

Time-Temperature-Transformation (TTT) Cure Diagrams: Relationship between T_g and the Temperature and Time of Cure for a Polyamic Acid / Polyimide System

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Synopsis

Glass transition temperatures (T_g) were obtained vs. isothermal temperature (T_{cure}) and time of cure for a polyamic acid/polyimide system. A time-temperature-transformation (TTT) isothermal cure diagram was constructed to include the time to vitrification and iso- T_g curves. As for epoxies, the relationship between T_{cure} and the time to vitrification is S-shaped. Plots of T_g vs. T_{cure} show that solvent evaporation and chemical reaction are controlled by vitrification.

INTRODUCTION

The TTT cure diagram has been developed to understand relationships between the conditions of cure and material behavior.¹ It provides an intellectual framework for comparing thermosetting systems in which low molecular weight liquids are converted to glassy solids by chemical reaction. Figure 1 is a representation of the TTT diagram which has been developed from measurements of the times of occurrence of the basic phenomena which are encountered in the cure of epoxy systems versus the isothermal temperature of cure (T_{cure}). Gelation, which corresponds to the incipient formation of an infinite molecular network that gives rise to long range elasticity in the macroscopic fluid, is characteristic of network-forming thermosets like epoxies. The gelation curve indicates the times required for a system to gel with respect to T_{cure} . Flory's theory on gelation predicts that this curve represents constant conversion, and therefore a single glass transition temperature (gel T_g), for a system which involves a single reaction. The S-shaped vitrification curve represents T_{cure} vs. the time needed for the glass transition temperature, T_g , to reach T_{cure} . Cure of epoxies at temperatures lower than $T_{g\infty}$ (the maximum value of T_g) for extended periods of time reveals T_g to be generally 20–40°C above T_{cure} which corresponds to reactions having proceeded isothermally in the glass transition region beyond the assigned vitrification time. At high temperatures, there is competition between cure and thermal degradation reactions. For epoxies this leads to a lowering of T_g with time in a process labeled devitrification on the TTT diagram.

Polyamic acids undergo intramolecular reaction during the change from liquid to solid. With heat, cyclodehydration of the relatively low T_g polyamic acids (T_g between 120 and 180°C) produces rigid semiladder polyimide structures with higher glass transition temperatures than epoxies without forming

**THE THERMOSETTING PROCESS:
TIME-TEMPERATURE-TRANSFORMATION CURE DIAGRAM**

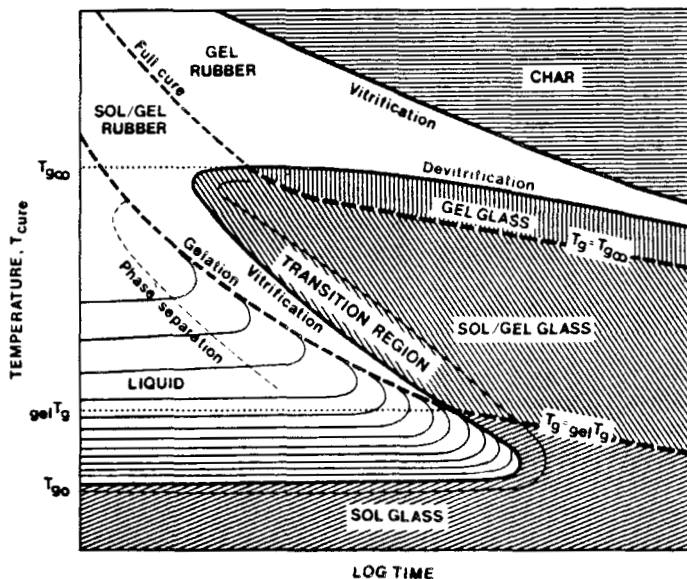


Fig. 1. Generalized time-temperature-transformation (TTT) isothermal cure diagram for epoxy thermosetting systems, showing three critical temperatures, i.e., $T_{g\infty}$, gel T_g , and T_{g0} , and the distinct states of matter, i.e., liquid, sol/gel rubber, gel rubber (elastomer), gelled glass, ungelled (or sol) glass, and char. The full-cure line, i.e., $T_g = T_{g\infty}$, divides the gelled glass region into two parts: sol/gel glass and gel (fully cured) glass. Phase separation, as in rubber-modified systems, occurs prior to gelation. Successive isoviscous contours shown in the liquid region differ by a factor of 10. The transition region corresponds to the half-width of the glass transition. T_{g0} , gel T_g and $T_{g\infty}$ are the glass transition temperatures of the reactants, the material at the composition corresponding to gelation, and the fully cured system, respectively.

crosslinked networks (Fig. 2). Thus gelation is not expected. The intramolecular nature of the imidization reaction perhaps facilitates cure in the glassy state and renders vitrification less controlling in terms of chemical conversion than is observed with the intermolecular reactions of epoxies. Study of polyamic acid/polyimide systems is complicated by the presence of solvents used to facilitate processing. Vitrification can occur by both chemical reaction and solvent evaporation. This paper represents an attempt to extend the

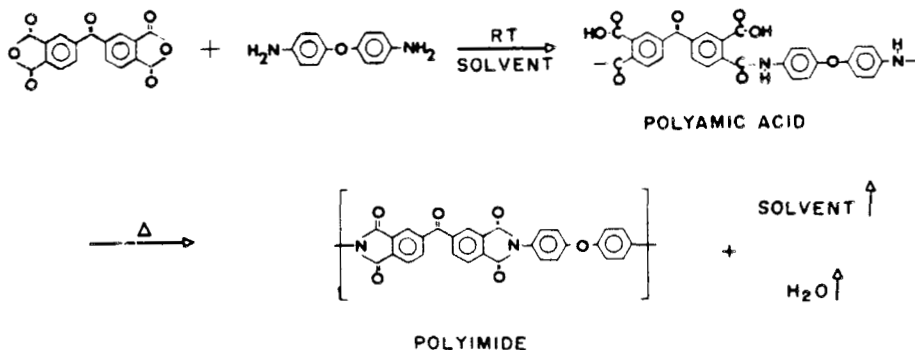


Fig. 2. Reaction scheme.

concept of the TTT diagram to a polyamic acid/polyimide system so as to examine the influence of vitrification on the rate of an intramolecular reaction and on solvent evaporation. A preliminary report has been published²; a more complete report is available.³

MATERIALS

A commercial solution (about 20% solids) of polyamic acid in *N*-methyl pyrrolidone (NMP) and petroleum distillates was examined. Comparison of the dynamic mechanical spectra of the cured system with those in the literature showed the polyamic acid/polyimide system to be based on benzo-phenone tetracarboxylic acid dianhydride (BTDA) rather than pyromellitic dianhydride.⁴ The well-defined T_g was 302°C (0.8 Hz) and a prominent glassy state transition (1.4 Hz) was centered on 140°C. In the discussions which follow, the chemical structure is taken to be that of the polyimide formed from BTDA and oxydianiline (Fig. 2).

EXPERIMENTAL TECHNIQUE AND PROCEDURE

The transformation of liquid polyamic acid solution to solid polymer during isothermal cure, and transitions characteristic of the isothermally cured samples were monitored using the torsional braid analysis (TBA) technique.⁵ Specimens were prepared using heat-cleaned multifilamented glass braids impregnated with a solution of the polyamic acid. The pendulum was intermittently set into motion to produce freely damped waves with frequencies ranging from 0.02 to 2.0 Hz. Measurements of frequency and decay constants characteristic of each wave provide two dynamic mechanical properties: relative rigidity and logarithmic decrement. These parameters were used to monitor changes in the material behavior of the specimens. Maxima in logarithmic decrement curves were used to identify the times and temperatures of transitions during isothermal runs and temperature scans, respectively. This paper reports data from a pendulum which has been automated using an IBM personal computer [Plastics Analysis Instruments, Inc., P.O. Box 408, Princeton, NJ 08540⁶].

A typical experiment consisted of two sequential parts: (1) a TBA specimen was cured isothermally for a preestablished time to determine the time to vitrify at T_{cure} ; (2) the specimen was then cooled from T_{cure} to -180°C , heated to 330°C , cooled a second time to -180°C , heated again to 330°C , and cooled to 25°C at a rate of $2^\circ\text{C}/\text{min}$. The first two ramps of the cycle were used to characterize the cured specimen. Additional ramping was used to determine the stability of T_g upon further heating. Most experiments were carried out for temperatures of cure ranging from 65 to 330°C and cure times of 12, 24, and 96 h. Figures 3 and 4 show spectra for the 24 h time scale, for the sequential isothermal and temperature scans, respectively.

Vitrification times in isothermal spectra which displayed multiple mechanical loss peaks were assigned using the definition that vitrification occurs when $T_g = T_{\text{cure}}$. Therefore, a temperature scan of a specimen which has been cured isothermally at T_{cure} for the time corresponding to vitrification will display its T_g at temperature T_{cure} .^{3,7}

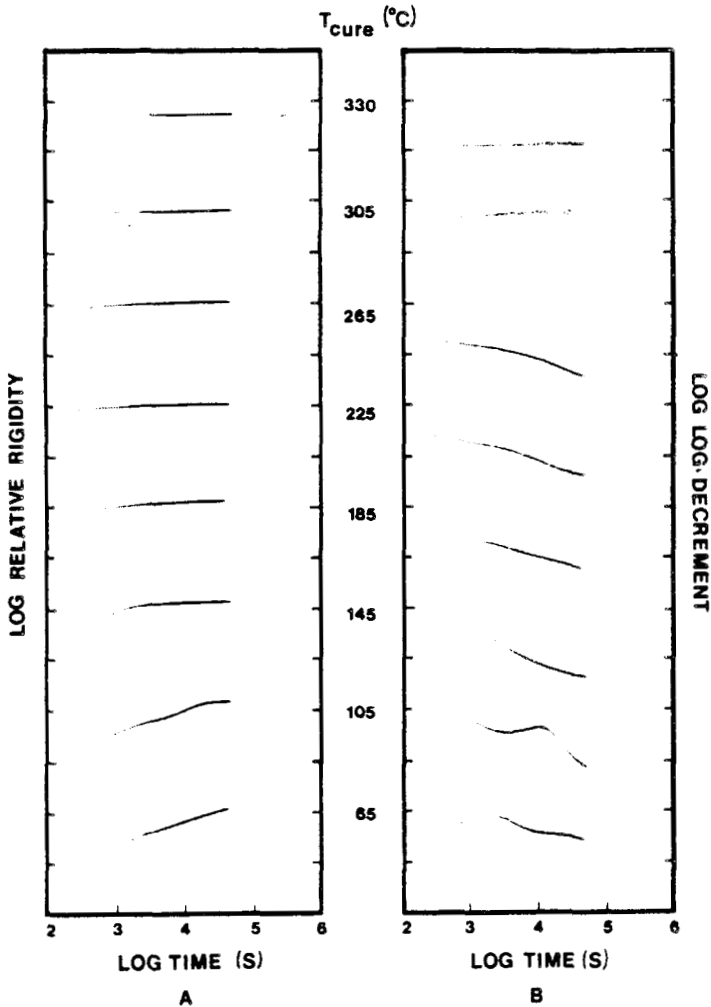


Fig. 3. TBA isothermal spectra for the polyamic acid/polyimide system: relative rigidity (A) and logarithmic decrement (B) vs. time for the 24 h time scale.

RESULTS

TTT Diagram

Figure 5 contains isothermal cure spectra for temperatures and times of cure that show distinct damping peaks. Times to vitrification determined from isothermal runs at these temperatures were used to construct a TTT diagram for the polyamic acid/polyimide system (Fig. 6). The S-shaped nature of the vitrification curve is evident when T_{cure} is plotted vs. time. Times to vitrification obtained for T_{cure} between 65 and 145°C show the time to vitrification decreases with increasing T_{cure} , thus forming the central diagonal of an S. Vitrification times for T_{cure} between 285 and 310°C increase rapidly with small changes in T_{cure} , and when plotted form the upper branch

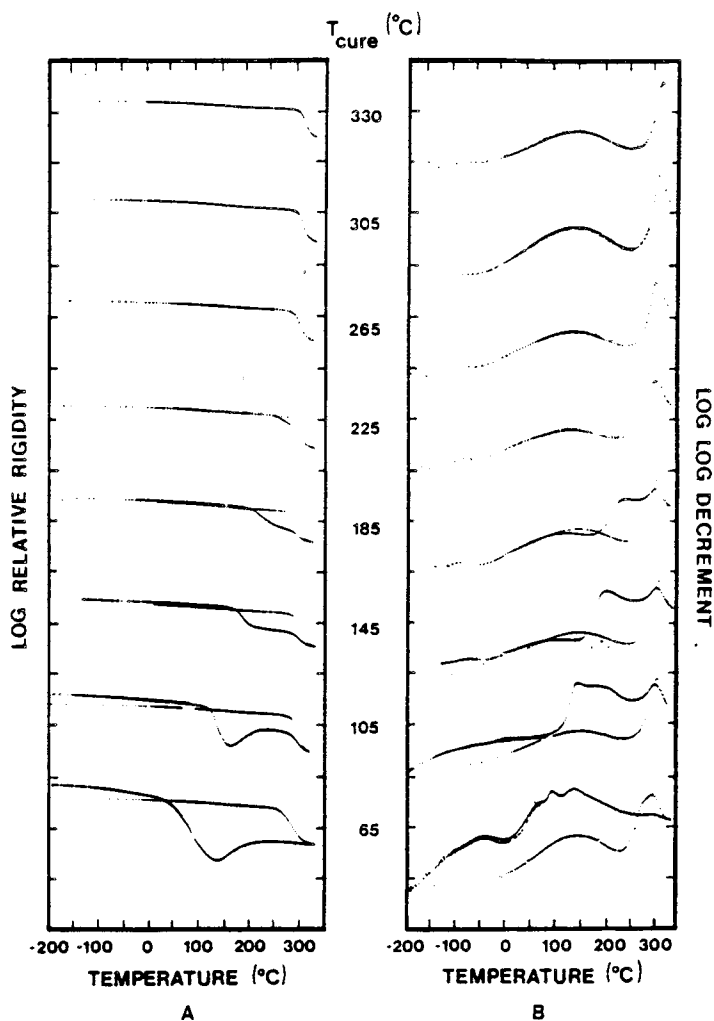


Fig. 4. TBA temperature scans of the polyamic acid/polyimide system after 24 h isothermal cure: relative rigidity (A) and logarithmic decrement (B) vs. temperature. Plots are shown for the temperature sequence: T_{cure} to -180 to 330 to -180°C at $2^{\circ}\text{C}/\text{min}$.

of an S. For T_{cure} between 140 and 280°C , times to vitrification are too short (< 5 min) for the TBA technique to follow (Fig. 3; 185 , 225 , 265°C). Vitrification times obtained for these temperatures would form the upper elbow of the S curve (dashed line). T_{g0} , the glass transition temperature of the polyamic acid solution before cure, is -75°C , as determined in a temperature scan (25 to -175°C). Thus in the temperature interval between -75 and 65°C the vitrification curve must form the lower elbow of an S curve (dashed line).

During the imidization reaction, the polyamic acid will lose up to 6.9% of its weight as water byproduct. Extended exposure of the polyamic acid/polyimide solution to high temperatures (300°C) shows that the system's weight levels off at 18% of its initial value. Thus, most of the weight lost is a result of solvent evaporation. The curve labeled 80% weight loss in Figure 6, which was

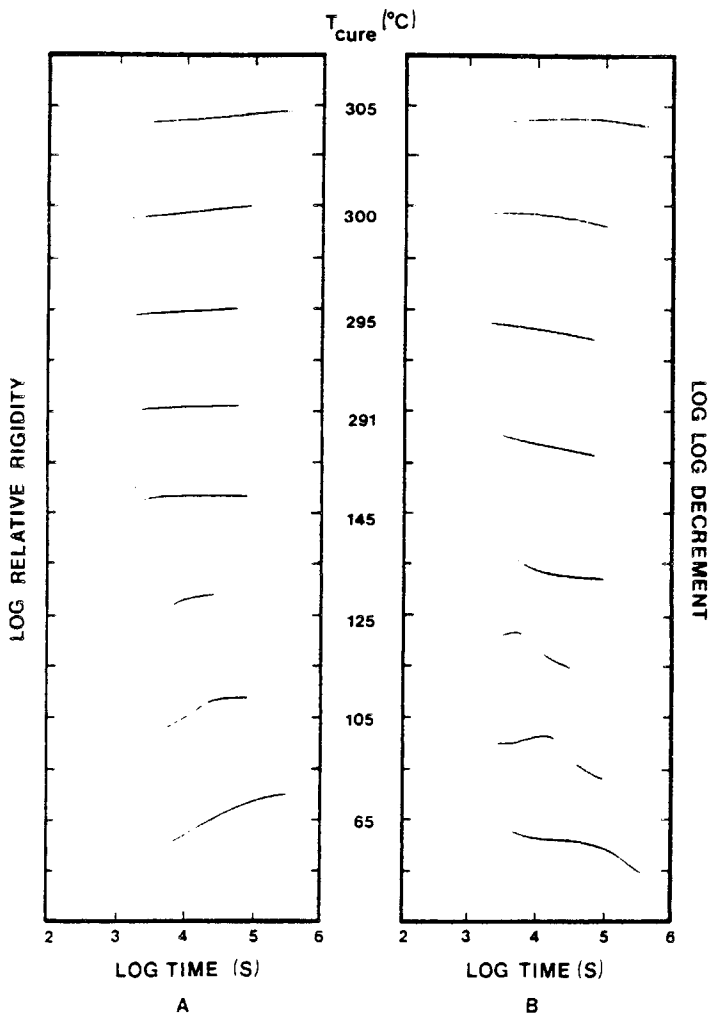


Fig. 5. TBA isothermal spectra for the polyamic acid/polyimide system: relative rigidity (A) and logarithmic decrement (B) vs. time for various time scales.

determined by monitoring weight loss as a function of time for fixed T_{cure} using thermogravimetric analysis (TGA), is therefore a good indication of the boundary between the solvent-free and solvent-laden system. A line representing the boiling point of NMP is also included in Figure 6.

Transition Temperatures

Two major transitions are distinguishable in the TBA temperature scans of the polyimide on the basis of the breadth and intensity of the loss peaks [e.g., Fig. 4(B), 265°C]. The more intense peak corresponds to T_g . Typically the numerical value of the logarithmic decrement at T_g ranges between 0.8 and 1.2; the value of the logarithmic decrement, corresponding to the broader peak centered on a temperature (T_{sec}) below T_g , is an order of magnitude less. Glassy-state transitions often occur at temperatures where side chains or

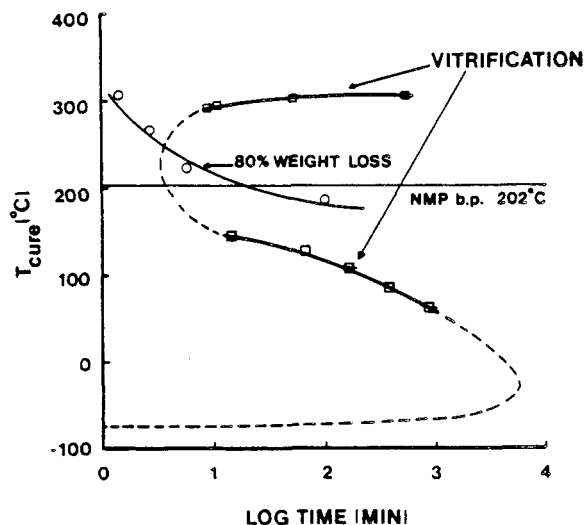


Fig. 6. TTT cure diagram for the polyamic acid/polyimide system: (□) vitrification; (○) 80% weight loss; boiling point of *N*-methyl pyrrolidone, 202°C. Horizontal error bars show repeatability of data.

small subgroups of a polymer chain become free to move or are immobilized. The shape of the loss spectra for the cured polyamic acid/polyimide system is similar in form to that of other amorphous polymers, such as polymethyl methacrylate.⁵ Minor transitions occur at about -90°C which are due to the presence of small amounts of water.^{4,8}

The Glass Transition Temperature (T_g)

In general, a reacting polyamic acid/polyimide system cured isothermally for prolonged times at temperatures below $T_{g\infty}$ will vitrify before reaching full

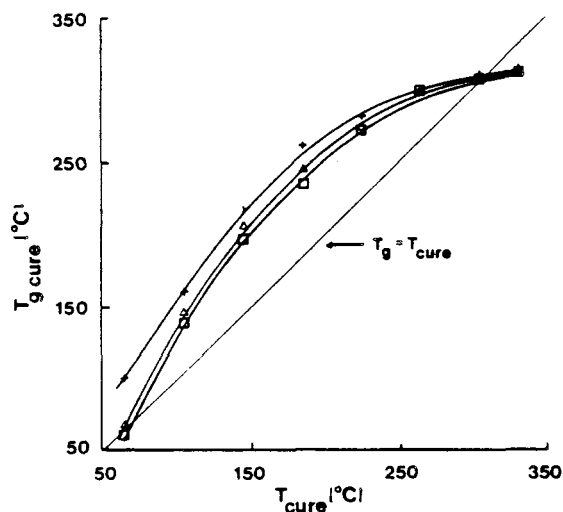


Fig. 7. T_g vs. T_{cure} for the polyamic acid/polyimide system for 12 (□), 24 (Δ), and 96 (+) h isothermal cure. The line $T_g = T_{cure}$ is also shown.

conversion. For low T_{cure} , upon heating in a subsequent temperature scan, the vitrified system devitrifies, revitrifies through further reaction and solvent loss, and finally redevitrifies as the slower rates of vitrifying processes allow the temperature to pass T_g (e.g., Fig. 4, 105°C). T_g of the isothermally cured sample ($T_{g \text{ cure}}$) can be identified on heating as the first damping maximum above T_{cure} provided that vitrification had occurred during isothermal cure. As T_{cure} increases $T_{g \text{ cure}}$ increases, and the damping peaks associated with $T_{g \text{ cure}}$ and revitrification become difficult to resolve (Fig. 4; 145, 185°C). For still higher T_{cure} , the $T_{g \text{ cure}}$ and revitrification peak begins to merge with the

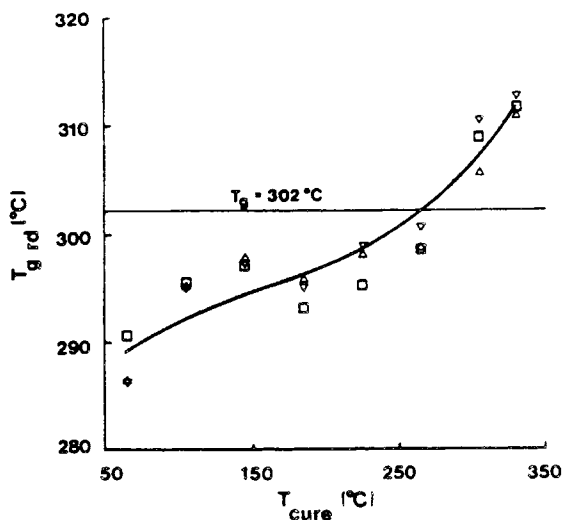


Fig. 8. $T_{g \text{ rd}}$ vs. T_{cure} for the polyamic acid/polyimide system for 12 (Δ), 24 (\square), and 96 (∇) h isothermal cure. The curve represents the general trend for the three time scales.

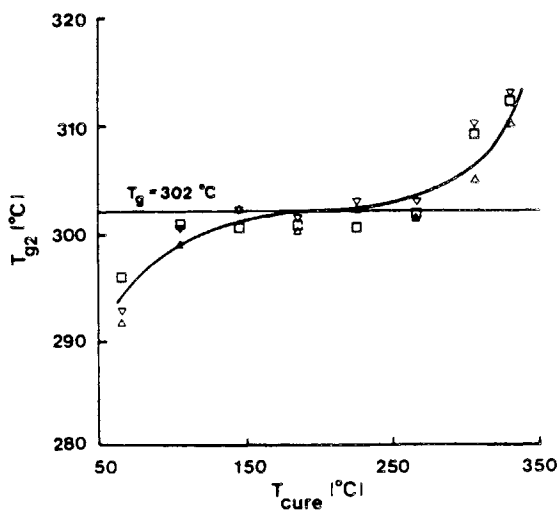


Fig. 9. T_{g2} vs. T_{cure} for the polyamic acid/polyimide system for 12 (Δ), 24 (\square), and 96 (∇) h isothermal cure. The curve represents the general trend for the three time scales.

redevitrification transition at T_{grd} (Fig. 4; 225°C) until these peaks become indistinguishable (Fig. 4; 265, 305, 330°C). Upon cooling from 330°C a new glass transition is passed which occurs at a slightly higher temperature (T_{g2}) than T_{grd} . This is not typical of high T_g epoxy systems for which T_{g2} becomes lower than T_{grd} when exposed to temperatures close to $T_{g\infty}$.⁹

Figure 7 is a plot of $T_{g\text{ cure}}$ vs. T_{cure} for 12, 24, and 96 h of isothermal cure. (The 24 h curve was obtained from the spectra in Fig. 4.) Points above the $T_{g\text{ cure}} = T_{\text{cure}}$ line are obtained when vitrification has occurred during isothermal cure. In contrast to the limited published data for epoxies,¹⁰ the relationship between $T_{g\text{ cure}}$ and T_{cure} is not linear [however, more extensive recent data on epoxies are also nonlinear¹¹]. Whereas $T_{g\text{ cure}}$ increases more rapidly than T_{cure} for low T_{cure} , at higher temperatures the $T_{g\text{ cure}}$ curves level off as they collapse into one curve. For $T_{\text{cure}} = 330^\circ\text{C}$, $T_{g\text{ cure}}$ lies beneath the $T_{g\text{ cure}} = T_{\text{cure}}$ line. For a fixed T_{cure} , $T_{g\text{ cure}}$ increases with time of cure.

The relationships between T_{grd} and T_{cure} , and T_{g2} and T_{cure} , are shown in Figures 8 and 9, respectively. Generally, both T_{g2} and T_{grd} increase with T_{cure} . Figure 9 shows that T_{g2} forms a plateau around 302°C for T_{cure} between 105 and 265°C. In this region, the increase in T_g from T_{grd} to T_{g2} seems limited. However, T_{g2} and T_{grd} for $T_{\text{cure}} = 330^\circ\text{C}$, are higher (312°C) than the nearly constant values attained for T_{cure} between 105 and 265°C.

The Glassy State Transition Temperature (T_{sec})

$T_{\text{sec cure}}$ is identified as the first broad transition encountered when cooling after vitrification has occurred at T_{cure} . Upon scanning to 330°C, as expected, little change is observed in the position of this transition. However, subsequent cooling reveals large changes in the secondary glass transition temperature (identified as $T_{\text{sec}2}$) for the polyamic acid/polyimide system cured at isothermal temperatures below 265°C. Figure 10 is a plot of $T_{\text{sec cure}}$ and $T_{\text{sec}2}$

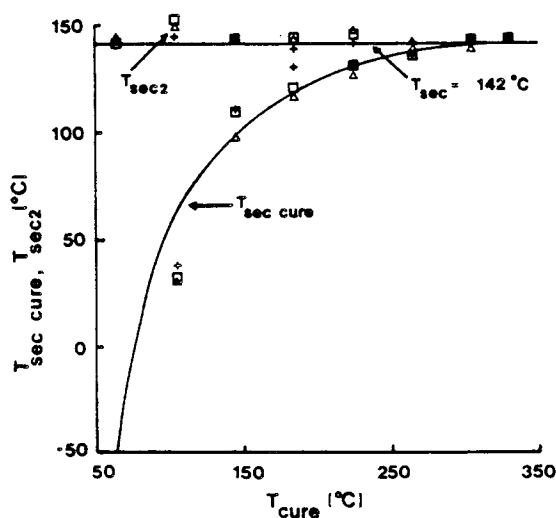


Fig. 10. $T_{\text{sec cure}}$ and $T_{\text{sec}2}$ vs. T_{cure} for the polyamic acid/polyimide system for 12 (Δ), 24 (\square), and 96 (+) h isothermal cure. The solid lines show general trends.

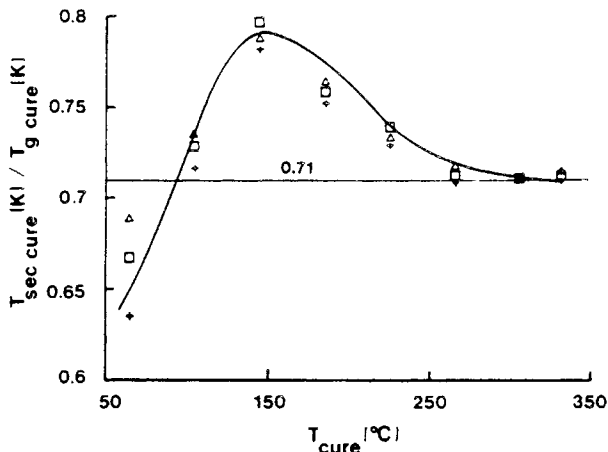


Fig. 11. $T_{\text{sec cure}} (\text{K})/T_{\text{g cure}} (\text{K})$ vs. T_{cure} for the polyamic acid/polyimide system for 12 (+), 24 (□), and 96 (Δ) h isothermal cure. The solid curve shows the general trend. The ratio approaches a stable value of 0.71 for $T_{\text{cure}} > 265^{\circ}\text{C}$.

as a function of T_{cure} for the 12, 24, and 96 h isothermal cures. The $T_{\text{sec cure}}$ curve is similar in shape to $T_{\text{g cure}}$ curves in Figure 7. In general, as with T_{g} , $T_{\text{sec cure}}$ increases with time of isothermal cure for a fixed temperature of cure. The relationship between the $T_{\text{sec cure}}$ and T_{sec2} curves shows that after scanning once to 330°C , regardless of cure prehistory, the glassy state transition temperature reaches a value around 142°C , which is characteristic of the polyamic acid/polyimide system studied. The ratio $T_{\text{sec}} (\text{K})/T_{\text{g}} (\text{K})$ approaches 0.71 with increasing T_{cure} (Fig. 11). This value is support for the molecular structure being based on BTDA with a *p, p'*-dianiline containing a flexible linkage [such as oxy, methylene, or carbonyl⁴].

T_{g} -Time-Temperature Relationships

Times to obtain specified values of glass transition temperatures for different values of T_{cure} were obtained by interpolating T_{g} data shown in Figure 7. The interpolated data have been incorporated into the TTT diagram shown in Figure 12 in the form of iso- T_{g} contours. Values of T_{g} were chosen such that data on the vitrification curve should be included in the contours (i.e., using $T_{\text{g}} = T_{\text{cure}}$ at vitrification). Such curves could be useful in determining proper curing procedures for the polyamic acid/polyimide system.

DISCUSSION

$T_{\text{g}\infty}$ (Full Cure T_{g})

For an ideal thermosetting system (i.e., one in which heating causes only the desired chemical cure reaction to take place), $T_{\text{g}\infty}$, the glass transition temperature corresponding to full cure, could be determined by reacting the system to full conversion and then measuring T_{g} . In principle such conversion could be attained by curing above $T_{\text{g}\infty}$ for extended periods of time. In real systems, however, the high temperatures needed to achieve full conversion provoke

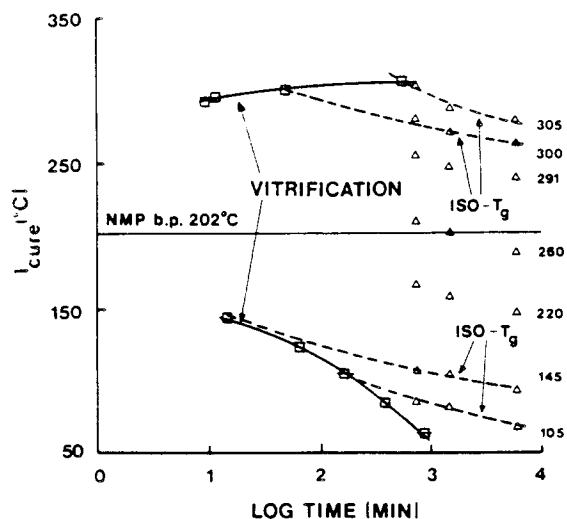


Fig. 12. The TTT cure diagram for the polyamic acid/polyimide system including iso- T_g lines (Δ) obtained using data from Figure 7.

competing thermal processes. In epoxies, the effect is an eventual decrease in T_g with time.⁹ A maximum value for T_g therefore occurs during the isothermal cure of such systems, the value of which varies with T_{cure} .^{10, 11} Exposure of polyimides to high temperatures increases T_g by crosslinking and/or ordering processes. This makes it difficult to separate the effects on T_g of the imidization and competing processes at high temperatures.

Nevertheless, the vitrification curve developed for the polyimide system (Fig. 6) provides a clue for determining a value of $T_{g\infty}$. For isothermal temperatures of cure between 290 and 310°C, the vitrification curve shows that times to vitrification increase "exponentially" with T_{cure} . This is interpreted as a consequence of the depletion of reactive groups when nearing full cure. Notwithstanding a very high rate constant at high T_{cure} , the concentration of reactive groups in the vicinity of vitrification is too low to cause substantial changes in T_g in the time frames shown. This is strong evidence that $T_{g\infty}$ lies between 300 and 310°C. That the ratio $T_{\text{sec}}(\text{K})/T_g(\text{K})$ levels off at 0.71 for $T_{\text{cure}} > 265^\circ\text{C}$ (Fig. 11) also suggests a limiting chemical state.⁴ The results of temperature scanning after isothermal cure support this attribution. Figure 9 shows that for temperatures of cure from 105 to 265°C, prehistory has very little effect on the T_g attained by specimens after scanning to 330°C. Most values of T_{g2} lie between 300 and 305°C and for this work $T_{g\infty}$ has been chosen as 302°C. A value of $T_g = 283^\circ\text{C}$ has been reported for the polyimide formed from benzophenone tetracarboxylic dianhydride and oxy-dianiline.⁴

Cure Processes and the "Glassy State"

Examination of the T_g data presented in Figure 7 shows that curing processes are not quenched by vitrification as defined. Glass transition temperatures measured after isothermal cure are consistently higher than T_{cure} . Before assuming that both reaction and solvent evaporation occur in the glassy state, an understanding of the state of the cured polyamic acid/polyimide system at the point which has been defined as vitrification is necessary.

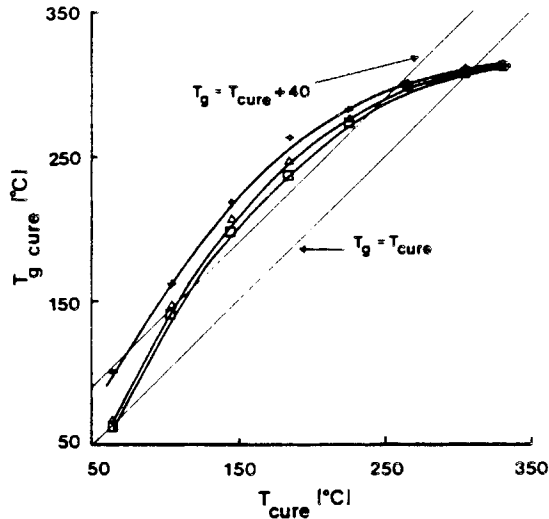


Fig. 13. $T_{g \text{ cure}}$ vs. T_{cure} for the polyamic acid/polyimide system for 12 (\square), 24 (Δ), and 96 (+) h isothermal cure. The lines $T_g = T_{\text{cure}}$ and $T_g = T_{\text{cure}} + 40^\circ\text{C}$ are also shown.

Glass transition temperatures were identified from logarithmic decrement plots as the temperatures at which loss peaks due to vitrification or devitrification attain maximum values. However, to pinpoint a temperature for this transition is misleading since the change from liquid to glassy solid is not instantaneous. Indeed, the rigidity plots vs. temperature for a fully cured system show that the changes in rigidity through T_g are gradual. The maximum value of the logarithmic decrement usually occurs at a temperature where rigidity is approximately halfway between its high and low levels. The width of the glass transition for $T_g = 300^\circ\text{C}$ is about 80°C (e.g., for $T_{\text{cure}} =$

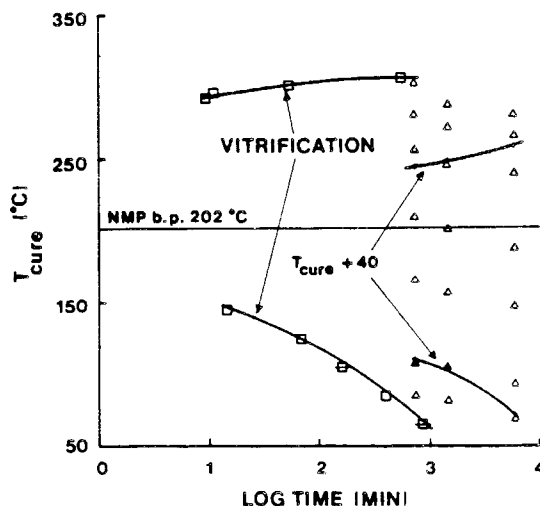


Fig. 14. The TTT cure diagram for the polyamic acid/polyimide system including the times for T_g to reach $T_{\text{cure}} + 40^\circ\text{C}$. The region between vitrification (\square) and $T_{\text{cure}} + 40^\circ\text{C}$ (+) is the glass transition region.

305°C, Fig. 4); thus before the material can begin to be considered glassy, it must be at least 40°C below its measured glass transition temperature.

Therefore, to claim to have observed curing in the glassy state, values of $T_{g \text{ cure}}$ must at least be greater than $T_{\text{cure}} + 40^\circ\text{C}$. The $T_{\text{cure}} + 40^\circ\text{C}$ line in Figure 13 distinguishes those values of $T_{g \text{ cure}}$ that are less than and greater than $T_{\text{cure}} + 40^\circ\text{C}$. Similarly, a time to reach $T_{\text{cure}} + 40^\circ\text{C}$ curve has been added to the TTT diagram in Figure 14. The state of a polyamic acid/polyimide system found between the vitrification curve and the $T_{\text{cure}} + 40^\circ\text{C}$ curve is certainly not glassy: It is in the glass transition region. Substantial data lie well above the $T_g + 40^\circ\text{C}$ line, which suggests that curing processes proceed well into the glassy state. However, the process of measuring T_g may change T_g . On heating to measure $T_{g \text{ cure}}$, reaction rates may increase enough both by an increase in the temperature and a decrease in diffusion control to contribute a rise in $T_{g \text{ cure}}$ that is not a result of glassy state reactions. Furthermore, it is noted that the width of the glass transition varies with the value of T_g .⁵

Single-Reaction Kinetics Analysis

Given a single reaction in the absence of diffusion control, it follows that for a fixed value of conversion (p) the log of time (t) is related inversely to the isothermal temperature needed to reach that conversion: $\ln t = (E/R)[1/T \text{ (K)}] + \ln g(p)$, where g is a function of p , E the activation energy for the reaction, and R the gas constant. For an ideal thermosetting system where cure proceeds by one reaction only, T_g for the system would be related to conversion in a one-to-one fashion. For such systems, the equation may be rewritten as, $\ln t = (E/R)[1/T_{\text{cure}} \text{ (K)}] + \ln h(T_g)$. However, the reactions are expected to be diffusion-controlled, especially beyond vitrification.

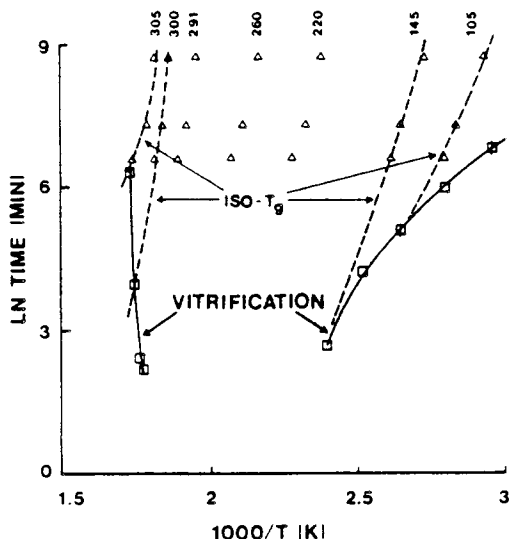


Fig. 15. The TTT cure diagram presented as \ln time vs. $1/T_{\text{cure}}$ (K): (□) vitrification; (Δ) iso- T_g .

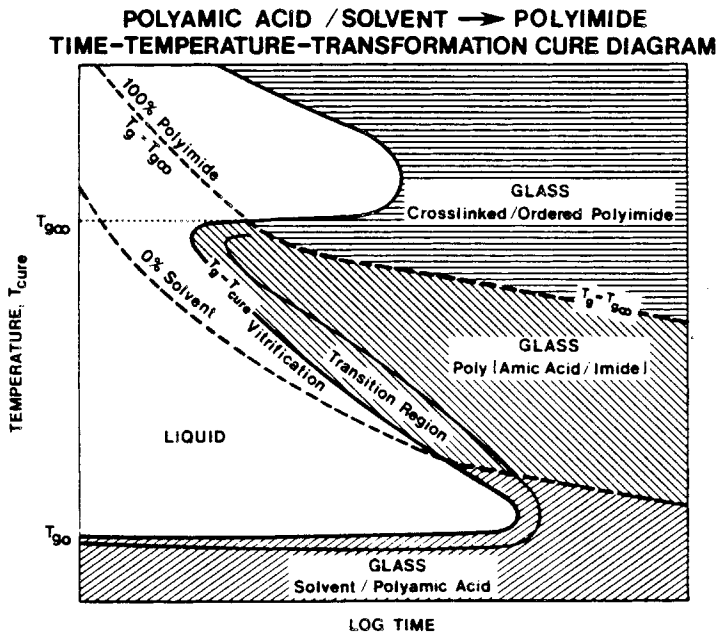


Fig. 16. Schematic TTT isothermal cure diagram for the polyamic acid/solvent/polyimide system.

The iso- T_g lines shown in Figure 12 have been recast in Figure 15 as functions of time and $1/T_{\text{cure}}$ (K). Since both the processes of imidization and solvent evaporation affect vitrification, the iso- T_g lines in the intermediate temperature range should be affected by this complexity. For an ideal system, once solvent is lost there should be a one-to-one correspondence between T_g and conversion for the polyamic acid/polyimide system; for example, as for the 305 and 291°C iso- T_g curves found in the high temperature range of Figure 15, where the presence of solvent is considered to be negligible.

The apparent activation energies calculated from the slopes of the iso- T_g curves increase with time. This is a result of changes in the physical state of the system. In the liquid state activation energies are those of the reaction [~ 25 kcal/mol¹²], whereas in the glassy state, apparent activation energies are indicative of processes that restrict reaction. Since vitrification is a gradual process, changes in the degree of diffusion control are also gradual and apparent activation energies increase with time through this transition, reaching a limiting value³ which is similar to that obtained for epoxies (~ 100 kcal/mol).¹⁰ In the limit it therefore seems that glassy state motions control the reaction rate.

SUMMARY

A summary of much of this work appears in Figure 16 in the form of a schematic TTT-cure diagram.

References

1. J. K. Gillham, in *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Wiley, New York, 1986, Vol. 4, p. 519.
2. G. R. Palmese and J. K. Gillham, *Proc. Am. Chem. Soc. Div. Polym. Mater., Sci. Eng.*, **55**, 390-395 (1986).
3. G. R. Palmese, Senior thesis, Princeton University, May 1986.
4. J. K. Gillham and H. C. Gillham, *Polym. Eng. Sci.*, **13**(6), 447 (1973).
5. J. K. Gillham, in *Developments in Polymer Characterisation-3*, J. V. Dawkins, Ed., Applied Science, London, 1982, pp. 159-227.
6. M. K. Gillham and J. B. Enns, 1986, unpublished results.
7. J. K. Gillham, in *Resins for Aerospace*, C. A. May, Ed., ACS Symposium Series No. 132, Am. Chem. Soc., Washington, DC, 1980, pp. 349-365.
8. Y. Ozari, R. H. Chow, and J. K. Gillham, *J. Appl. Polym. Sci.*, **23**, 1189 (1979)
9. L. C. Chan, H. N. Naé, and J. K. Gillham, *J. Appl. Polym. Sci.*, **29**, 3307 (1984).
10. X. Peng and J. K. Gillham, *J. Appl. Polym. Sci.*, **30**, 4685 (1985).
11. K. P. Pang and J. K. Gillham, *Proc. Am. Chem. Soc. Div. Polym. Mater., Sci. Eng.*, **55**, 64-68 (1986).
12. J. A. Kreuz, A. L. Endrey, F. D. Gay, and C. E. Sroog, *J. Polym. Sci., A-1*, **4**, 2607 (1966).

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