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TORSION IMPREGNATED CLOTH ANALYSIS (TICA) OF EPOXY CURE

Polymer Branch
Nonmetallic Materials Division

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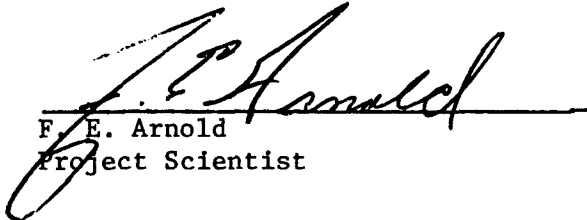
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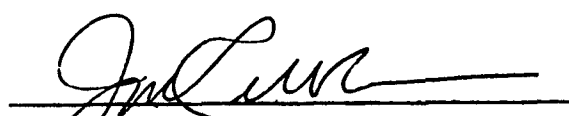
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The technique of Torsion Impregnated Cloth Analysis (TICA) has been developed to allow continuous monitoring of the cure behavior of thermoset systems. Epoxy 3501-A has been used as the material in the feasibility study. The thermal scan of an incompletely cured epoxy specimen has shown that further curing effect during experimentation cannot always be ignored. The cure phase diagram and an isocure state curve have been constructed from the experimental results. Combining both results, it is concluded that an epoxy sample cured at 135°C for 5 hours will have an intrinsic cured glass transition of 158°C.		

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, "Nonmetallic and Composite Materials," Task No. 241904, Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the AFML Project Scientist. Co-authors were Dr. C. Y.-C. Lee, Mr. T. D. Henes, and Mr. T. E. Grossman of the University Dayton Research Institute and Dr. I. J. Goldfarb, Air Force Materials Laboratory (AFML/MBP).

This report covers research conducted from April 1977 to April 1978.

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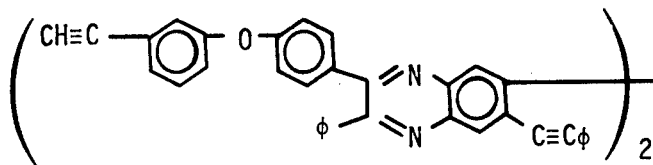
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SECTION I

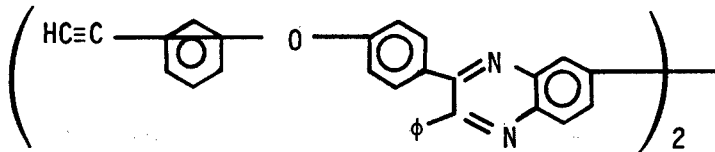
INTRODUCTION

In the Intramolecular Cycloaddition (IMC) Resin program, a candidate resin has been prepared. This resin, named BA-DABA-BA (Reference 1) is structured as follows



and has two types of reactive acetylene groups. The groups attached to the end will induce crosslinking reaction during cure to form a network structure like most of the acetylene terminated systems. The two groups in the middle will react with each other to form aromatic rings. This IMC reaction will stiffen the backbone of the polymer and should raise the T_g of the system to a higher temperature. Since the two reactive groups in the middle are permanently attached to adjacent sites on the resin, chain immobility of the polymer will not hinder the progress of this reaction. Unlike the chain extension reaction of the acetylene groups at the end of the resin, the IMC reaction is not diffusion controlled, and can continue after vitrification of the polymer. This type of IMC reaction allows the possibility of curing a polymer at a low temperature with the usable temperature limit at a much higher value.

To evaluate the effectiveness of this IMC reaction, another resin, BA-DAB-BA (Reference 2)



was prepared as a reference. This resin is identical in structure to BA-DABA-BA, except for the absence of the IMC groups in the middle. It was desirable to study the T_g attained from these two resins after curing

at identical temperature. To help eliminate confusion between the two, BA-DABA-BA will be called BA/IMC, and BA-DAB-BA will be called BA in this report.

A BA rectangular bar sample was made by melting the resin in a mold, then curing at 204°C for one hour. A temperature scan was run on the rheometrics mechanical spectrometer to study its dynamic mechanical properties. Up to 350°C, there was no sign of a T_g transition; G' did not drop from its glassy value of about 10^{10} dynes/cm², and G'' and $\tan \delta$ showed no sign of a maximum peak.

This result can lend itself to two different interpretations. The simple one is that the T_g of the cured bar sample has a T_g above 350°C. This would mean that the IMC reaction is unnecessary since a cure temperature of ~200°C will yield a specimen with an extremely high T_g . This is contrary to the view that the crosslinking reaction of the terminal acetylene reaction, or most of the crosslinking reactions of thermoset resins, will stop after the polymer vitrifies.

Another explanation is that the kinetic rate of the curing reaction in this system is very fast. As the temperature was increased during the temperature scan, further reaction occurred when the temperature was close to T_g . This would push the T_g of the specimen to a higher value. If the rate of temperature increase in this experiment were slower than the rate of T_g increase due to further reaction, no T_g transition will be observed. This explanation is highly plausible since the BA system is believed to have a high kinetic rate of reaction, as observed from DSC studies (Reference 3).

This point of view not only means that T_g cannot be detected in these particular systems with the conventional thermal scan method; it even casts doubts on the observed " T_g - transition" on other incompletely reacted thermoset polymers. Let's define "intrinsic cured T_g " as the T_g associated with a particular cured state if its measurement is feasible without changing the cured state of the specimen. The observed transition is the intrinsic cured T_g of the partially cured specimen only if the

kinetic rate of further reaction is so slow that the amount of further reaction is insignificant during the course of the measurement. If not, the observed value will always be higher, and a different temperature scanning rate will yield a different observed value. This is even more complicated if a comparison of T_g -after-cure between two different systems is being made. System A may have a lower intrinsic cured T_g than system B, but because the reaction rate of A is much faster than B, under identical experimental conditions, system A may show a higher observed T_g value.

Since direct measurement of the intrinsic cured T_g is not possible, an alternate approach is proposed. This approach involves studying the isothermal cure of the resin at different temperatures. The result will yield a phase diagram relating the different phases of the matter, e.g., liquid, rubbery, and glassy phases, with temperature and time. A different study relating the extent of reaction as a function of time and temperature will then be done with other experimental methods. By combining the two results, we can interpolate the intrinsic cured T_g of a thermoset resin. The detailed explanation of this approach will be given later.

This report is the result of the development of the torsion impregnated cloth analysis (TICA) technique which will allow the study of isothermal cure with the rheometrics mechanical spectrometer. Epoxy Resin H-3501-A, lot No. 12 KV10, is chosen as the material used in this technique-feasibility test. The reasons are: 1) the material is readily available from the Composite Branch in "quantities," and 2) TBA studies on this resin have been made by J. K. Gillham at Princeton, so his result can be used as a reference.

SECTION II

BACKGROUND

1. TORSION IMPREGNATED CLOTH ANALYSIS (TICA)

The experiment described in this report is similar to Torsional Braid Analysis (TBA) developed by J. K. Gillham. The idea is to impregnate a stack of glass fiber cloth, with the resin to be studied either by "melt-prepreg" or "solvent prepreg" method. "Melt prepreg" method is to heat the resin to a high enough temperature to allow the resin to flow and wet the cloth. This method has the advantage of potentially depositing a lot more sample on the cloth and eliminating the troublesome process of extracting the solvent, as in the case of "solvent prepreg." But because high temperature may be needed to achieve this, the resin could have advanced somewhat during the impregnating process. The "solvent prepreg" method is to wet the cloth with a solution of the resin and then extract the solvent by prolonged pumping under vacuum.

The method of determining G' and $\tan \delta$ is different from that of TBA. In TBA, the resin-impregnated braid is set in free oscillatory motion and its damping decay characteristic is recorded. The frequency of oscillation can be related to the G' of the resin, while the log of the amplitude decrement is proportional to the $\tan \delta$. In the TICA experiment in this report, the cloth is cut into a rectangular bar shape and is mounted on the rheometrics mechanical spectrometer, as in the torsional bar mode (Reference 4). The cloth is undergoing an oscillatory strain at a fixed frequency and the resultant torque is analyzed by a frequency response analyzer to give both the in-phase and out-of-phase components' amplitudes. The resultant torque is a response of the composite: the cloth and the resin. The torque from the cloth itself is presumably small in comparison with that from the resin. Also the contribution from the cloth is very much a constant over a wide range of temperature. Any changes in the total response will be assumed to arise from the resin itself.

The results obtained from TICA measurements are not absolute modulus values of the resin studied. But this mode of measurement has the advantage over the conventional torsion bar or parallel plates measurement on the rheometrics instrument, in that a much wider range of modulus change can be covered on the same specimen. Torsion bar experiments require the samples be sufficiently stiff to support themselves structurally in the sample chamber. Thus, for a material that has a modulus value lower than that of the rubbery state, one has to use a parallel-plates measurement. But because of the geometry of the parallel plates, slippage may occur for materials having a modulus value above the rubbery state. The two methods are complementary to each other to cover the full range of behavior of a material, but not on the same specimen (Reference 4). The TICA measurement is like the torsional bar measurement, but when the resin is in the liquid state, the glass fiber will provide the structural support. This feature makes TICA ideal for monitoring the isothermal cure of a resin which may go through the liquid state and the glassy state.

2. CURE BEHAVIOR OR THERMOSET RESIN

The general dynamic modulus behavior of a thermoplastic is shown in Figure 1. At low temperature, the material is in the glassy state, characterized by a high modulus value in G' . As the temperature approaches T_g , the G' value starts to drop, while the $\tan \delta$ value begins to rise ($\tan \delta$ is used here instead of G'' because TBA results give $\tan \delta$, not G'' ; and, also, it is not certain if $T_{\ell,\ell}$ has a G'' maximum) (Reference 4). At $T=T_g$, $\tan \delta$ attains a maximum value. The polymer is in the rubbery region as temperature is further increased. The temperature range of this region depends on the molecular weight of the polymer: the higher the molecular weight, the wider is the range. At a sufficiently high temperature, the modulus is dropped even further, while the $\tan \delta$ shows another peak. This transition has been referred to as $T_{\ell,\ell}$ (Reference 5). It has also been interpreted as the transition temperature between the rubbery state and the liquid state (Reference 6). In a highly crosslinked system, this transition is absent, presumably because the rubbery state will reach an equilibrium plateau and the polymer will never change into the liquid state. In a thermoplastic system, the molecular weight and the T_g of the system is a constant. Depending on

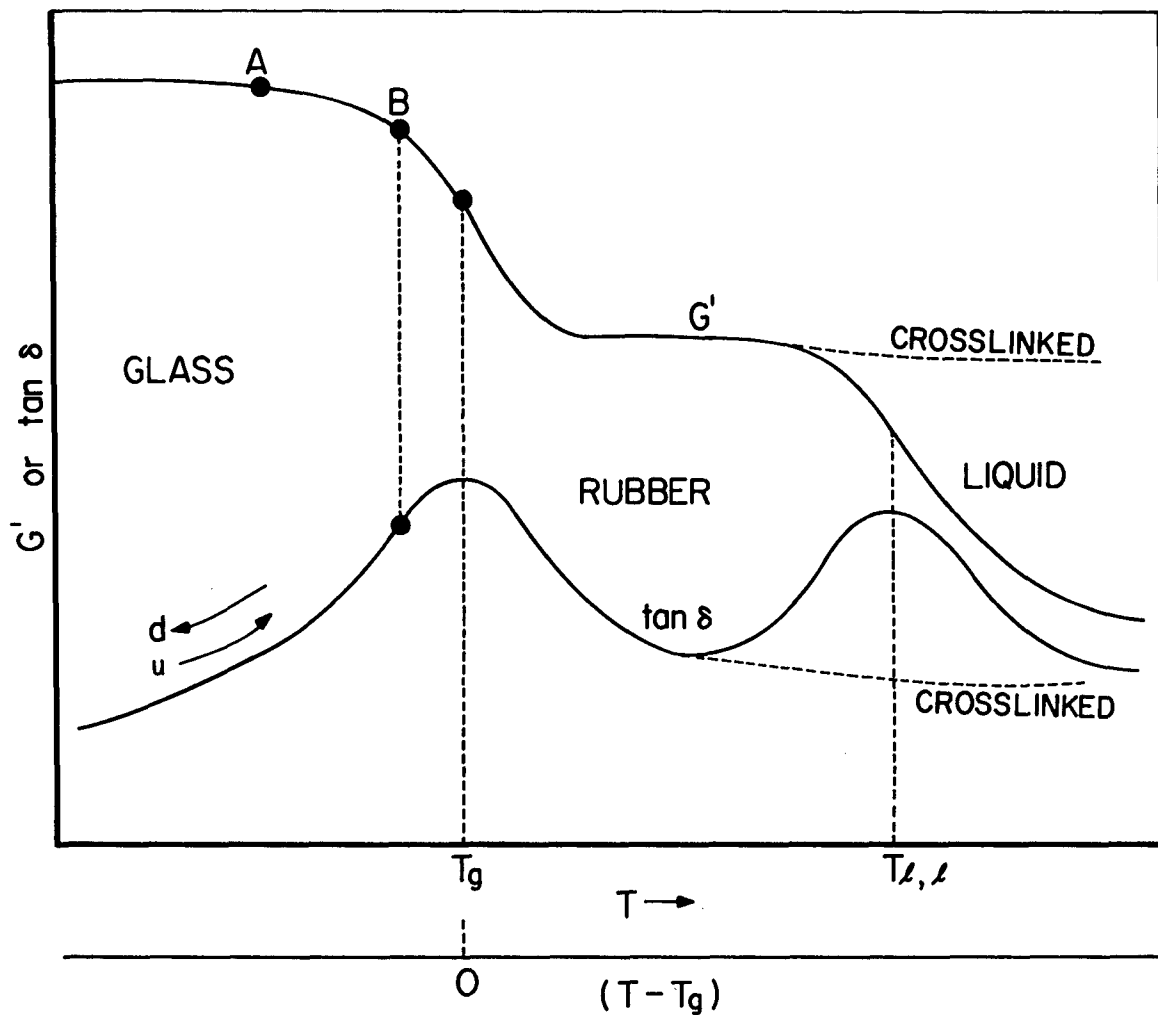


Figure 1. Dynamic Mechanical Response of a Polymer Near The Glass Transition Temperature

the measurement temperature, T , one of the three states of the polymer can be in effect and the corresponding behavior observed. This description of general behavior is applicable to any thermoplastic system of any molecular weight value by replacing the temperature scale by a reduced temperature scale $(T - T_g)$.

In an isothermal cure experiment of a thermoset resin, the measurement temperature, T , is a constant. As the material cures with increasing time, the T_g of the material increases. The reduced temperature $(T - T_g)$ then decreases as a function of time. If the polymer starts off at the beginning as a liquid, its behavior as a function of time will be like tracing the curve of the thermoplastic in Figure 1 from the right to the left. The first $\tan \delta$ maximum observed is when the system is advancing from the liquid state into the rubbery state, or called the gel point. If this resin could be stopped from further reaction at this point, a temperature scan of this polymer would yield a $T_{\ell, \ell}$ at the cure temperature. The second maximum during the cure is then the transition into the glassy state. At the maximum, $T = T_g$, and at that point in cure time one would have a specimen whose intrinsic cured T_g is equal to the cured temperature T .

The reference of $T_{\ell, \ell}$ being equivalent to the gel point deserves further discussion. Since a thermoset resin usually cures by crosslinking, and $T_{\ell, \ell}$ is absent from crosslinked materials, it seems impossible that they could be equivalent. The molecular interpretation of $T_{\ell, \ell}$ as proposed by Boyer and Gillham may be used to help clarify this point. According to this picture, the $T_{\ell, \ell}$ transition of a thermoplastic is when the center of gravity of the whole molecular chain starts to become mobile. For a cross-linked network, the whole bulk of polymer has to be moved for this to happen. However, in thermoset cure, the resin starts out as low molecular weight oligomers. At the initial cure, many small networks start to grow, with the center of gravity of each network being freely mobile. As the cure is advanced, these networks increase in size as well as in numbers. Eventually they will become immobile, thus causing the maximum in loss tangent. This is not yet the glass transition, because though the center of gravity of each network is immobile, the segments on the networks are mobile.

3. PHASE DIAGRAM AND ISOCURE STATE CURVES

With the isothermal cure curves, we can denote the times for gelation and T_g transition by monitoring the loss behavior. These data can be used to construct a cure phase diagram as suggested by Gillham (Reference 7). Figure 2 is a typical phase diagram. For a cure temperature T ($T_{gg} < T < T_g(\infty)$), the cure curve will exhibit both the gelation and T_g peaks. T_{gg} is defined as the temperature where time to gelation is the same as the time to T_g transition. Below this temperature the cure curve will exhibit only the T_g transition peak. $T_g(\infty)$ is the maximum T_g a system can attain after it is "completely" cured. A cure curve above this temperature will show only the gelation peak.

A specimen cured at temperature T_1 would have attained a certain cure state, n , after a cure period of t_1 (Figure 2). If the times for attaining the same cure state at different temperatures are known, an isocured state curve (the dotted line on Figure 2) can be drawn on the phase diagram. The temperature at which this curve crosses the T_g transition line, T_2 , will then be the intrinsic cured T_g of the specimen with the said cure history (cured at T_1 for t_1). This method of T_g interpolation allows an intrinsic cured T_g value of a specimen to be deduced without the conventional thermal scan measurements if its cured state can be identified.

The isocured state curves would have to be constructed from a separate series of experiments where bulk cure kinetics can be monitored as a function of time. This can be accomplished by spectroscopy; e.g., FTIR can monitor the disappearance of the vibrational band of the reactive moiety or the appearance of the product band. With the new development of the solid state NMR measurements, this method is even more promising as a tool to construct isocure state curves.

A simpler way is to monitor the heat of reaction by DSC. By subjecting a series of samples to various cure times, the unreacted material will show up in subsequent DSC scans on these samples as different amounts of heat of reaction. This method of measurement assumes that two samples with the same amount of remaining heat of reaction are in the same cured state. The validity of this assumption will be explored further in detail when such data are reported.

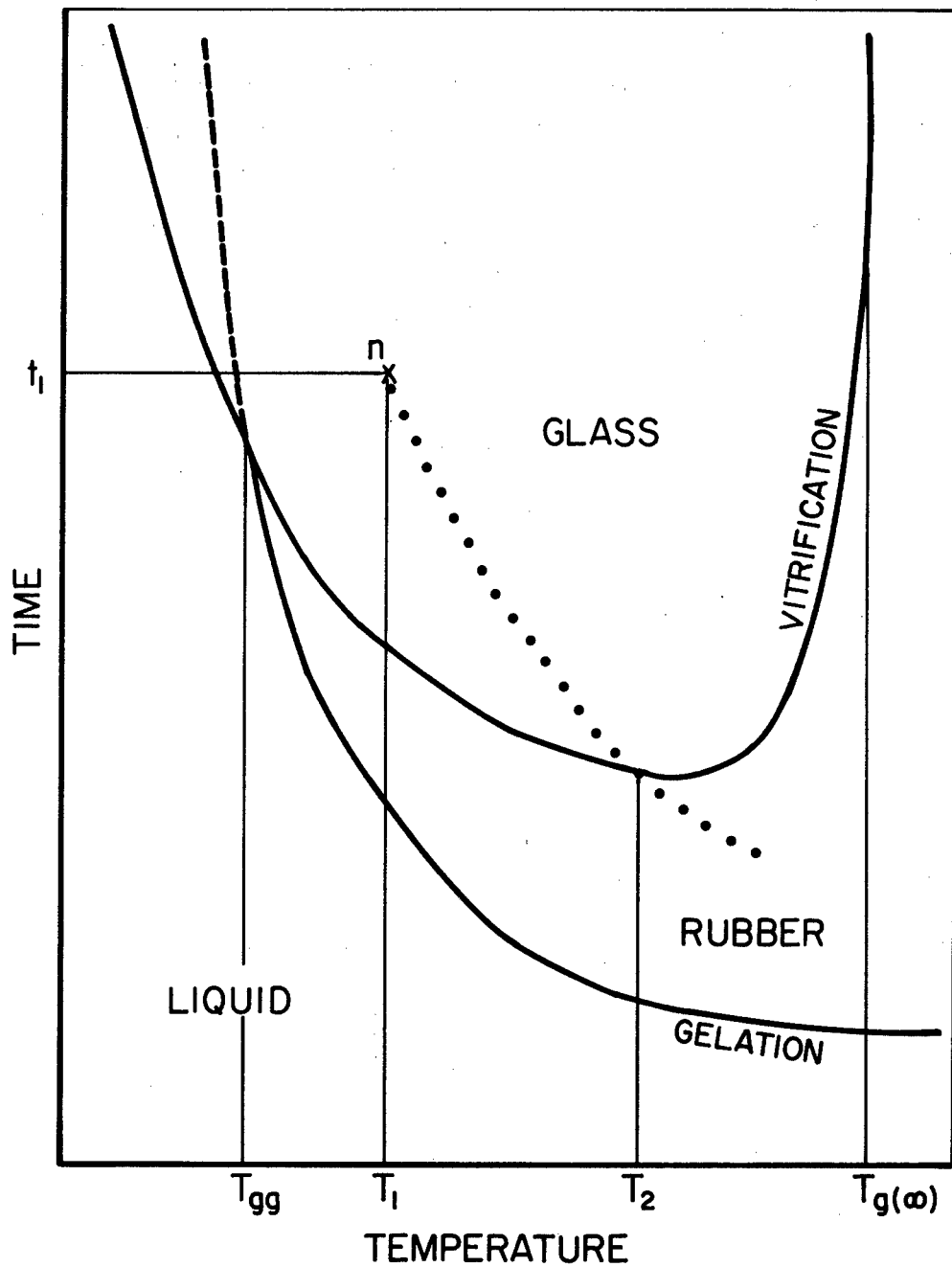


Figure 2. A Cure Phase Diagram of Thermoset Systems

This method of T_g interpolation has an underlying assumption that T_g is only affected by the cured state as measured by the extent of reaction with whatever method chosen. It further assumes that two specimens cured at two different temperatures will have the same T_g if the extent of reaction is the same for both. Topological and morphological effects are neglected. These assumptions will be seriously strained when dealing with copolymers, where cure temperature has much effect on the resultant properties of the cured product. For homopolymers, however, morphology and thermal history usually have more effect on properties other than T_g .

SECTION III

EXPERIMENTAL

1. SAMPLE PREPARATION

Hercules' epoxy system 3501A-12KV10 subplot was obtained and the material was used "as is." Two techniques have been used to prepare the resin-impregnated cloth. The first attempt was to use the "melt-prepreg" technique. The resin was heated to 80°C to lower the viscosity and the individual cloth was wetted with epoxy. The impregnated cloths were then stacked to the desirable thickness. The heated resin was very "tacky." It was difficult to align the warp of the cloths along the same axis. In this technique there tends to be too much resin on the cloth, so that when the specimen was in the high temperature liquid state, excess resin ran off and bonded to the sample holding fixtures. Melt-prepreg also requires heating the resin to a higher temperature so that some cure advancement may have occurred. This may cause specimens from different preparations to be in different cured states.

The "solvent-prepreg" technique was used to prepare all specimens used in the experiments. Four layers of cloth were stacked together with the warps aligned in the same direction. The ends of the cloth were clamped together with glass plates and binder paper clips. The cloth was then dipped into a solution of epoxy in dichloromethane. The wet cloth was hung in the exhaust hood overnight. Then it was subjected to vacuum extraction of the solvent for a week before use.

2. FIXTURES AND TEST SPECIMENS

Fixtures were designed to hold the impregnated cloth in the sample chamber of the RMS. An earlier version of the design was more elaborate. It allowed the cloth to be folded back over the edge of the fixtures to prevent slippage. Later, it was found that such a feature was not necessary. A simpler design was used which allows more layers of cloth to be incorporated in each test specimen. The fixtures are plates of stainless steel of dimension: 1.78 x 1.26 x 0.23 cm (length x width x thickness). The cloth ends were sandwiched by two fixture plates which

were held together by a screw at the center. Aluminum foil was used to separate the fixtures from the cloth so that the cured resin will bond to the foil instead of the fixtures.

Test specimens were cut from the solvent-extracted impregnated cloth. The dimensions of the specimens were 6.35 cm long and 1.26 cm wide. Holes were punched at both ends to allow the passage of the screws holding the fixtures. An aluminum jig was built to help the mounting of the fixtures. This will ensure the fixture-mounted specimens to be more uniform in dimensions. The resultant specimens had dimensions at both ends similar to those of the torsion bar specimens, and they were mounted on the sample holding chucks of the RMS the same way as the torsion bars.

3. EXPERIMENTAL CONDITIONS

All measurements were made at 1.6 Hz frequency and the voltage for oscillation amplitude was set at 0.3V. Other experimental parameters were developed during the series of experiments. It is found that a 700 to 1000 gm tension on the sample is desirable at room temperature. Together with the temperature expansion compensator, this setting will not give too much tension at low temperatures and will not cause sample compression at high temperatures. Tension level on the sample is the most troublesome experimental parameter in TICA measurements. Too high tension will cause transmission of the tensile force into torque through the oscillatory motions. Too low tension will cause buckling of the cloth. Because of the exploratory nature of this series of experiments, the qualities of the results are not uniform.

SECTION IV

RESULTS AND DISCUSSION

The isothermal cure curves gave two peaks during cure as expected. Figure 3-a shows the cure curves at 155°C as a function of time. Figure 3-b shows the same set of data on log time. Three curves are shown, a is the in-phase component, b the out-of-phase component, and $\tan \delta = b/a$. The a and b are proportional to G' and G'' respectively.

The first $\tan \delta$ peak at about 1400 sec. is the gel peak. Both a and b values are rising at this time, and there is no corresponding b peak, similar to the $T_{g,2}$ observation on Radel (Reference 6). At about 2300 sec. there is an inflection point on a. This is like the rubbery state of a low molecular weight thermoplastic. At 2500 sec. there is a $\tan \delta$ maximum. In the TBA experiment, where $\tan \delta$ is measured, this time is called t_{Tg} . At 4850 sec., b shows a maximum. If the G'' maximum instead of the $\tan \delta$ maximum is chosen as the criterion for glass transition, the latter time would become t_{Tg} . Thus, in general, for each isothermal cure, we can identify three points, gel peak (t_{gel}), $\tan \delta$ maximum (t_{δ}), and b maximum (t_{vit}). After about 3 1/4 hours, the three values a, b, and $\tan \delta$ are still changing, but at a very slow rate.

The T_g transition as measured by TICA is verified by comparing with results from conventional torsion bar measurements (results will be presented in a later section). There is no good way to verify the vitrification transition. Since resin-cloth interaction will likely be affecting the component a, spurious $\tan \delta$ maxima can occur. Therefore, it is better to identify vitrification with the b maximum.

Gillham had defined a time longer than t_{Tg} as the vitrification time, which is when the "relative rigidity (corresponding to G') levels off" (Reference 7). This definition of vitrification is difficult to measure experimentally, as stated in Gillham's report. The basic implication in that definition is that vitrification is a condition occurring when further reaction is stopped because of hindered movements of the

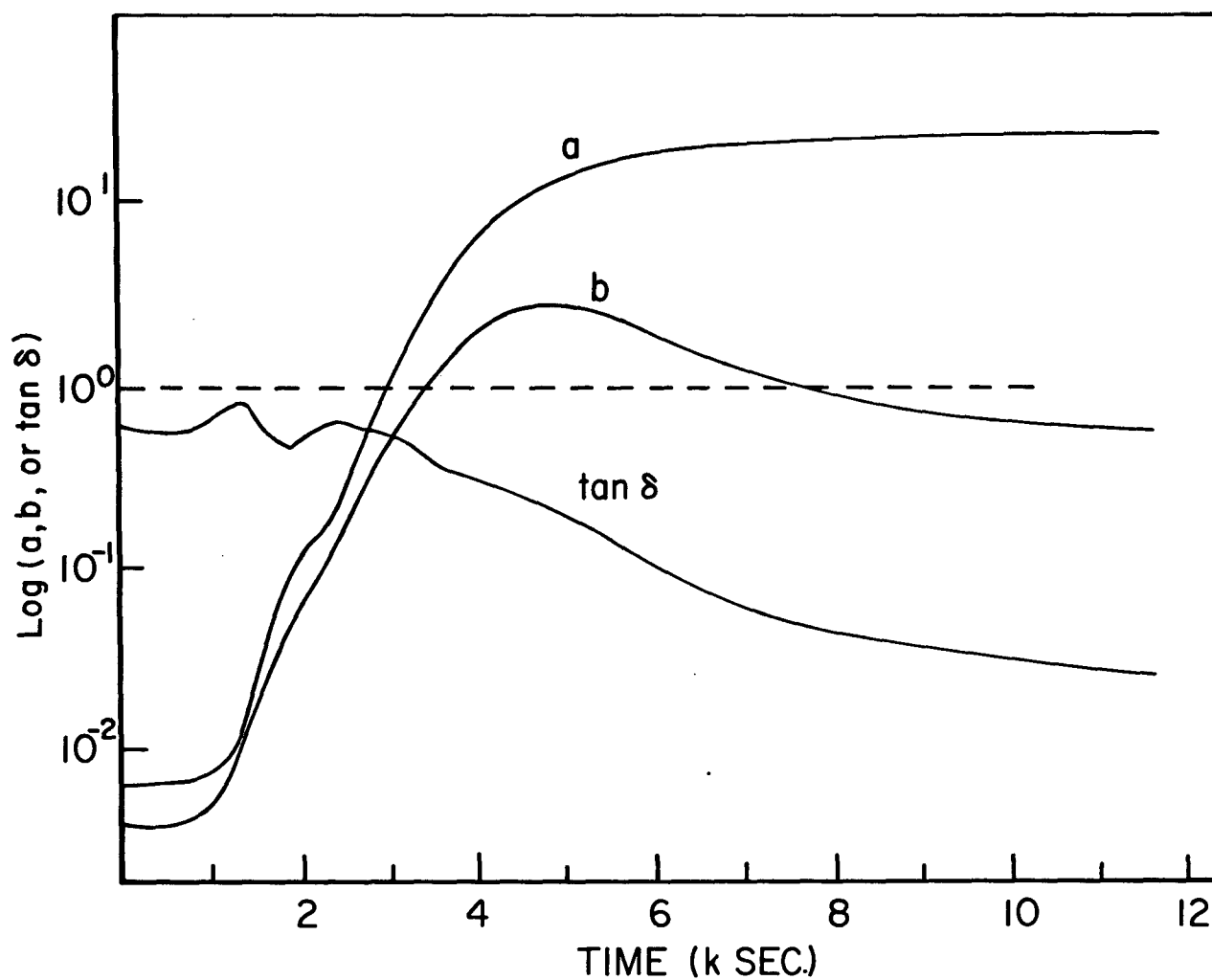


Figure 3a. TICA Isothermal Cure Curve of an Epoxy Specimen. The in-phase component (a), out-of-phase component (b), and their ratio $\tan \delta$ are plotted (a) vs time, and (b) vs log time

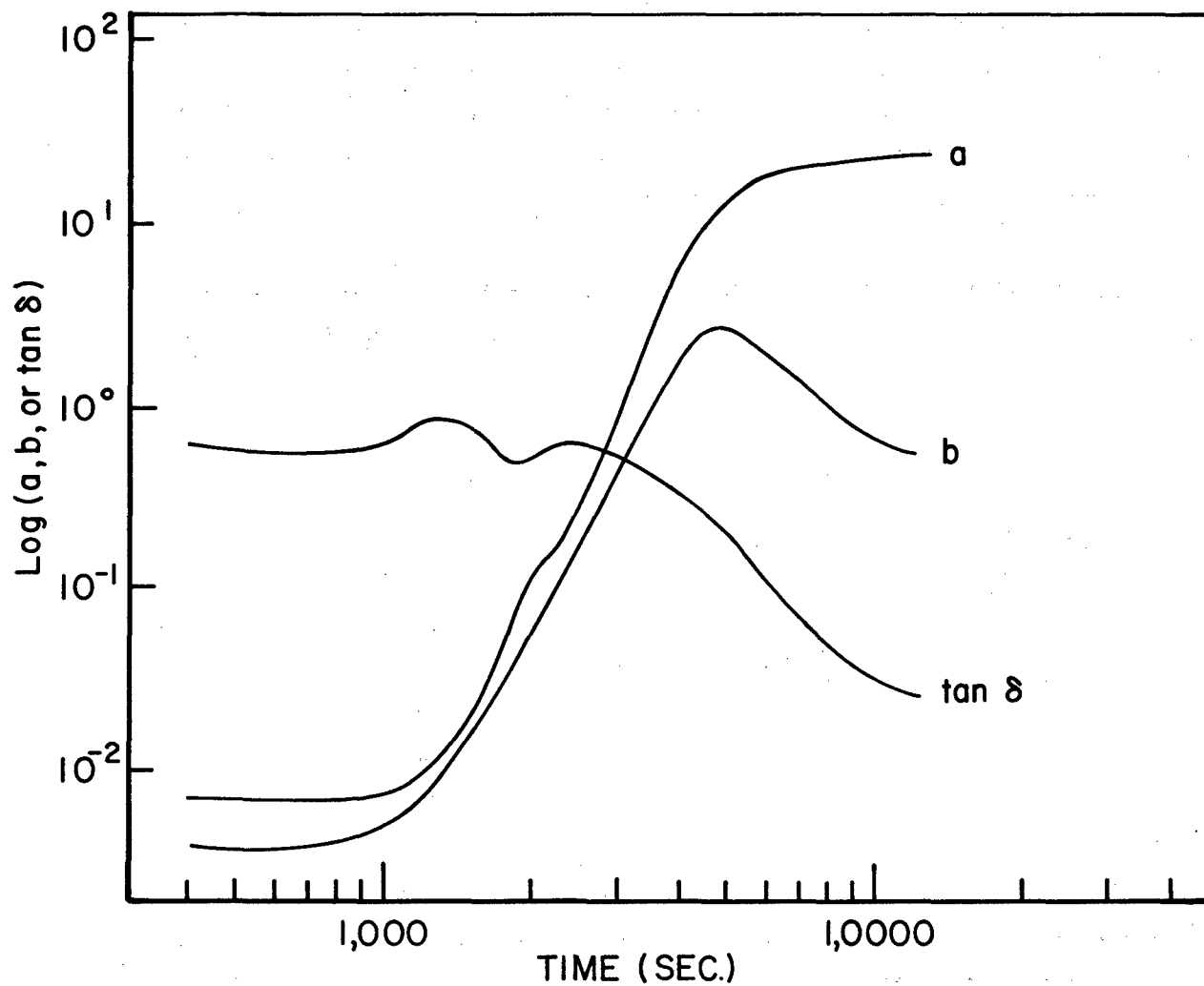


Figure 3b. Isothermal Cure Curve of an Epoxy Specimen. The in-phase component (a), out-of-phase component (b), and their ratio $\tan \delta$ are plotted (a) vs time, and (b) vs log time

reactive segments in the glassy state. Depending on the ability of the reaction to proceed in the glassy state, that point can be anywhere to the left of T_g in Figure 1. If that point is before the glassy modulus plateau is reached, like at point B (Figure 1), the leveling off of rigidity does indicate the termination of further cure. But if point A is reached, the rigidity levels off even if cure is still continuing. This may be the case if IMC curing occurs. If vitrification is taken to mean the transition of a rubbery state material into the glassy state, it should be the same as the glass transition. The authors propose that the later definition be adopted, making the vitrification time $t_{vit} = t_{Tg}$.

Different isothermal cure curves have been obtained at 135°, 155°, 175°, 195°, and 207°C. The results from these curves are listed in Table 1.

TABLE 1
RESULTS FROM ISOTHERMAL CURE CURVES

Cure Temp (°C)	Cure Time (hr)	t_{gel} (sec)	t_{δ} (sec)	t_{vit} (sec)
135	5	2300	5300	9000
155	3 1/4	1400	2500	4850
175	2 1/4	600	1600	3700
195	1	200	900	1900
207	1	---	560	1200

Because of the time needed to heat the sample chamber to the required temperature, the short time values in Table 1 are usually not reliable. The air temperature in the sample chamber is heated in steps of 10°C/5 sec. from 0°C. It takes usually another 20 to 40 sec. for the air temperature to become regulated at the desired temperature after that value is reached. The temperature of the test specimen itself of course will come to the desired temperature at a later time. The estimation of this time is about two to four minutes. The values obtained in this series of experiments are not the real isothermal cure times, but, rather, the time it takes to reach a certain state under a certain experimental procedure. For long time values, where the heat-up times are comparatively short and become insignificant, the results approach the real isothermal cure times.

Figure 4 is a plot of the TICA results of t_{gel} and t_{vit} in log time vs. temperature. The TBA results of Gillham's are also shown (Reference 7). Since the TBA experiments do not measure the out-of-phase component, only $\tan \delta$ maximum times for gel and vitrification are available. Agreement between the two sets of data is poor, but the general features are similar. The results indicate that the temperature region under study is in a region between T_{gg} and $T_g(\infty)$.

Another way to compare the results is to compare the time between gelation and vitrification. If the gelation occurs after the specimen has come to equilibrium with the cure temperature, the time between gelation and vitrification should agree between the two sets of measurements regardless of the heat up rate or the states of the starting materials. Figure 5 shows such time intervals for both sets of data. For the TICA data, both vitrification times have been used. Since TBA measured the $\tan \delta$, the circles from TICA data should be used for comparison. Again, the agreement between the two sets of data is poor. As a matter of fact, the time intervals calculated with the b maxima (the triangles) at low temperature agree better with the TBA data. For the two measurements at 175°C and 195°C, it could be argued that the gel times are too short; that when gelation occurs, the temperature of the test specimen was below the supposed cure temperature. This comparison supports the identification of the TICA b maximum with vitrification.

It should be noted that if the gel peak arises from the $T_{\ell,\ell}$ type of molecular transition as suggested earlier, then it is not the same as the conventional gel point in network theory, which implies a fixed chemical conversion state for any given system. Assuming that they are the same, then a plot of $\log(t_{gel})$ vs $1/T$ will be a straight line and the slope will yield the activation energy for the curing reaction. The plot is shown in Figure 6. The slope gives an activation energy of 15.7 kcal/mole as compared with the value of 18.0 kcal/mole obtained by Gillham with TBA measurements (Reference 7). Although the activation energy from TICA experiments seems smaller, the difference, which is actually within the experimental error limit, is probably due to the heat up time effect of the TICA experiment.

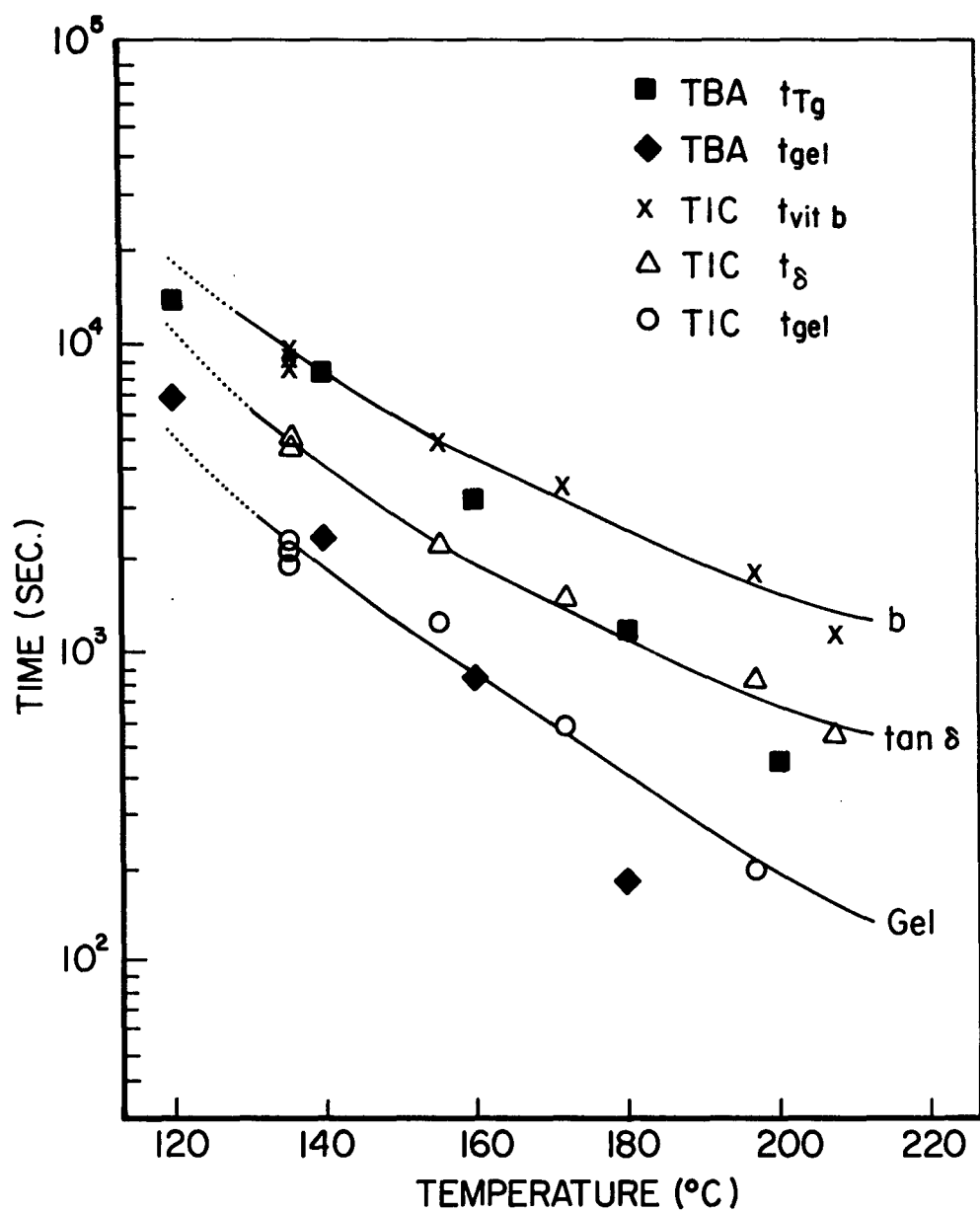


Figure 4. The Cure Phase Diagram of the Epoxy System Obtained Via TICA

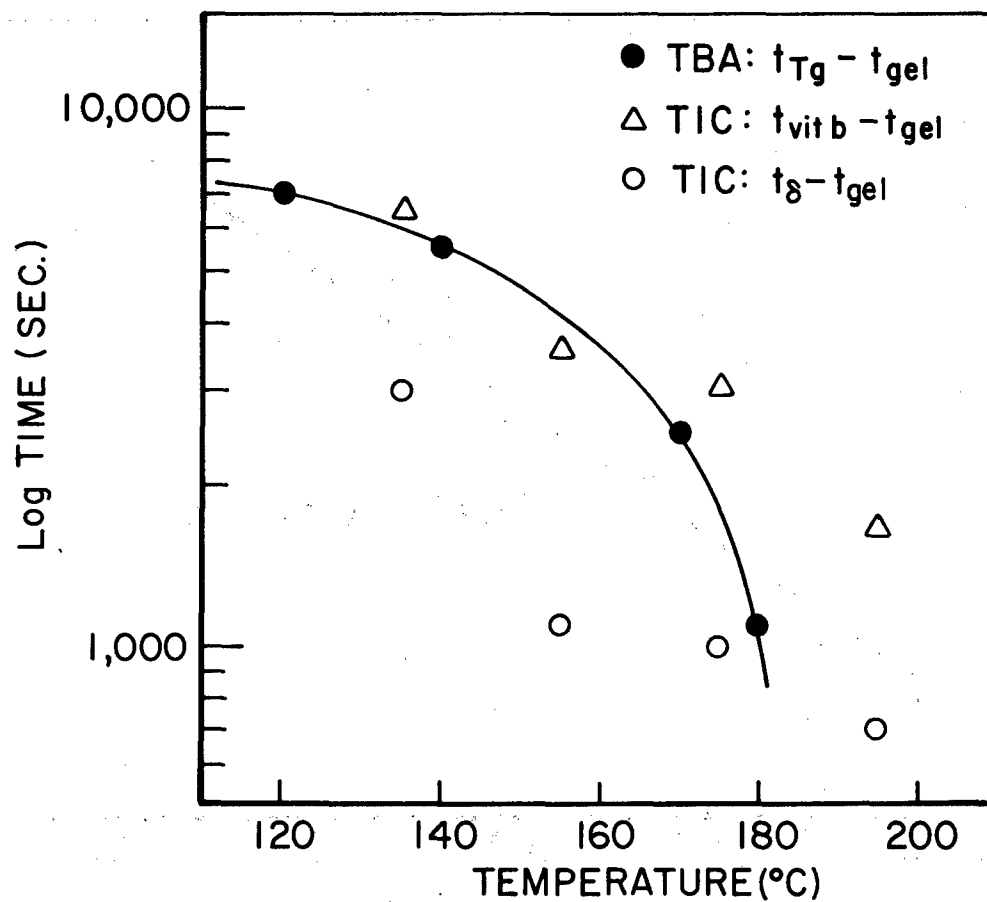


Figure 5. Plot of Time Intervals between Gel and Vittrification Times vs Temperature. Both TBA and TICA data are shown

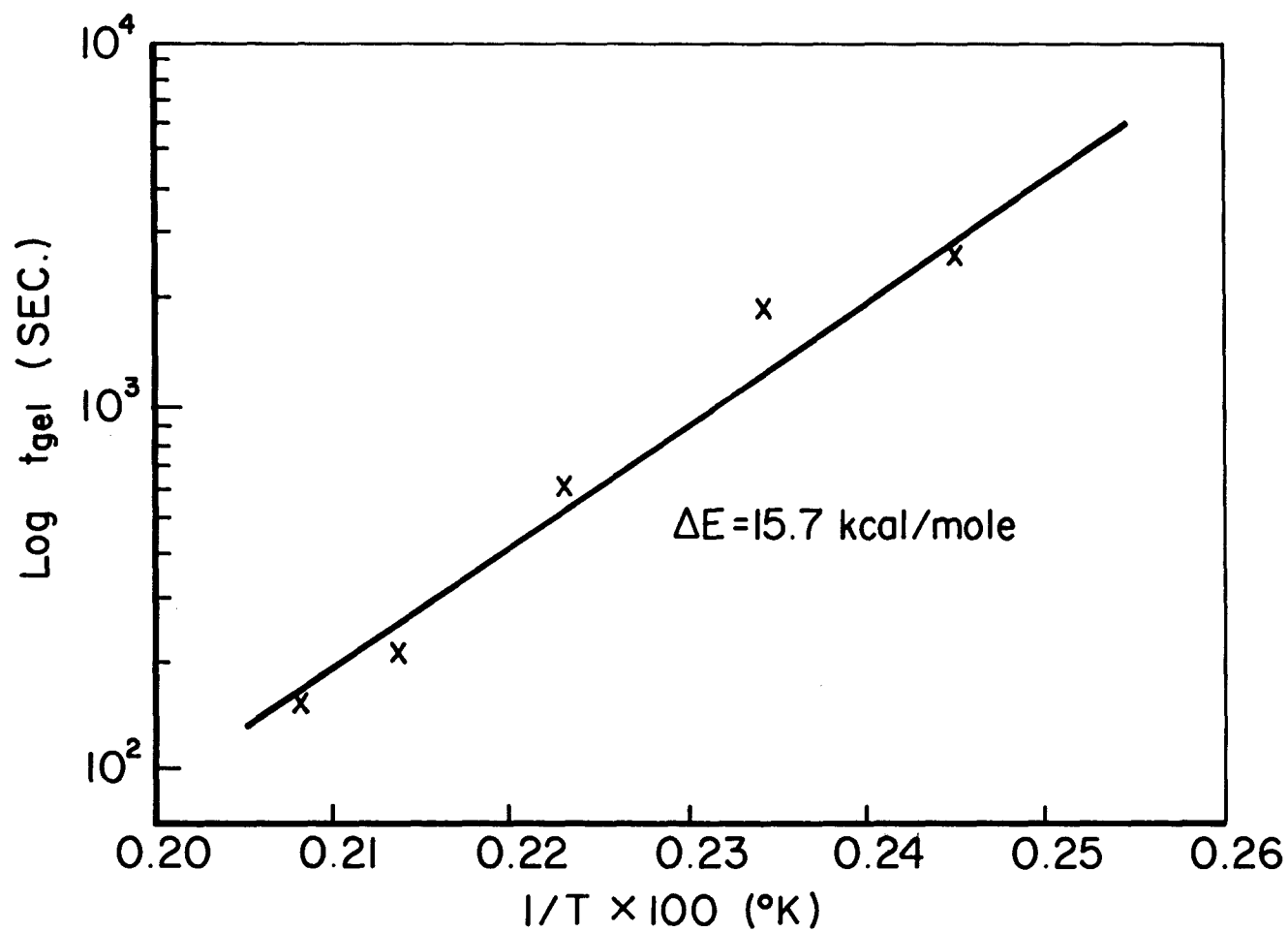
Figure 6. Plot of Log t_{Gel} vs $1/T$

Figure 7 is the plot of a temperature scan of a specimen which has been cured at 135°C for two hours. After two hours of curing, the $\tan \delta$ vitrification is already past, but the b value is still rising. That means the specimen has a $T_g < 135^\circ\text{C}$, if measured by $\tan \delta$, but $< 135^\circ\text{C}$ if measured by b maximum. The temperature scan is at the rate of $1^\circ\text{C}/\text{min}$. The a value starts to drop at about 100°C , and b starts to rise, indicating the T_g transition is near. The a value reaches a minimum at 155°C where both the b and $\tan \delta$ reach a maximum. A similar run was performed with TBA by Gillham, and the maximum of the $\tan \delta$ was denoted at the T_g for the specimen which had been treated with a given cure history. This is ignoring the further cure effect during the measurement. The result presented here clearly demonstrates that the effect is not always negligible. Furthermore, the value 155°C may not be any transition temperature at all in this particular instance. The argument is presented as follows.

Let's consider the experiment as a continuous measurement of the modulus as a function of time. Experimentally, the temperature is also changing. The response changes observed in the experiment can be expressed mathematically as:

$$\frac{d G(n, T)}{dt} = \left(\frac{dG}{dT} \right)_n \frac{dT}{dt} + \left(\frac{dG}{dn} \right)_T \frac{dn}{dt} \quad (1)$$

where G is whatever properties the experiment is monitoring, T is the temperature, n is the state of the tested sample, and t is time. For a temperature scan of most thermoplastic materials, the state of the sample is a constant when no chemical aging occurs, so the second term is zero. Then the observed mechanical spectrum will be just like Figure 1. This would not be the case for a thermoset resin because the second term is not always negligible.

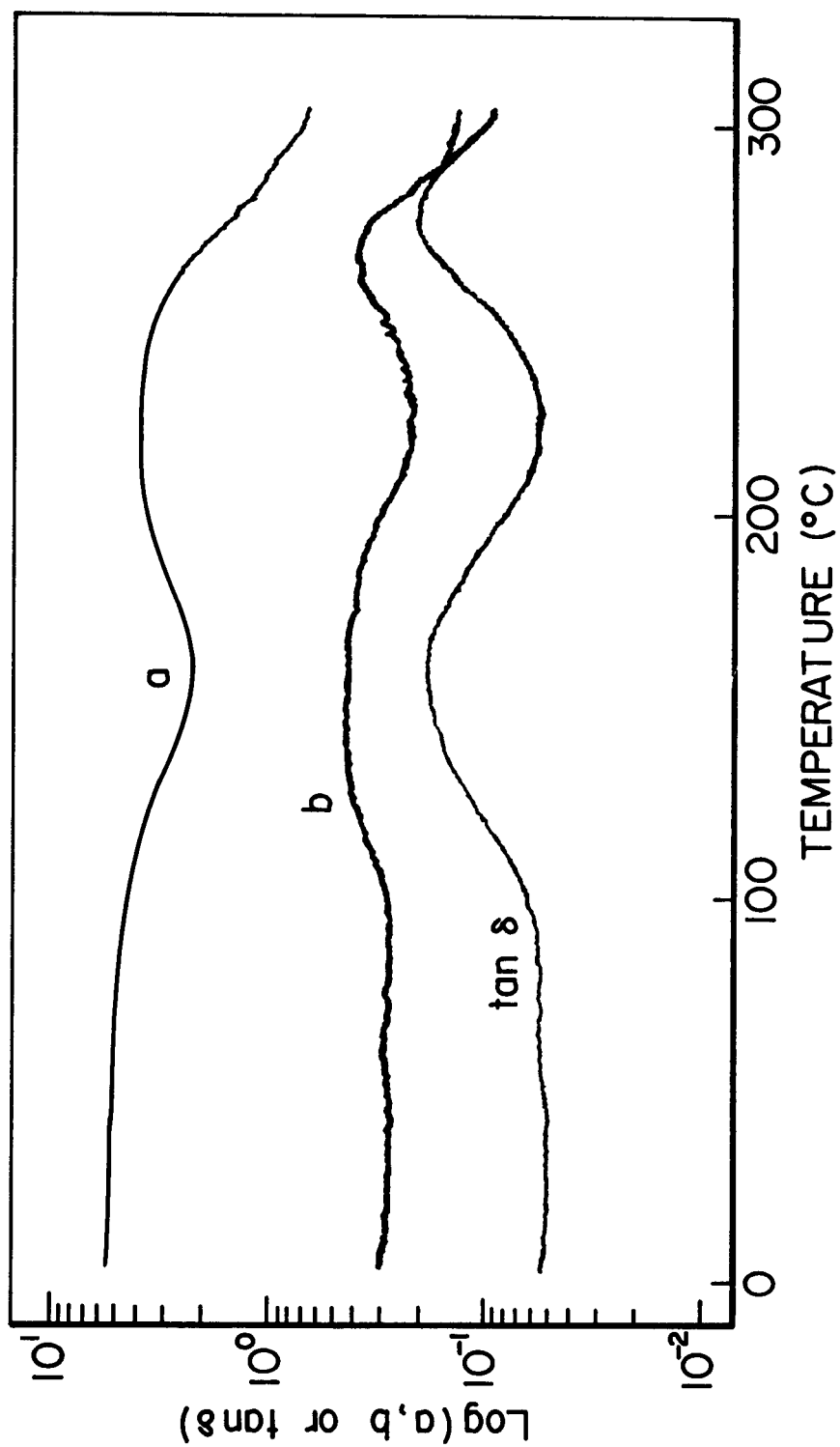


Figure 7. TICA Thermal Scan Plot of a Partially Cured Specimen (135°C - two hours). Scanning rate 1°C/min

The same diagram can be utilized if the assumption is made that curing will only increase the T_g value of the specimen but leave the shape of the response curve unchanged. The abscissa then has to be changed to a reduced variable $(T-T_g)$, and Equation 1 can be rewritten as:

$$\frac{d G(T-T_g)}{dt} = \frac{dG}{d(T-T_g)} \left[\frac{dT}{dt} - \frac{dT_g}{dt} \right] \quad (2)$$

A temperature scan will still yield a spectrum similar to Figure 1 if the term $\frac{dT_g}{dt} < \frac{dT}{dt}$ at all times. The abscissa, however, will become nonlinear with time because $d(T-T_g)/dt$ is no longer a constant.

At the beginning of a temperature scan, $d(T-T_g)/dt = dT/dt$ (the scanning rate), because the specimen is sufficiently below T_g so that no further cure is occurring. The experimental observation with time will be like following the arrow u in Figure 1. When $(T-T_g)$ approaches zero, further cure starts to occur. The function $d(T-T_g)/dt$ becomes less than dT/dt as shown at point B in Figure 8. If the kinetics of the specimen are fast enough, it is conceivable that $dT_g/dt > dT/dt$ at some point, as in point D. Then the slope $d(T-T_g)/dt$ will become negative. Instead of arrow u, the trajectory will become arrow d (Figure 1). A peak of $\tan \delta$ will have appeared when $dT/dt = dT_g/dt$, but the maximum is not an indication of any glass transition.

This is indeed the case at 155°C, as shown in Figure 7. The curve a indicates a minimum at this temperature. Using Equation 1 to describe the behavior of a, we can see $(da/dT)_n$ is always negative and $(da/dn)_T$ is always positive.* The presence of the minimum of a indicates the change of sign of the function $da(n,T)/dt$.

After 155°C, the cure kinetics are faster than the temperature increase of the experiment. The specimen is going back into the glassy state. Eventually, the available reactive groups are being used up,

*-Assuming that no effects like antiplasticization are present, and that increase in modulus with temperature due to entropy is negligible (which is true in the glassy state).

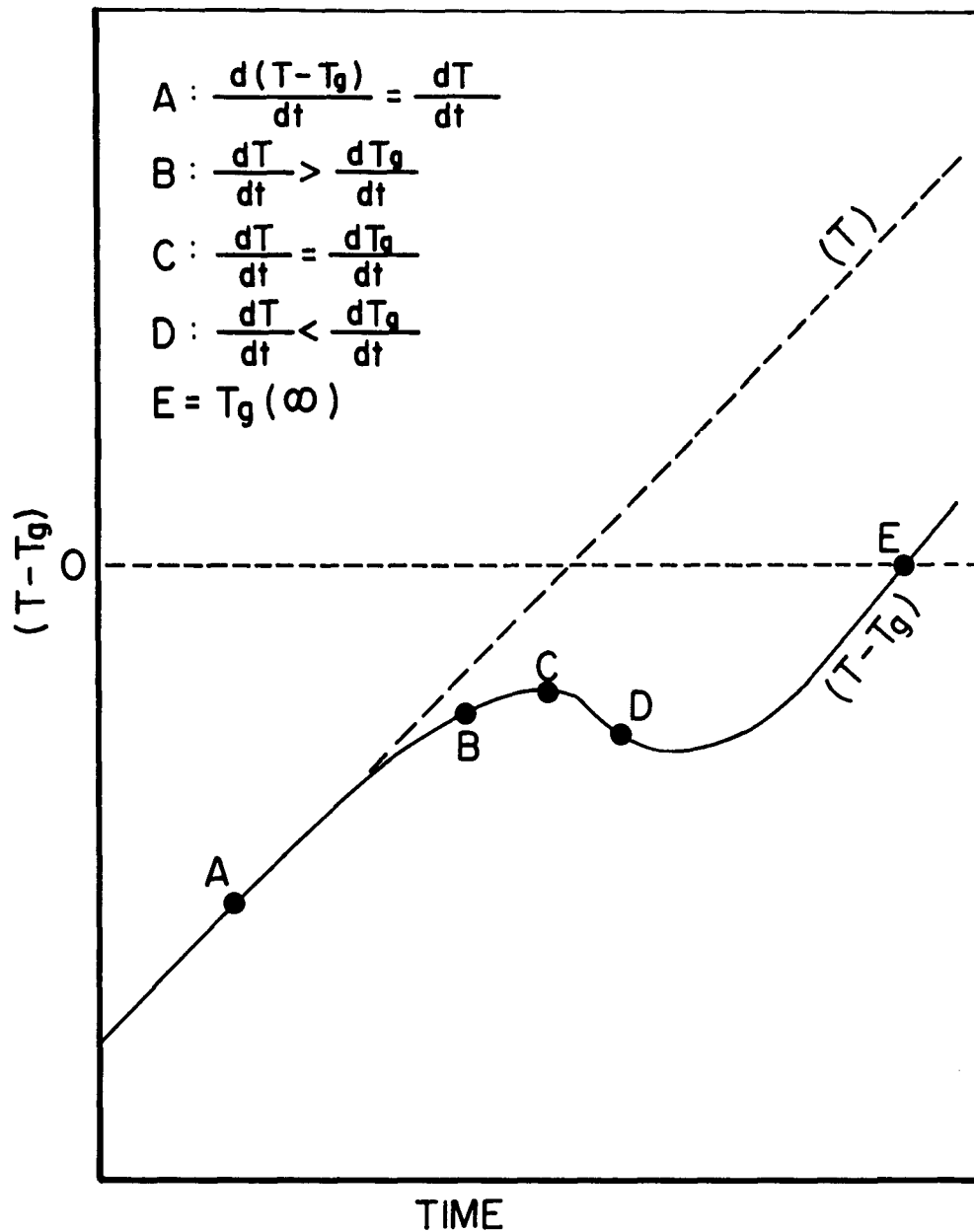


Figure 8. $(T - T_g)$ vs Time of a Partially Cured Specimen During a Thermal Scan Experiment

causing dT_g/dt to decrease again. The function $d(T-T_g)/dt$ increases again and finally at about 274°C , $(T-T_g) = 0$, point E in Figure 8 is reached, and the glass transition occurs. This glass transition should be close to the $T_g(\infty)$, the maximum glass transition temperature for the completely cured specimen. Another scan of the same specimen between 200°C to 300°C gives identical transition temperatures: b maximum at 253°C and $\tan \delta$ maximum at 265°C . A specimen post cured at 207°C and subsequently scanned up in temperature yields similar values: 252°C and 260°C respectively.

Each of the specimens cured isothermally were subsequently post cured at 207°C . The time needed to reach the b maximum at the post cure temperatures (t_{pc}) was recorded. The values are plotted in Figure 9. The value at 25°C is the time measured from virgin sample, which presumably has been curing at room temperature for an extended period of time. The value at 207°C is taken to be zero, and no value was obtained from the 195°C cure. The specimens cured at a particular temperature would have a T_g higher than the cure temperature. No significance can be attached to the seemingly straight line relationship between the points. But it should be noted that the increase in cure temperature does shorten the required cure time to reach the 207°C b maximum. The plot suggests an alternate method to measure the T_g of a specimen. If the low temperature cures of a similar series of experiments were stopped at the times of b maxima, the cure times measured at the post cure temperature, or the reference temperature (in the case, 207°C), will be directly related to known T_g 's, the cure temperature values. With this relationship known, the measurement of the cure time of an unknown specimen at the reference temperature will yield its T_g . All t_{pc} values are smaller than $(t_{vit} - t_\delta)$ values at 207°C . This fact also supports the notion that the $\tan \delta$ maximum is probably due to resin-cloth interaction, not vitrification.

The full temperature scan of a specimen cured at 175°C , post cured at 195°C and 207°C for one hour each is shown in Figure 10. Secondary transitions below T_g are observed at -42°C . A rectangular bar sample cured with the recommended cure history (8) shows, at 1.6 Hz , a $T_g(G'')$ at 234°C , $T_g(\tan \delta)$ at 246°C , a weak β transition at 74°C , and a stronger γ

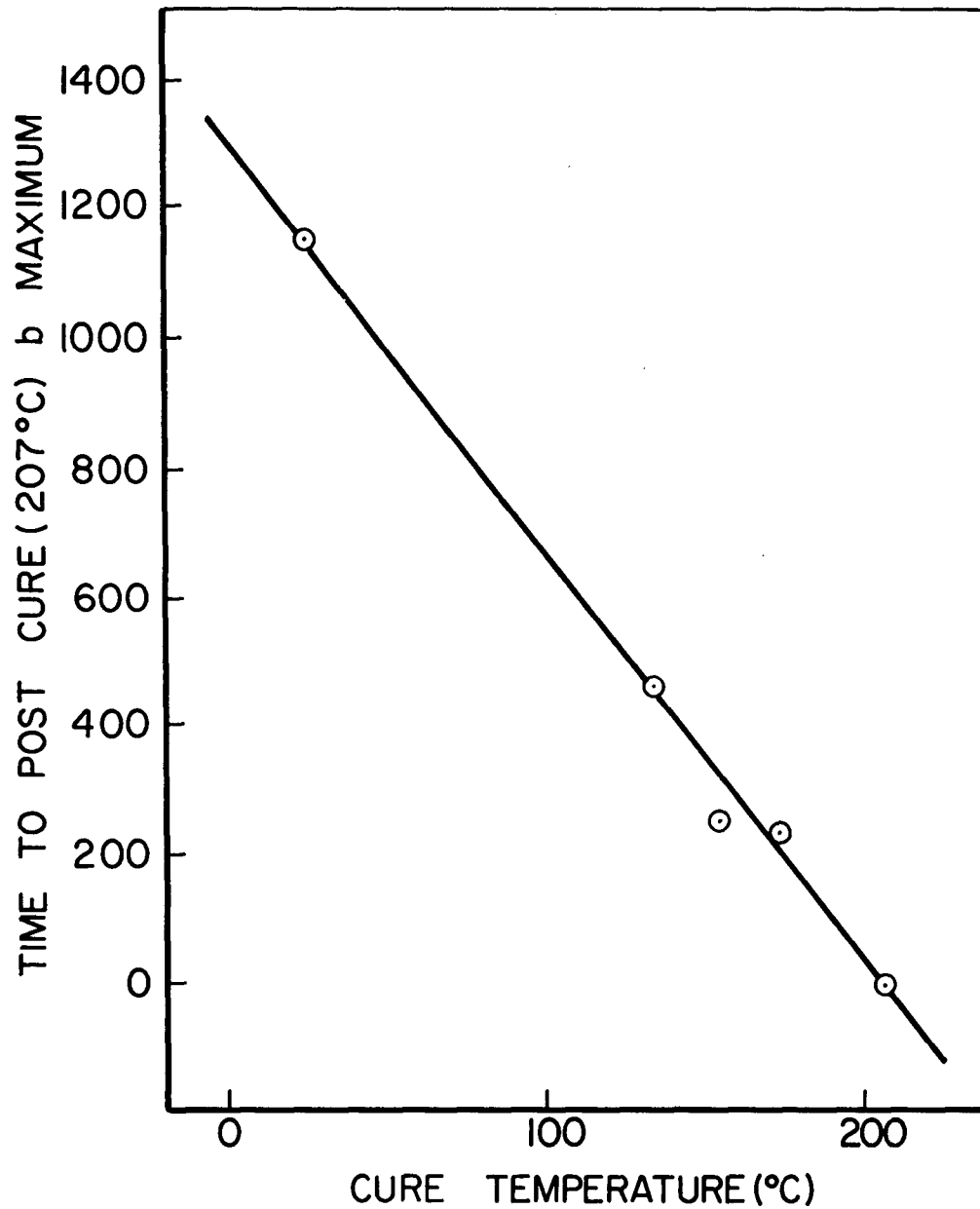


Figure 9. Post-Cure Times vs Cure Temperatures

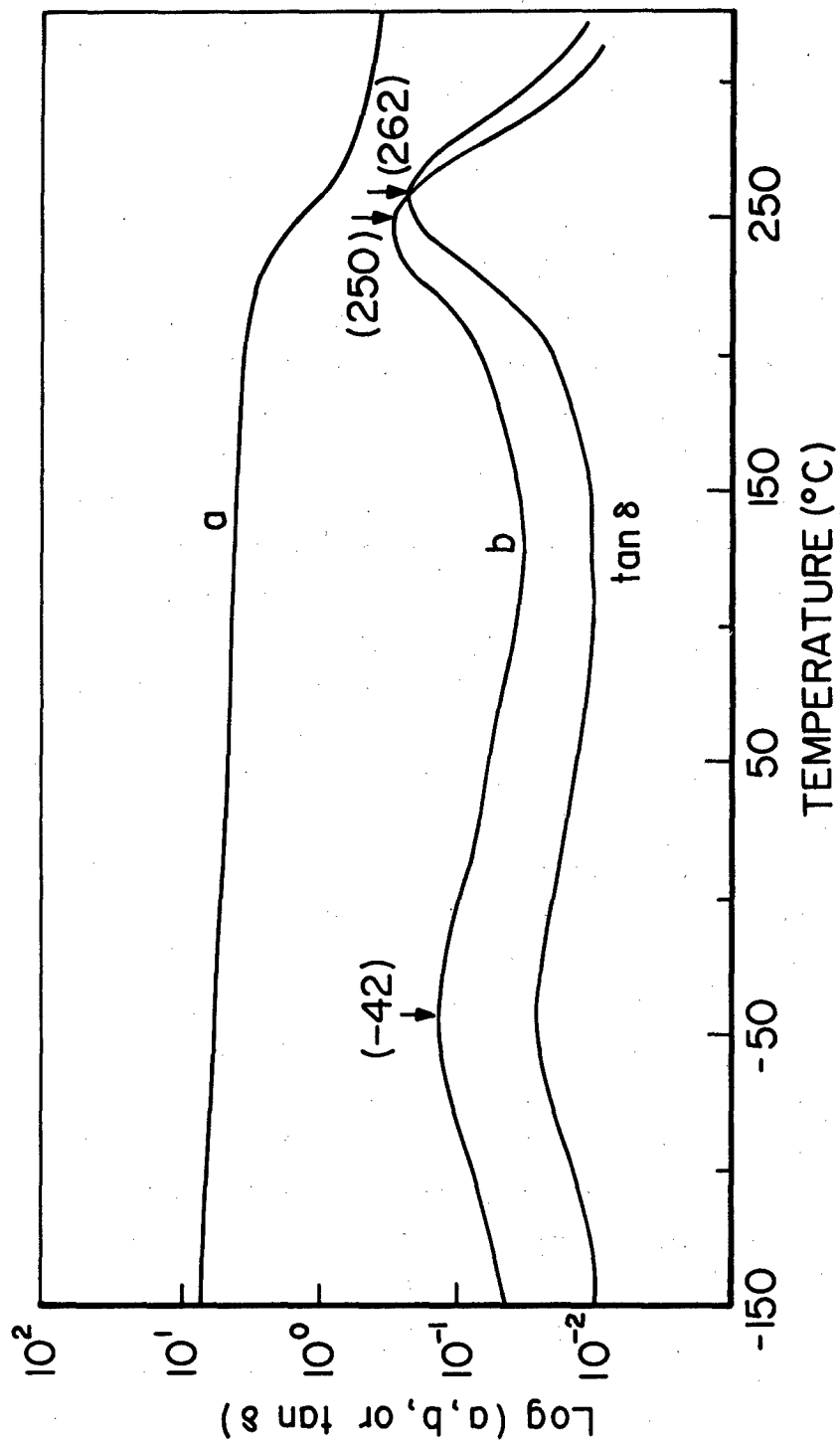


Figure 10. TICA Thermal Scan of a Cured Epoxy Specimen

transition at -60°C . The TICA sample shows the stronger γ transition, but the weak β transition is indeterminable. This presumably is due to the lower sensitivity of the TICA experiment in comparison with the torsion bar experiment. The T_g transition at 252°C and 260°C (b and $\tan \delta$ values respectively) is very close to the $T_g(\infty)$ values.

The temperature values of the γ transition after different cure histories are measured. They are listed in Table 2, in increasing temperatures. The states of cure are estimated based on the cure history and are numbered sequentially; a higher number implies a more advanced cure state. The data seems to show a correlation of increasing transition temperatures with advancing cure states. This also suggests another method of T_g determination. If different specimens with known T_g can be made by stopping at the maxima of the b values in isothermal cures, and their corresponding secondary transition temperatures are measured, the correlation between the transition temperature and T_g can be established. The measurement of the secondary transition temperature of an unknown specimen can give T_g information without further advancing the cure state.

A series of specimens are cured at 135°C for five hours. Then isothermal post cures are carried out at 155° , 175° , 195° , and 207°C . The time required for the post cure experiments to reach the b maximum are noted. Ignoring the heat-up effect, this time (t_{pc}) represents the cure time required at the post cure temperature, for a cure state (n_1), which is reached after five hours at 135°C , to advance to a cure state with a T_g equal to the post cure temperature (T_2). The time difference between t_{pc} and t_{vit} is then the cure time to reach state n_1 at post cure temperature T_2 . These values are plotted in Figure 11 as log time versus temperature. The value at 155°C is estimated since no b maximum corresponding to the vitrification is observed. Comparing with the cure behavior of the 155°C isothermal cure, it is estimated that the n_1 state is reached about 600 sec. past the 155°C isothermal cure - b maximum state. The curve joining these points represents an isocure state curve. The vitrification curve is also shown. The intersection point at 158°C then represents the intrinsic cured T_g value for a specimen that has been cured five hours at 135°C . This method of isocure state curve construction will be called two step cure technique.

TABLE 2

CURE HISTORY AND SECONDARY TRANSITION TEMPERATURE

<u>HISTORY</u>	<u>RANKING</u>	<u>TRANSITION TEMPERATURE</u>
155°C - 3 1/4 hr	④	-77°C
135°C - 4 1/2 hr	①	-70°C
135°C - 5 hr	② ③	-62°C
173°C - 2 1/4 hr	⑤	-60°C
193°C - 1 hr	⑩	-57°C
135°C - 5 hr	② ③	-56°C
135°C - 5 hr; 175°C - 1 3/8 hr	⑦ ⑧	-50°C
135°C - 5 hr; 175°C - 1 3/8 hr	⑦ ⑧	-45°C
135°C - 5 hr; 175°C - 2/3 hr	⑥	-42°C
207°C - 1 hr	⑪	-42°C
135°C - 5 hr; 175°C - 1 2/3 hr; 175°C - 1 1/4 hr	⑨	-40°C
135°C - 5 hr; 175°C - 13/8 hr; 207°C - 1/2 hr	⑫	-37°C

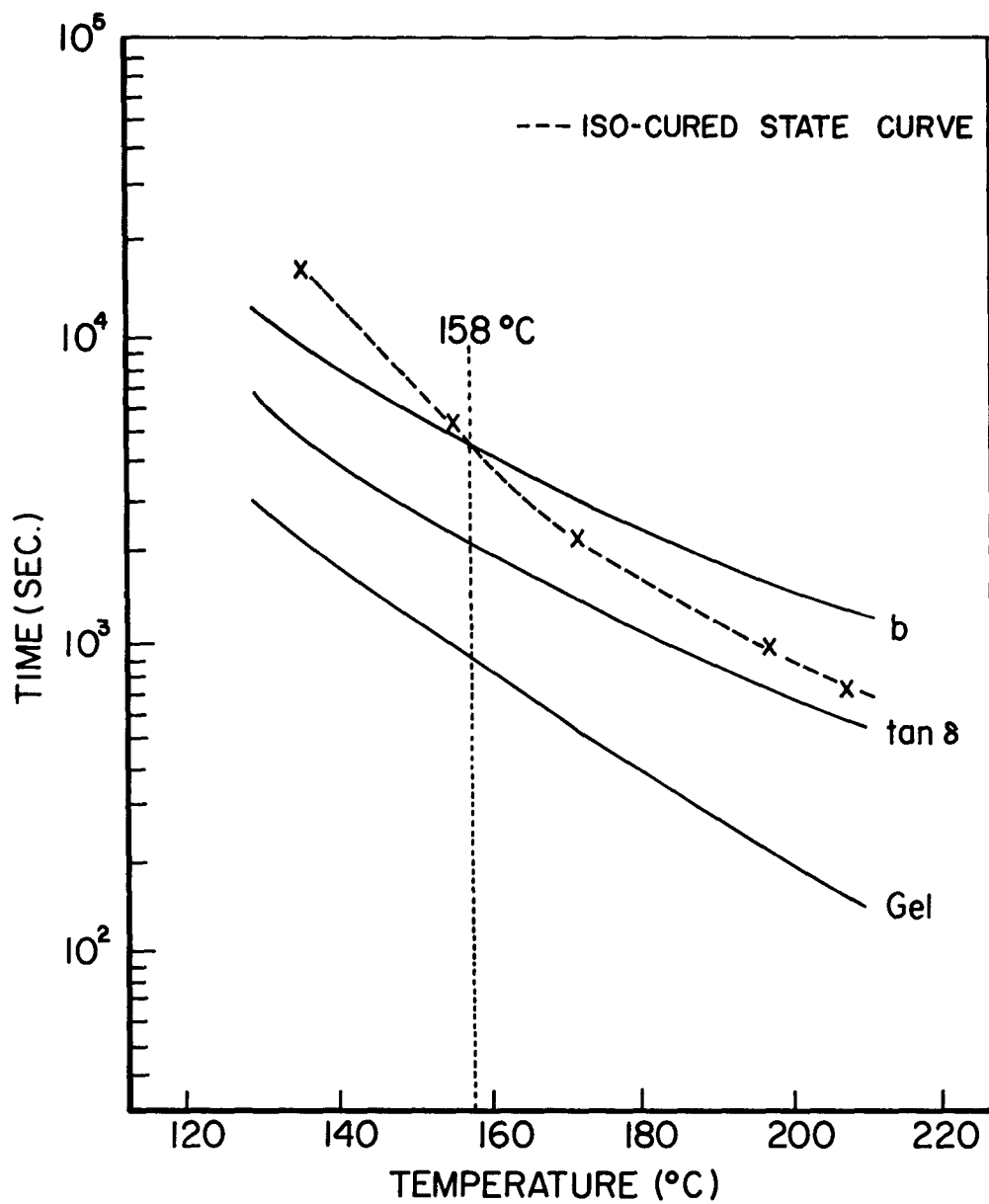


Figure 11. Isocure State Curve of an Incompletely Cured (135°C, five hour) Epoxy Specimen

SECTION V

CONCLUSION

This work reports the development of the torsional impregnated cloth analysis (TICA) technique with the rheometrics spectrometer. Its usage as a mean to follow the mechanical properties changes during cure is demonstrated. This technique has less sensitivity than the conventional torsion bar measurements, but it allows the continuous measurement on a single specimen over its various states of matter. The technique tends to be less sensitive than TBA, when the resin is in the liquid state, but its advantage over TBA lies in the constant frequency during the whole course of the experiment. This feature makes TICA a desirable technique to measure transition temperatures which are usually frequency dependent. This technique also allows the in-phase and out-of-phase components of the dynamic response to be measured simultaneously.

Hercules 3501A, 12KV10 epoxy has been used as the material for the feasibility test. A cure phase diagram has been constructed. It has the same general feature as the one produced by Gillham using TBA with the same epoxy system. Both sets of data agree that between 100°C to 210°C, the system is above T_{gg} but below $T_{g(\infty)}$.

The series of experiments has also demonstrated the possibility of the conventional thermal scan technique giving erroneous T_g results when used with an incompletely cured thermosetting system. The result also points out that some loss maxima observed in such cases do not correspond to the glass transition, but rather to the point where two separate terms of a time derivative function being equal. This equation will be useful in the interpretation of results from incompletely cured systems.

The successful construction of the phase diagram with TICA measurements make the first step towards interpolating the intrinsic cured T_g of a partially cured specimen as proposed originally. However, isocure state curves have to be constructed from other experimental results. This work has shown three alternate ways to interpolate the same information

by using only the TICA technique. They are: (1) estimation of isocure state curve by a two-step cure technique, (2) correlation of secondary transition temperatures with T_g , and (3) correlation of post-cure times at a reference temperature with T_g .

The completion of this work will allow the commencement of the TICA study of the IMC program candidate BA/IMC (BA-DABA-BA).

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