reported in earlier work from this laboratory on high- T_g epoxy/amine systems was suggested to be associated with gelation,⁷ as another researcher has suggested for cyanate ester/polycyanurate systems.¹ However, as shown in Figure 5, the maximum occurs at the conversion corresponding to gelation only at an isothermal temperature of 25°C. Rather, the maximum in isothermal modulus (relative rigidity) appears to correspond to the end of the glass transition region, i.e., where T_g is approximately 50°C higher than the temperature of the measurement as indicated by the diagonal dashed line.^{22,23} Thus, it was only a coincidence that, in the earlier work, the end of the glass transition region corresponded to gelation at the temperature at which measurements were made. The same conclusion was found for other work from this laboratory on an epoxy/amine system.^{8,9}

It is considered that the maximum in the isothermal modulus (relative rigidity) is the result of the competition between the increase in modulus due to vitrification during cooling and the decrease that occurs with increasing conversion. Of the two explanations suggested in earlier work for the decrease in isothermal modulus with increasing conversion,⁷ kinetic and nonkinetic, it is considered that the kinetic argument (i.e., that material with a higher conversion has a lowered ability to relax on cooling through the glass transition region and to dissipate excess free volume) is of lesser importance. The decreasing magnitude of the glass transition, the difference between the modulus at the glass/glass transition and glass transition/rubber boundaries, decreases with increasing T_g [Fig. 3(a)] and corresponds to the decrease in the isothermal glassy-state modulus (relative rigidity) with increasing conversion. This decreasing magnitude of the glass transition cannot be attributed to the relaxation on cooling through T_g since the most prevalent (mode) relaxation time at T_g is constant, independent of T_g ($=1/\omega \approx 1$ s), and since the mean relaxation time correlates with the breadth of the glass transition that passes through a maximum with increasing

conversion. Consequently, it is considered that non-kinetic steric factors associated with the developing molecular structure are the primary cause of the decreasing modulus in the glassy state with increasing conversion. That the volume vs. conversion relationship is nonlinear at the curing temperature^{15,21} also supports the conclusion reached.

The data of Figures 4 and 5 are replotted in Figure 6 using a measure of the departure from equilibrium, $T_g - T$, as the x -axis. A vertical solid line at $T_g = T$ marks the glass transition temperature and the point of vitrification on cooling, whereas a vertical dotted line indicates the approximate maximum in isothermal modulus and the boundary between the glass transition and glassy states. [The width of the glass transition region, which is dependent on how the boundaries are defined, actually passes through a maximum with increasing T_g , as discussed and indicated in Figure 3(b).] To the right of the glass transition region, the material is in the glassy state. Three dashed iso-conversion contours are shown on the diagram. The upper and lower dashed contours correspond to T_{g0} and $T_{g\infty}$, respectively, with the $T_{g\infty}$ contour being estimated. The intermediate dashed line corresponds approximately to macroscopic gelation ($T_g =_{\text{gel}} T'_g \approx 80^\circ\text{C}$) and to the change in slope of the isothermal modulus vs. T_g data. Above the gelation line, the material is sol; below it and until the full-cure line, the material is a mixture of sol and gel.

Figure 6 summarizes the behavior of the isothermal glassy-state modulus with increasing conversion, as measured by $T_g - T$. In the initial stages of cure and at temperatures below T_{g0} (-18°C), the modulus of the material decreases rapidly with increasing cure, whereas at intermediate conversions, the modulus decreases more gradually with increasing conversion. At conversions above macroscopic gelation, the modulus decreases more rapidly with increasing conversion. For measurement temperatures above T_{g0} , the competition between vitrification during cooling and the isothermal decrease in glassy-state modulus with increasing conversion results in the maximum in modulus with increasing conversion. The same trends are observed for a material in which the quench rate during the temperature cycling experiments was $2^\circ\text{C}/\text{min}$ (rather than $5^\circ\text{C}/\text{min}$ as in this work).⁴⁰

It should be noted that in work on a high- T_g aromatic epoxy/aromatic amine in this laboratory^{8,9} the behavior of the isothermal glassy-state modulus was generally observed to be more complicated than for the dicyanate ester/polycyanurate system stud-

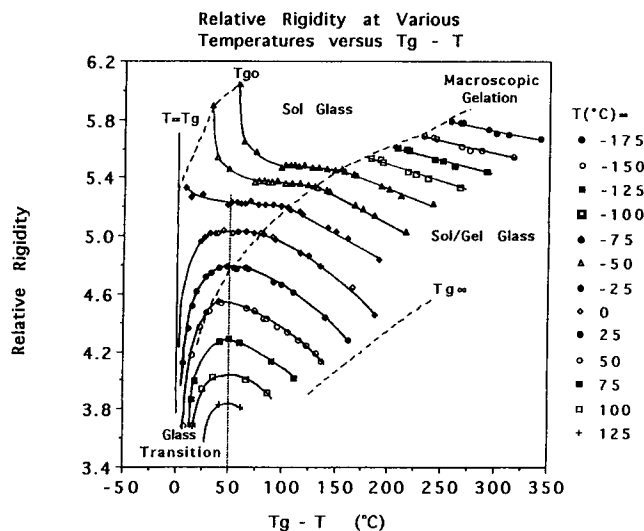


Figure 6 Isothermal relative rigidity (modulus) vs. extent of conversion, as measured by $T_g - T$. The glass transition temperature is marked by a vertical solid line ($T_g = T$). The vertical dotted line approximately marks the maximum in isothermal modulus vs. conversion and the glass transition/glass boundary ($T_g = T + 50^\circ\text{C}$). Dashed contours also mark T_{g0} , $T_{g\infty}$ (estimated), and macroscopic gelation. A change in slope in the isothermal modulus vs. conversion is attributed to macroscopic gelation.

ied here. In that work, the isothermal glassy-state modulus increased prior to gelation with increasing conversion.^{8,9} After gelation, the isothermal glassy-state modulus decreased with increasing conversion when the isothermal temperature was between T_β and T_g since the number of segments associated with the β process increases with conversion; however, the glassy-state modulus increased at a low rate after T_β was greater than the measurement temperature.^{8,9} In contrast, in this work, the isothermal glassy-state modulus is not affected by the β -transition; instead, the modulus decreases monotonically with increasing conversion prior to gelation for all temperatures. The different behavior observed in the vicinity of the β -transition is suggested to be due to the much stronger β -transition in the epoxy system. In the dicyanate ester system where there is no apparent effect of T_β , the decrease in the modulus due to the decrease in packing density is considered more significant than the increase in the modulus due to the freezing out of β motions as the β -transition temperature rises above the measurement temperature. In both works, the isothermal modulus measured at temperatures above T_{g0} passes through a maximum at the conversion corresponding to the boundary between the glass transition and glass regions due to competition between the increase in the modulus due to the freezing out of segmental motions as the glass-transition temperature rises above the mea-

surement temperature and the decrease in the modulus due to the decrease in packing density.

Conversion-Temperature-Property (T_g TP) Diagram

The T_g TP diagram in Figure 7 summarizes the discussed experimental results for the dicyanate ester/polycyanurate system with a cooling rate of $5^\circ\text{C}/\text{min}$. The x -axis of the diagram is conversion, as measured by T_g . The y -axis is temperature (i.e., measurement temperature). The major transitions that affect material properties, gelation and vitrification, are straight lines simplifying the diagram. A similar diagram has been constructed for the dicyanate ester/polycyanurate system from data in which the cooling rate was $2^\circ\text{C}/\text{min}$.⁴⁰

Vitrification is a heavy solid diagonal line in the T_g TP diagram, corresponding to $T_g = T$. Although marked by a single line, the process of vitrification actually occurs throughout the glass transition region and separates the rubbery and glassy states. Note that vitrification does not follow an iso-relative rigidity contour. Rather, the relative rigidity at which vitrification occurs decreases the higher the conversion (i.e., T_g). From a simple order of magnitude calculation incorporating the effect of volume changes with temperature, the shear modulus at vitrification is expected to also decrease with increasing conversion.

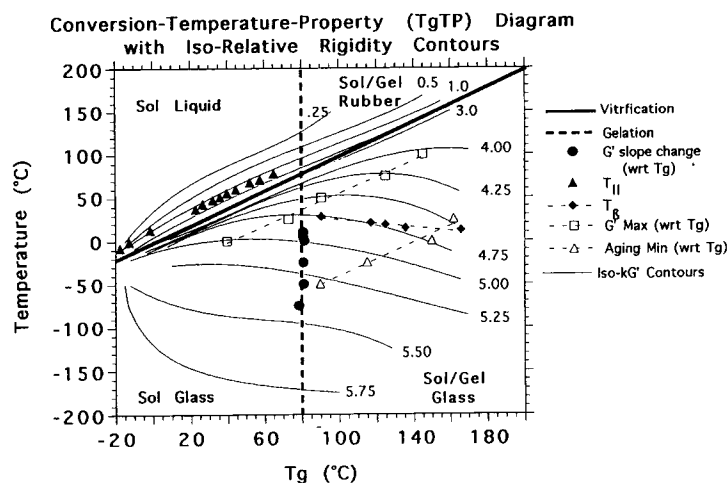


Figure 7 Conversion-temperature-property, T_g TP, diagram with iso-relative rigidity contours, summarizing the effects of temperature and conversion (T_g) on the properties of the thermosetting material.

Macroscopic gelation is a vertical dashed line on the T_g TP diagram separating the sol and sol/gel regions at $_{gel}T'_g \approx 80^\circ\text{C}$. Macroscopic gelation was determined by the change in slope of the isothermal modulus with conversion; the experimental data points are plotted. Note that macroscopic gelation affects the discernible limits of the secondary transitions, T_β and T_{II} , which are also plotted in the T_g TP diagram.

Iso-relative rigidity (\approx iso-relative modulus) contours are also constructed on the T_g TP diagram. The T_g (conversion) corresponding to the maximum in the isothermal modulus is marked (labeled G' Max). The minimum in the isothermal physical aging rate with respect to T_g at constant T is also plotted from data presented in other work (labeled Aging Min).^{36,48} Both contours, denoting the maximum in the isothermal modulus with respect to T_g and the minimum in the isothermal physical aging rate with respect to T_g , are approximately parallel to the vitrification line. Consequently, cross-linking is not considered to be responsible for the conversion dependence of these phenomena. Rather, the data suggest that the isothermal properties in the glassy state are influenced by the vitrification process and by the interval from equilibrium, i.e., $T_g - T$. Previous work from this laboratory has also shown that the rate of physical aging depends on the interval ($T_g - T$).¹¹

CONCLUSIONS

The effects of temperature and conversion on the dynamic mechanical properties (at ≈ 1 Hz) of a

new liquid dicyanate ester/high- T_g polycyanurate material have been investigated. The isothermal modulus decreases with increasing conversion in the glassy state below T_{g0} . The maximum in the isothermal glassy-state modulus with increasing conversion above T_{g0} results from competition between the increase in the modulus during cooling due to vitrification and the decrease observed below T_{g0} considered to result primarily from network constraints on packing. Macroscopic gelation results in a change in the slope of the T_g vs. glassy-state modulus data at a conversion of 0.66. The experimental results are summarized in a T_g TP diagram that demonstrates the effects of the transitions encountered during cure (gelation, vitrification, etc.) on material properties.

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