

# Dynamic Mechanical Properties of an Acetylene-Terminated Quinoxaline System under Air/Nitrogen Cure

C. Y-C. LEE, *Materials Laboratory (AFWAL/MLBP), Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio 45433*

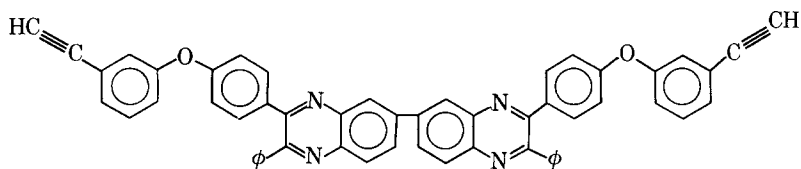
## Synopsis

Torsional impregnated cloth analysis (TICA) temperature scan results of an acetylene-terminated quinoxaline system indicated the presence of two different reactions with different activation energies. Two additional effects are delineated when cure is carried out in the presence of air. Curing at low temperature in the presence of air will lower the final  $T_g$ , but at high temperature it will have the opposing effect. The two reactions that can occur under nitrogen are affected differently by air curing. It appears that one is prohibited by the lower temperature curing in air while the other is not.

## INTRODUCTION

Acetylene-terminated (AT) resin can cure without evolving volatile products, and is being studied as a new technology to form high performance structural materials.<sup>1</sup> Air curing effects on the physical properties of some AT systems are recognized<sup>2</sup> based on other works, yet no systematic study of this effect has been undertaken.

A series of torsional impregnated cloth analysis (TICA)<sup>3</sup> experiments was initiated using a quinoxaline resin (3,3'-bis(4-[3-ethynylphenoxy]phenyl)-2,2'-diphenyl-6,6'-biquinoxaline)<sup>4</sup> to study the air/nitrogen curing effect:



The experimental results are very interesting and seemingly complex. A four-reactions interpretation which can satisfactorily account for all the features observed is presented. Recognizing this interpretation may not be unique in being able to explain the observations, care is taken to separate the experimental results from the interpretation as much as possible so other workers who will attempt to present an alternate interpretation can go through the data with ease.

## EXPERIMENTAL

The TICA sample preparation procedure has been described elsewhere.<sup>3</sup> The measurements were made with the Rheometrics Mechanical Spectrometer (RMS-7200). The frequency of measurement was kept constant for all experiments (1.6 Hz, 10 rad/s).

The resin to be studied was dissolved with an appropriate solvent. A fiber glass cloth about 10 cm wide was wetted with the solution. After it had been hung in an exhaust hood overnight, the cloth was put under vacuum for solvent extraction at room temperature for a week before use. The cloth was cut into rectangular patches of 10 cm  $\times$  7.5 cm, and they were folded into strips 10 cm long and 1.25 cm wide, with the cut edges folded inside the strips. Three strips were stacked together to make one TICA specimen.

The resulting specimens have dimensions at both ends similar to that of torsion bar specimens of the RMS, and they are mounted on the sample holding chucks of the RMS the same way as torsion bars. The sample is subjected to forced torsion deformation. The stress generated is converted to a voltage signal, which is in turn analyzed by a frequency analyzer to give the magnitudes of both the in-phase ( $a$ ) and out-of-phase ( $b$ ) components. The loss  $\tan \delta$  is obtained by taking the ratio of the two values ( $b/a$ ).

Normally, the temperature programmer on the RMS unit presently installed in this laboratory is coupled with the Rheophaser which controls the mechanical measurements. An electronic clocking device was built to decouple the two units. The temperature programmer was run in a local mode with temperature increase in steps of 2°C/min. The clocking device then synchronized the Rheophaser to take measurement every minute. The clocking device was programmed as such that the measurement was taken just before the temperature step increase. This way the data does not contain the noises caused by the temperature step increase.

All specimens were cured exclusively with the RMS environmental chamber. Air or nitrogen was used as the convecting medium. The specimen was placed in the chamber at room temperature, and the same temperature increase procedure used in isothermal curing measurements<sup>5</sup> was employed to bring the chamber up to the curing temperature. An earlier attempt to cure specimens in a Vac-line oven gave unacceptable data scattering and poor correlation between specimens. This was because of the long time required for the Vac-line to equilibrate at the controlling temperature after each disturbance, like opening the oven door.

All scanning experiments were repeated with a scan-down in temperature at the same scanning rate after the upper temperature limit was reached.

## RESULTS

### Effect of Scanning under Air/Nitrogen Environment

An uncured TICA specimen of the resin was scanned in temperature under nitrogen atmosphere at a rate of 2°C/min with the procedure described in the previous section. The results is shown in Figure 1.

The scan-up result can be explained by a four-stage scheme forwarded by Lee and Goldfarb.<sup>6</sup> The scheme is designed for experiments where  $T_g$  is not a con-

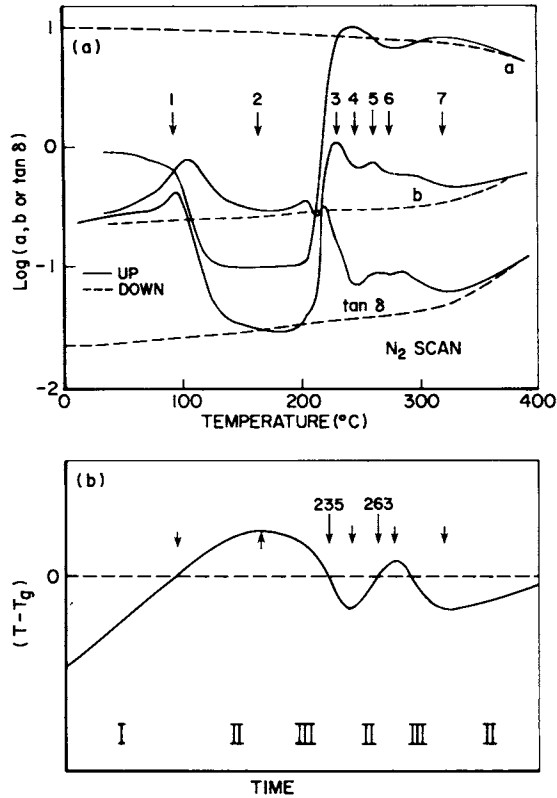


Fig. 1. Nitrogen scan results of an uncured specimen. (—) Scan-up; (---) scan-down.

stant during the measurements. The scanning rate of such an experiment ( $dT/dt$ ) is assumed to be a constant. Depending on the rate of change of the  $T_g$  value ( $dT_g/dt$ ), the experiment can be at either one of the following four stages:

- (I)  $dT_g/dt = 0$ ,
  - (II)  $0 < dT_g/dt < dT/dt$ ,
  - (III)  $0 < dT/dt < dT_g/dt$
- or (IV)  $dT_g/dt < 0$ .

Briefly, Stage I is when the glass transition temperature is a constant. Stages II and III are when  $T_g$  is increasing, but they are further distinguished by comparing with the constant scanning rate. Stage IV is when  $T_g$  is actually decreasing in value. A rate conversion point is defined as the point when the experiment is transiting from Stage II to Stage III. At such a point, the scanning rate  $dT/dt$  is the same as the  $T_g$  increasing rate  $dT_g/dt$ ; and the time derivative of the parameter  $(T - T_g)$  is zero.

In Stage II,  $(T - T_g)$  is increasing, but in Stage III, the parameter is decreasing. The scheme is modified here to include a Stage R which is a region where the specimen remains at the rate conversion point. In the R Stage, the  $(T - T_g)$  parameter is a constant, and the dynamic responses do not appear to change with temperature.

Thus, for a given scanning rate, the curing rate is increasing in the order of Stage II, Stage R, and Stage III. An experiment can be classified according to

the sequence of the stages appearing during the scan. Curing rates in different experiments can be compared by noting the stages involved.

The scan-up result in Figure 1 can be classified as a I-II-III-II-III-II experiment. The corresponding  $(T - T_g)$  curve is shown in Figure 1(b). At the beginning of the experiment,  $T_g$  was not changing, so the experiment was in Stage I, and the  $(T - T_g)$  parameter was increasing at the experimental scanning rate. At point 1, the  $b$ -component was showing a peak maximum corresponding to the uncured  $T_g$  of the system. Between point 1 and 2, the system was in the liquid state. Somewhere in that region, additional cure started to occur and the experiment proceeded into Stage II. At about 200°C, the  $a$ -component rose sharply, accompanied by the corresponding  $b$  and  $\tan \delta$  peaks. The system was vitrifying, and the  $(T - T_g)$  parameter was decreasing to a negative value. The experiment was obviously in Stage III, and had passed the first rate conversion point. The second rate conversion point was encountered at point 4. The experiment was back in Stage II, and the system was again above  $T_g$  after point 5. A third rate conversion point was encountered at point 6, with the system back in Stage III again. The fourth rate conversion point was at point 7. After that, the system was in Stage II, and eventually Stage I. Thus, the experiment can be described as a I-II-III-II-III-II type.<sup>6</sup>

The scan-down result indicated that the  $a$ -component had decreased with the additional cure, and the  $T_g$  of the system had been advanced to above 390°C. It is possible that the decrease in the  $a$ -component is due to thermal degradation of the network. TGA results did not indicate weight loss until over 550°C and the  $T_g$  is increasing instead of decreasing. On scan down, all the  $b$  peaks and  $\tan \delta$  peaks have vanished, supporting the interpretation that they are due to the additional cure effect.

It is not uncommon for an uncured, or a partially cured specimen to give a I-II-III-II-I type result which involves only two rate conversion points. The first would of course be due to additional cure, and the second be the result of depletion of reactive sites. The result described above is the first known example of a I-II-III-II-III-II type experiment. This feature is not exclusive to this quinoxaline resin; similar results have been observed with other acetylene terminated resins. So it seems that the four-rate conversion feature is common among acetylene-terminated systems.

Scanning the specimen in air produced a different result (Fig. 2). The experiment should be classified as a I-II-III-II-R-II-III experiment. The corresponding  $(T - T_g)$  plot is shown in Figure 2(b). The system went through the early I-II-III stages like the nitrogen scan experiment, with the vitrification peak occurring at about the same temperature. After that, the system never went back above  $T_g$ . The second  $a$ -component peak in the nitrogen scan experiment was reduced to a plateau, and the valley between the  $a$  peaks had disappeared. This changes the succeeding II-III-II stages of the nitrogen scan experiment to become II-R-II stages. The  $b$  and  $\tan \delta$  features observed in the nitrogen scan result were absent, and the presence of the additional cure was only indicated by the plateau of the  $a$ -component.

An additional Stage III was observed in the air scan result, and the corresponding rate conversion point (the fifth one) was at 355°C. The decrease of the  $b$ -component above that temperature was the result of the decrease of the parameter  $(T - T_g)$ . This is verified by the scan-down result which indicated that the  $T_g$  had been advanced to well above 390°C.

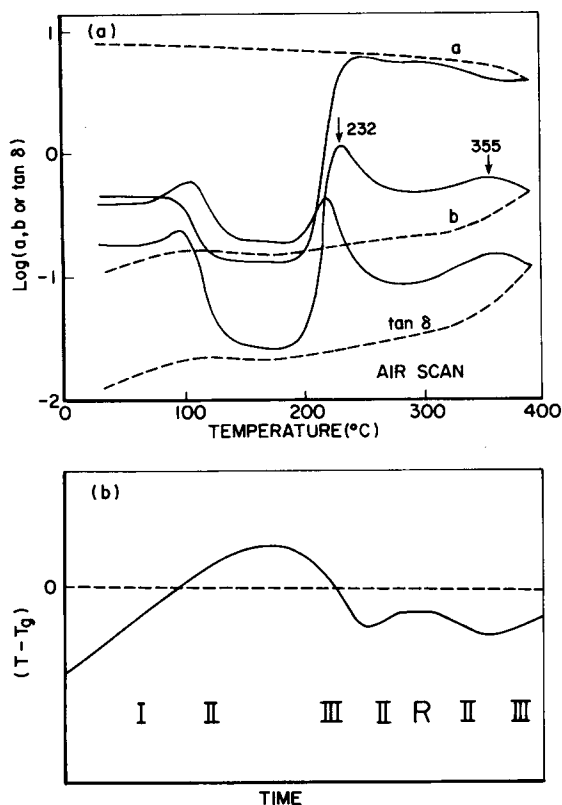


Fig. 2. Air scan result of an uncured specimen. (—) Scan-up; (---) scan-down.

### Effect of Curing Under Air/Nitrogen Environment

A TICA specimen of the quinoxaline resin was cured under nitrogen at  $160^{\circ}\text{C}$  for 24 h. The thermal scan of the specimen under nitrogen is shown in Figure 3. Comparing with the nitrogen scan of the uncured specimen (Fig. 1), it is obvious that the liquid stage was gone. The specimen was glassy during the whole experiment, with a limited degree of softening at about  $285^{\circ}\text{C}$ . The curing at low temperature had changed the experiment to a I-II-R-II-III-II experiment. The third rate conversion point was obviously at  $285^{\circ}\text{C}$  and the fourth at  $350^{\circ}\text{C}$ .

Again, the result is not the type of I-II-III-II-I experiment one observes with epoxy samples. The hum of the *b*-component at  $213^{\circ}\text{C}$  means additional cure was occurring at that temperature. The curing rate was as fast as the scanning rate in the next  $30^{\circ}$  region so that the parameter  $(T - T_g)$  was almost a constant or in the R stage, with little changes in the *a* and *b* components. Then the specimen went above  $T_g$  at  $260^{\circ}\text{C}$ , indicating that the curing rate had slowed to a value smaller than the constant scanning rate. The experiment momentarily slipped back into Stage II, and then proceeded into Stage III after  $285^{\circ}\text{C}$ . It is difficult to justify that the reaction that slowed down at  $260^{\circ}\text{C}$  is the same reaction that increases the  $T_g$  so rapidly around  $300^{\circ}\text{C}$ .

The *a*-component decreased after  $350^{\circ}\text{C}$  during the scan-up. The *b*-component changed relatively little in that region. The scan-down result suggested

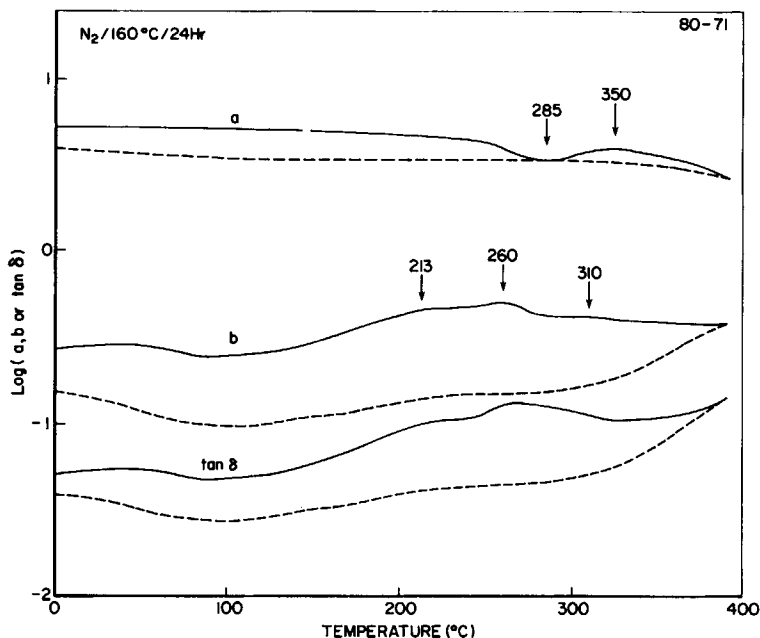


Fig. 3. Scan of a Specimen that has been cured at 160°C for 24 h under nitrogen. (—) Scan-up; (---) scan-down.

that the  $T_g$  was advancing during the scan-up, and, as a result, the  $a$ -component had also decreased. So the negative slope in the  $a$ -component above 350°C in the scan-up result can either be interpreted as a Stage II effect, where  $(T - T_g)$  was a decreasing function, or as a Stage III effect, where the additional cure caused the  $a$ -component to decrease.

The scan-down result showed that the  $T_g$  of the system after the scan was above 390°C; and all the features exhibited by the  $a$ - and  $b$ -components in the scan-up were caused by additional cure.

Another specimen was cured at 160°C for 24 h in an air environment. The subsequent thermal scan result under nitrogen is shown in Figure 4. The result is different from that of Figure 3. The scan-up curves give the appearance of a three-phase system: with three distinct regions of  $a$ -component decrease, each accompanied by a corresponding  $b$  peaks. However, the result should actually be classified as a I-II-R-II-R-II-I experiment. Additional curing of a partially cured specimen giving an appearance similar to a two-phase system had been observed before.<sup>6</sup> In this case, the process was repeated twice due to two different reactions.

The first  $b$  peak maximum was at 213°C, the same temperature as the first  $b$  shoulder in the nitrogen cure result. The peak in the air cure was much more intense, and the drop in the  $a$ -component in that region was much more significant. The peaks in both the air cure and the nitrogen cure results signified an abrupt change in the curing rate, and both were occurring at the region where  $(T - T_g)$  was negative. The air cure specimen, however, was having the event occurred at a large  $(T - T_g)$  value or closer to the glass transition temperature. This could either be interpreted as the additional curing rate in the air cure specimen was slower than that of the nitrogen cure, thus the  $(T - T_g)$  parameter was in-

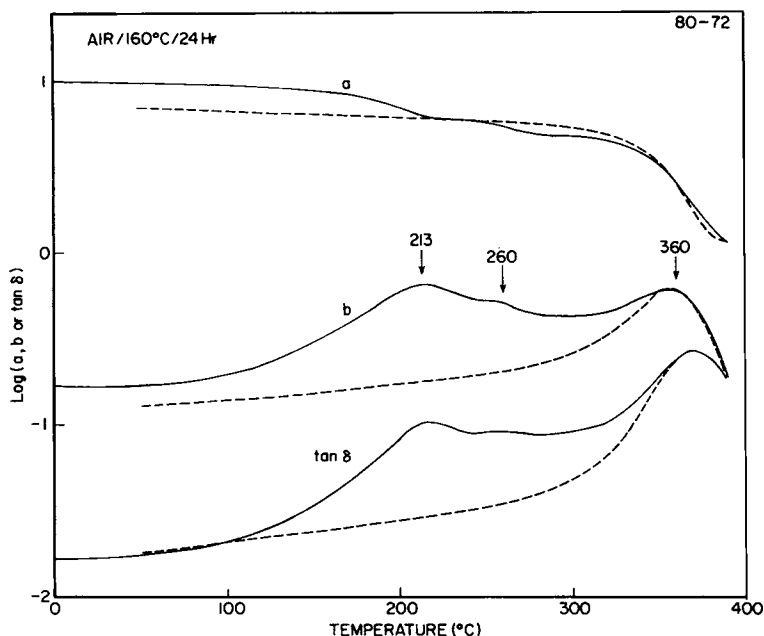


Fig. 4. Scan of a specimen that has been cured at 160°C for 24 h under air. (—) Scan-up; (---) scan-down.

creasing with a steeper slope, or as the air-cure specimen had a lower  $T_g$  to begin with.

A  $b$  shoulder was again observed at 260°C, which could be interpreted as an indication of the limitation of the first reaction, like depletion of reactive groups. After additional cure at about 300°C, the  $(T - T_g)$  parameter increased to a positive value (above  $T_g$ ) at 360°C. The second reaction was less intense than the corresponding nitrogen cured result as indicated by the Stage R effect rather than the Stage III effect in that region.

The scan down result retraced the scan-up curves in the region above 350°C. This means in that region the system was back in Stage I during the scan up. The completely cured  $T_g$  of this particular specimen was 360°C.

Two specimens had also been cured at 200°C for 1 h, with one being under nitrogen and the other in air. The subsequent scans of these specimens under nitrogen are shown in Figures 5 and 6. The features are very similar to those that had been cured at 160°C for 24 h (Figs. 3 and 4). Again, peak maxima of the  $b$ -component at about 210°C were observed, followed by another at about 260°C. The final  $T_g$  of the nitrogen cure specimen was above 390°C, but that of air cure was at 375°C.

### Isothermal Cure Time to $b$ -Maximum

TICA specimens were cured isothermally at different temperatures and their dynamic mechanical properties were continuously monitored. The time to  $b$ -maximum can be noted as an indication of the isothermal curing rate. The procedure used was already outlined elsewhere.<sup>3</sup> In the range of 200–350°C, the reaction rate is very fast, so the heat-up times are not negligible. However,

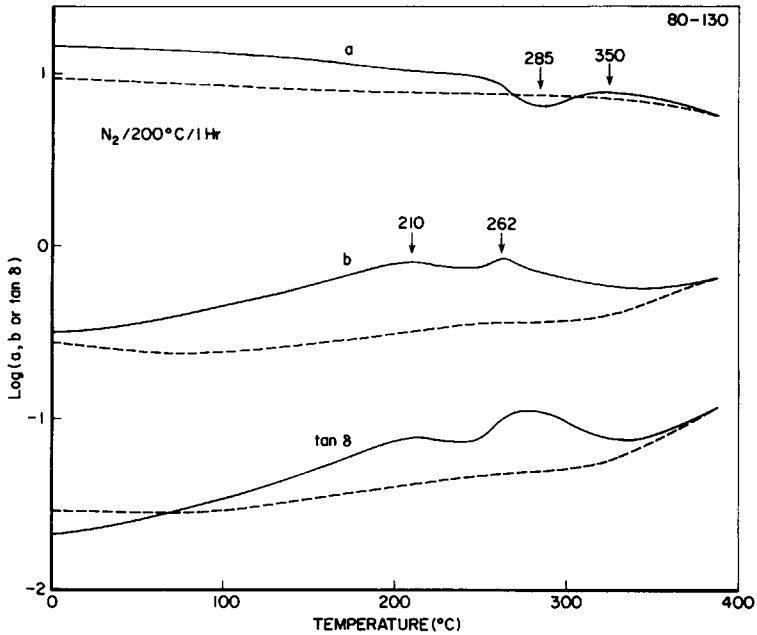


Fig. 5. Scan of a specimen that has been cured at 200°C for 1 h under nitrogen. (—) Scan-up; (---) scan-down.

if the temperature increase profile is kept constant at each curing temperature, reproducible results can be obtained. It should be emphasized that in cases where heat-up times are not negligible, the times to *b*-maximum are not the real isothermal curing times.

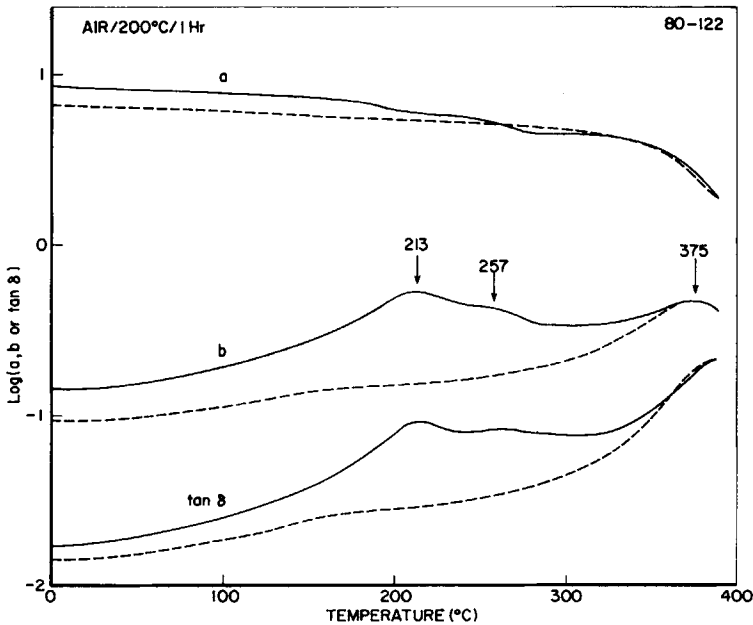


Fig. 6. Scan of a specimen that has been cured at 200°C for 1 h under air. (—) Scan-up; (---) scan-down.



The times to *b*-maximum under nitrogen atmosphere are plotted in Figure 7. At first inspection, all the points seem to be falling on a curved line. On closer examination, however, one can argue that there is an abrupt change in slope of the curve at about 250°C.

Three data points using air as the controlling atmosphere are also included in Figure 7. In all instances, the air-cure times are slightly below the nitrogen-cure curve. The differences, however, are slight. Evaporated nitrogen from a liquid nitrogen reservoir was used as the convection medium in the environmental chamber of the RMS during the nitrogen cure experiments. The low temperature gas was heated to the controlling temperature in a heat-element compartment just before it was forced into the sample area. In the air cure experiment, however, room temperature compressed air was used. Because of the vast difference in input air temperatures, the temperature increase profiles of the two sets of experiments can be different. The air-cure profile will be expected to be higher and can possibly account for the slightly shorter curing times in those experiments.

The samples that were cured in air at 200°C, 250°C, and 300°C were quenched to stop the air curing shortly after the *b*-maximum peaks. Then they were postcured in nitrogen at 350°C for half an hour. The subsequent temperature scans of these specimens under nitrogen revealed an identical final glass transition temperature at 380°C. There is insufficient data to claim the significance of this fact, or it may just be a coincidence.

#### Effect of Postcure under Nitrogen/Air Environment

The specimen that had been cured in air at 160°C for 24 h had a  $T_g$  of 360°C after it was scanned under nitrogen up to 390°C and was found essentially in Stage I ( $dT_g/dt = 0$ ) at the end of the scan (see Fig. 4). The specimen was

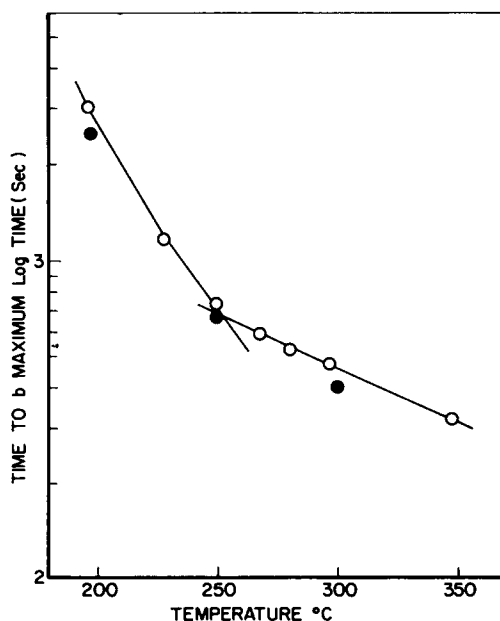


Fig. 7. Time to *b* maximum vs. cure temperature. (O) N<sub>2</sub>; (●) air.

postcured again in nitrogen for 1 h at 380°C. The subsequent nitrogen scan of this specimen is shown in Figure 8. The glass transition temperature remained at 360°C and no detectable change in either the *a*- or *b*-component was observed before and after the postcure. The specimen was then postcured at 380°C in air for another hour. The subsequent scan under nitrogen is also displayed in figure 8 (the dotted lines). The glass transition temperature had been increased to beyond 390°C and both the *a*- and *b*-components had decreased.

This showed that the specimen had reached a  $T_g(\infty)$  of 360°C under nitrogen cure. The  $T_g$  is so high, however, that it is overlapping with the oxidation temperature range. If care was not taken to exclude the oxidation effect, the specimen would have appeared to be not completely reacted even though it was.

### Effect of Cure Time in Air

Four specimens were cured at 200°C in air for various lengths in time (0.5 h, 1 h, 2 h, and 24 h). The thermal scans of these specimens under nitrogen are shown in Figure 9 (0.5), Figure 10 (2 h), and Figure 11 (24 h) (the 1-h result has already been shown in Figure 6).

The half-hour cure result in Figure 9 is clearly a I-II-III-II-III-II-I experiment. It shows two minima in the *a*-component. The first minimum at 195°C was also accompanied by a *b*-component maximum and can easily be identified as the first rate conversion point. At the second Stage II, the *b*-component went through a maximum at 258°C before it converted back into Stage III at 290°C. The peak at 258°C is again a sign of the limitation of the first reaction as discussed before. The specimen was finally in Stage I again at the end of the scan with a final  $T_g$  of 383°C.

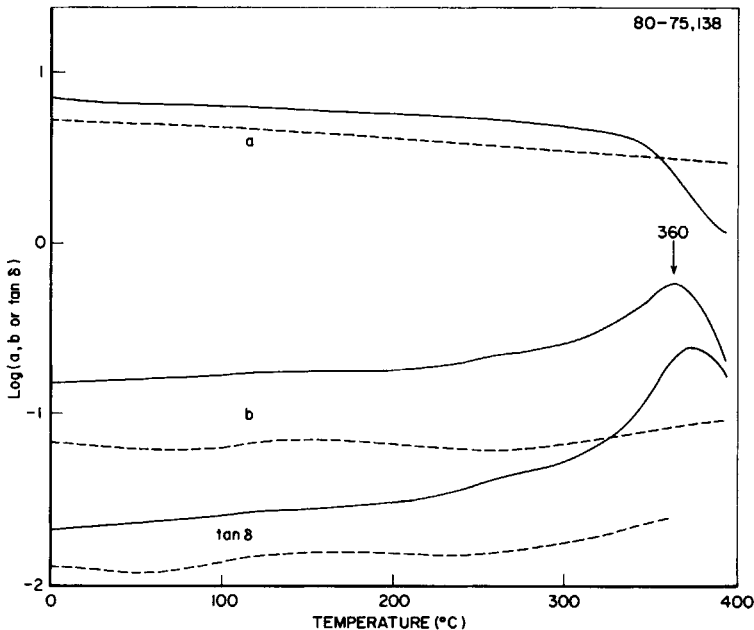


Fig. 8. Scans after postcuring in nitrogen (—) and air (---).

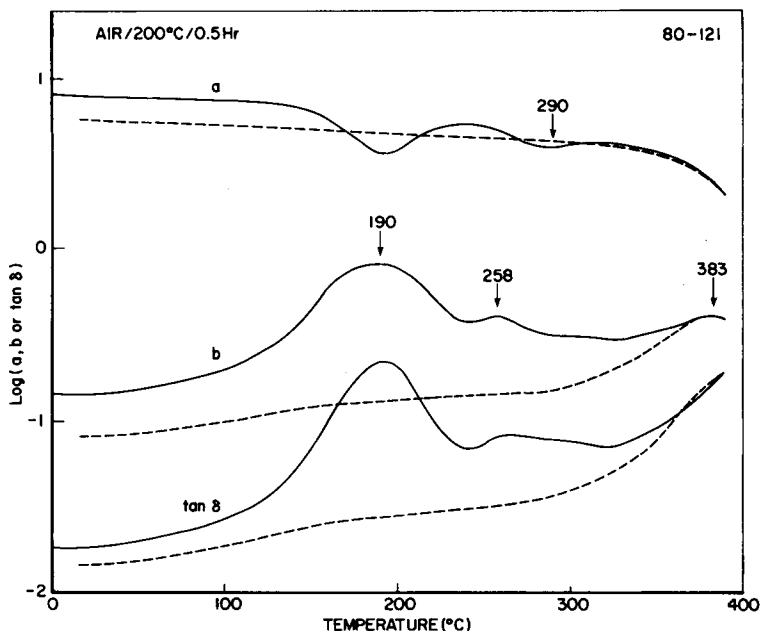


Fig. 9. Scan of a specimen that has been cured at 200°C for 0.5 h under air. (—) Scan-up; (---) scan-down.

The 1-h cure result (Fig. 6) has been discussed before. It is worthwhile to restate here that the first *b*-component maximum had been increased to 213°C with a shoulder of the *b*-maximum showing at 257°C. The valleys of the *a*-

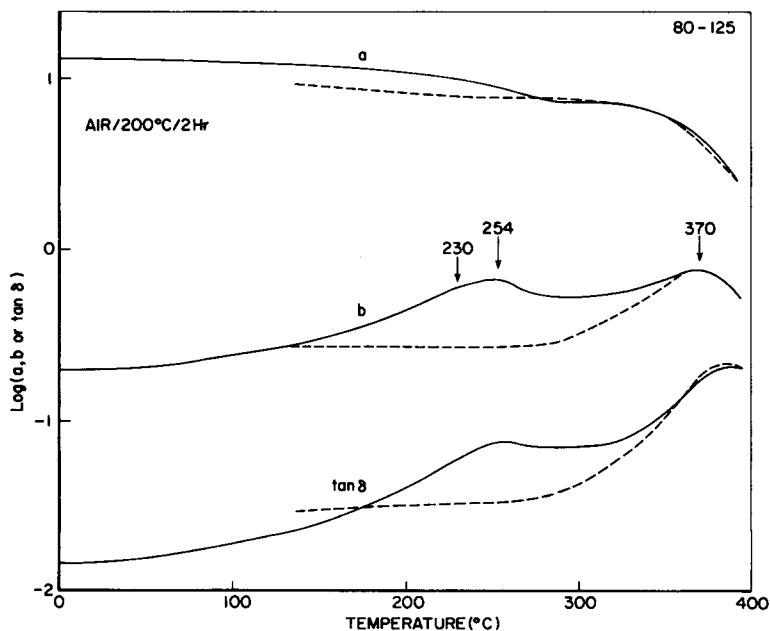


Fig. 10. Scan for a specimen that has been cured at 200°C for 2 h under air. (—) Scan-up; (---) scan-down.

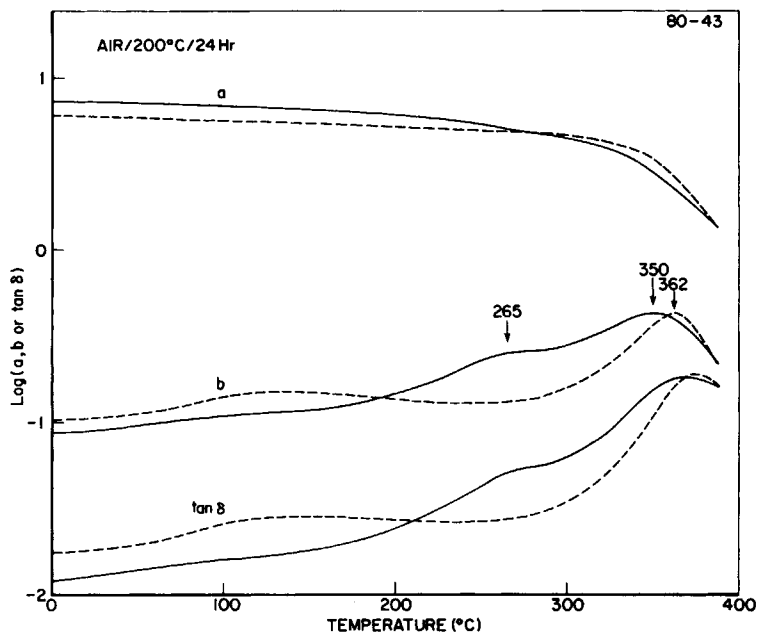


Fig. 11. Scan of a specimen that has been cured at 200°C for 24 h under air. (—) Scan-up; (---) scan-down.

component had been reduced to plateaus and the final  $T_g$  was lowered to 375°C.

The 2-h cure result (Fig. 10) showed that the first valley of the  $a$ -component was not detectable anymore but a  $b$ -component shoulder was still observed at 230°C. Again a  $b$ -maximum was shown at 254°C accompanied by the drop of the  $a$ -component. The final  $T_g$  was lowered to 370°C. The scan-down result suggested that the specimen was in Stage I at the end of the scan-up.

The 24-h cure result (Fig. 11) showed that the first  $b$ -maximum had disappeared. A  $b$ -component shoulder remained at 265°C. An apparent glass transition peak was observed at 350°C in the scan-up. The scan-down result, however, showed that the glass transition temperature had moved up to 362°C. The experiment was not in Stage I at the end of the scan-up.

## DISCUSSION

From the data presented in the previous section, it is obvious that curing under different conditions, will yield specimens with permanent changes as evidenced by the different  $T_g(\infty)$  the systems attained.

Combining all the data, we can empirically hypothesize that there are four distinct effects due to curing. Each effect may be a distinct reaction itself. The natures of these reactions are not known, so they are labeled alphabetically as A, B, C, and D. A summary of these effects is listed in Table I.

Reactions A and B can occur under nitrogen. Reaction A is occurring at low temperature, and Reaction B is at a higher temperature. The rate of Reaction B is not comparably faster than the scanning rate of 2°C/min until the temperature is above 270°C. The nitrogen scan experiment (Fig. 1) best exemplifies

TABLE I  
Summary of the Four Reaction Hypothesis

Reaction	Conditions	Remarks
A	in N <sub>2</sub> ; <270°C	(1) $T_g^A(\infty) = 260^\circ\text{C}$ (2) $T_g^A(\infty)$ not affected by precure
B	in N <sub>2</sub> ; >270°C	(1) $T_g^B(\infty) > 400^\circ\text{C}$ (2) $T_g^B(\infty)$ affected by precure (3) decreases $a$ -component
C	in air; low temp	(1) prohibits B (2) decreases $T_g^B(\infty)$ (3) no effect on $T_g^A(\infty)$
D	in air; >350°C	(1) increases $T_g(\infty)$ (2) decreases $a$ -component

the two reactions. The first II–III–II Stages are typical of a further reaction during a temperature scan, and the total reaction rate is slowed down (second Stage II) because of depletion of reactive groups. The glass transition observed after the Stage III is usually also the final  $T_g$  of the system, or  $T_g(\infty)$ .<sup>6</sup> The fact that Stage III occurred again after the Stage II implies either that the slowing down of the reaction rate in Stage II is not due to the depletion of reactive groups that causes the first Stage III, or that the second Stage III is the result of a different reaction. The result of the additional Stage III is a double-peak appearance in the  $a$ -component.

The appearance of the double peak in the  $a$ -component during a temperature scan is first observed in a TICA specimen of a blend of two different resins. At first, the double peak feature was thought to be either an experimental artifact or a complication due to a blend of two materials. The feature is experimentally reproducible. TGA experiments did not show weight loss in that temperature region, which means the second transition of Stage II to Stage III cannot be due to the loss of low-molecular-weight materials which act as plasticizers in the specimen. A thermocouple was embedded in another specimen, and no anomaly was observed between the temperatures of the sample chamber and the interior of the specimen during the scan. This rules out the notion of the temporary softening in the Stage II being a result of an intense exotherm due to the curing reaction. The two-peak feature was again observed in other single system resins. All these favor the explanation of two different reactions, which are common to most acetylene-terminated systems.

The fact that the two reactions can be so vividly separated by a valley of the  $a$ -component means the two reactions must have very different activation energies. One can argue that B will necessarily follow A if B is a reaction of the products formed in A. But without the difference in activation energies, the two reactions would be merged together, and mechanical properties scan should not be able to separate their effects. The notion of two separate reactions are involved is further supported by the appearance of two intersecting lines in the time to  $b$ -maximum plot.

If the specimen is cured and also scanned in nitrogen, the final  $T_g$  of the specimen is above 400°C. Because we cannot observe the  $T_g(\infty)$  in these cases, it is not certain if the  $T_g(\infty)$  is affected by the low temperature curing. Judging from the intensity of the second  $a$ -component peak, reaction B does not seem to be affected by the initial curing under nitrogen (Figs. 3 and 5). The effect of

reaction B is not only increasing the  $T_g(\infty)$ , but also decreasing the  $a$ -component.

The other two reactions required the presence of air. The effect of  $D$  is best demonstrated by the air-scan experiment (Fig. 2) and the postcure experiments (Fig. 8). Only at high temperature is the reaction rate of  $D$  comparable with the scanning rate. The most likely explanation of reaction  $D$  is oxidative crosslinking. The crosslinking can be at the backbone of the resin (the quinoxaline part) or the "joint" that extended the resins to a longer chain through the acetylene reaction. Regardless of the nature of reaction  $D$ , its effect is to raise the final  $T_g$  to above  $400^\circ\text{C}$  and at the same time lower the  $a$ -component.

The fact that reaction  $D$  is significant only at high temperature does not mean it does not occur at lower temperatures. The "significance" in observation is highly dependent on the experimental time scale, in this case, the scanning rate. At lower scanning rate, or long time exposure at use temperature, the temperature where reaction  $D$  is significant should be lower.

Reaction  $C$  is not directly observed in this series of experiments, but its effect can be observed by comparing with the nitrogen cure data. There is no *a priori* reason to say whether reaction  $C$  is different or the same as the reaction  $D$ , but the effect observed in this series of experiments is different, so it is treated accordingly. However, one can say that they are unlikely to be the same, considering that reaction  $C$  can occur at  $140^\circ\text{C}$ , while reaction  $D$  is not observed until  $370^\circ\text{C}$ .

Looking over the thermal scan results, we can see a persistent pattern of behavior in the  $b$ -component. First there is a shoulder or peak resulted from the additional curing because of the competing effects of the curing rate and the constant experimental scanning rate on the parameter  $(T - T_g)$ . This peak is labelled as  $T_c$  because it is a sign of the additional cure. It can also be used as a rough indicator of the extent of cure prior to the scanning experiment. The reason it is a rough indicator is that additional cure probably occurs before the  $T_c$  is reached.

The second and third peak are the  $T_g(\infty)$  of Reactions  $A$  and  $B$  respectively, so they are labeled as  $T_g^A(\infty)$  and  $T_g^B(\infty)$ . For the  $T_g^B(\infty)$  that are below  $400^\circ\text{C}$ , the value obtained during the scan-up is usually the same as that during the scan-down, with the exception of the specimen that has been cured at  $200^\circ\text{C}$  in air for 24 h. All  $T_c$ ,  $T_g^A(\infty)$  and  $T_g^B(\infty)$  are listed in Table II along with the curing conditions.

The  $T_g^A(\infty)$  values do not appear to be affected by the curing conditions. The average of all the  $T_g^A(\infty)$  values listed is  $260^\circ\text{C}$ , with the scattering within a  $\pm 5^\circ\text{C}$  range. The scatter is within the experimental errors and the uncertainty in identifying the peak locations due to the sloping characteristics in the region. The  $T_g^A(\infty)$  values are not affected by air or nitrogen cure, cure time or cure temperature.

It is interesting to note that in a previous study of the same resin<sup>8</sup> the  $T_g$  increase as a function of cure time at  $200^\circ\text{C}$  was measured with the calibration technique.<sup>5</sup>  $T_g$  was found to reach a value of  $250 \pm 10^\circ\text{C}$  after about 2 h of curing and stop increasing. At the time, the diffusion control of the reaction was thought to be the cause of the  $T_g$  remaining at a constant value. In light of the finding here, it is possible that the previous experiment was reaching the limit of Reaction  $A$ .

TABLE II  
Tabulation of *b*-Component Features with Curing Conditions

Curing conditions	$T_c$ (°C)	$T_g^A(\infty)$ (°C)	$T_g^B(\infty)$ (°C)
N <sub>2</sub> /160°C/24 h	213	260	>400
Air/160/24	213	260	360
N <sub>2</sub> /200/1	210	262	>400
Air/200/1	213	257	375
Air/200/1/2	190	258	383
Air/200/2	230	254	370
Air/200/24	—	265	<sup>a</sup> 350↑
	—		362↓
N <sub>2</sub> /scan	—	263	>400
Air/140/24	180	260	380
		Avg 260 ± 5	

<sup>a</sup> The 350°C value is the *b* maximum of the temperature scan up, and the 362°C of the scan down.

Reaction C does not have effect on  $T_g^A(\infty)$ , but its effect on Reaction B can readily be demonstrated. The *a*-component scans as a function of initial curing time and temperature are reproduced in Figure 12. The second peak of the *a*-component is diminished with increasing cure time in air, and also with increasing cure temperature. The feature does not seem to be affected if the curing was done under nitrogen. This implies that Reaction C, which requires air, will prohibit Reaction B.

$T_c$  and  $T_g^B(\infty)$  as functions of cure time and cure temperature are plotted in Figures 13 and 14, respectively.  $T_c$ , being a rough indication of the extent of Reaction A, increases with increasing temperature and time as expected. The  $T_g^B(\infty)$ , however, decreases with the higher temperature or longer time exposure in air during the initial curing. This is another indication of Reaction C prohibiting Reaction B.

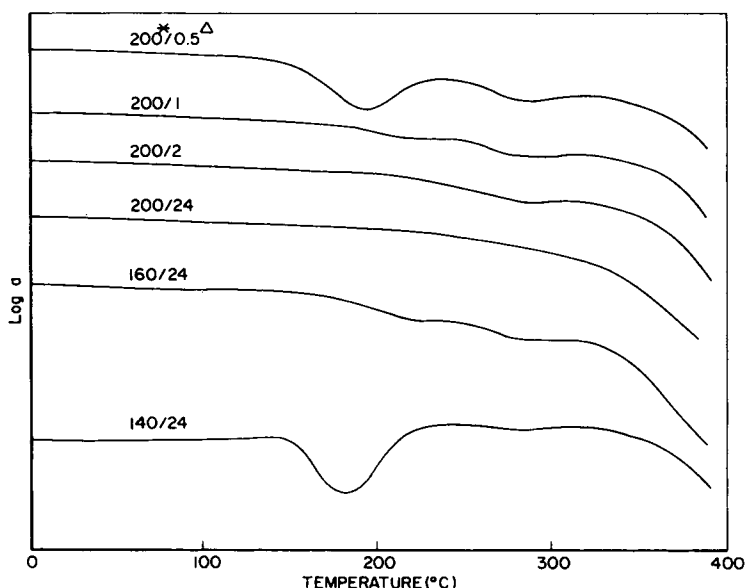


Fig. 12. *a*-component curves after different curing conditions. (\*) °C.

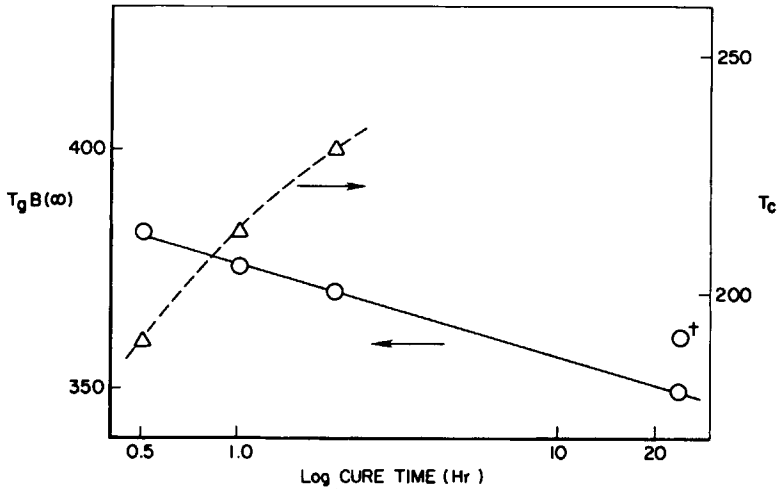


Fig. 13.  $T_c$  and  $T_g^B(\infty)$  vs. cure time at 200°C. (†) Scan-down result.

Several issues are raised from this study. It is clear that curing in air can impart permanent changes on the AT system as evidenced by the changes in  $T_g^B(\infty)$ . More important is how these permanent changes will affect the ultimate properties of the partially cured materials. Works are planned to measure the ultimate properties as a function of air/nitrogen cure.

Mechanical properties can reveal the effects of the reactions but such experiments are inadequate in shedding lights on the nature of the reactions. Such information however, is invaluable in fully understanding the acetylene cure technology. Other techniques, like spectroscopy, should be employed to explore this area.

The cure effects reported here should be taken into consideration in any experiments relating to the AT systems. Especially true are the experiments designed for correlation purposes. The cure cycles should then be designed in such a way as to minimize the confusion from different effects. The question of completeness of reaction should be carefully considered as well.

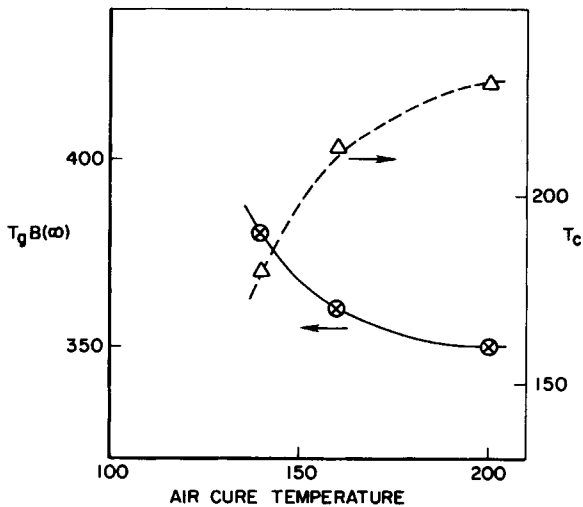


Fig. 14.  $T_c$  and  $T_g^B(\infty)$  vs. cure temperature for 24-h cure.



Reactions C and B are considered as curing reactions here. Cure cycles can be designed to exclude them from the cure. However, for fabricated components exposed in air at their designed use temperature, these reactions can occur and in such instances they will be considered as aging reactions. So these reactions' effects on properties should be carefully studied and should not be ignored.

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