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THERMAL MECHANICAL ANALYSIS STUDY OF
ACETYLENE TERMINATED QUINOXALINE RESINS

C. Y-C. LEE
Polymer Branch
Nonmetallic Materials Division

E.J. SOLOSKI
University of Dayton Research Institute

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Final Report for Period March 1981 to December 1981

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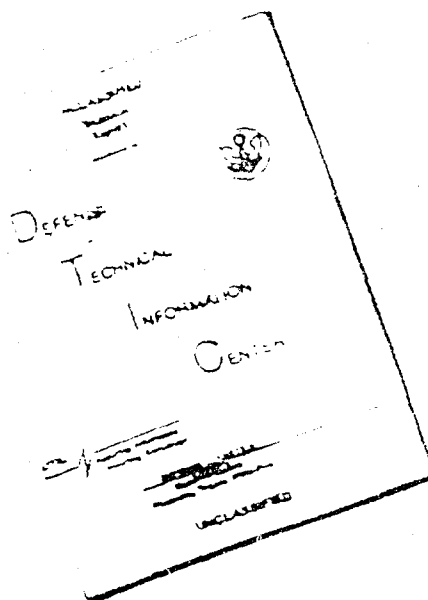
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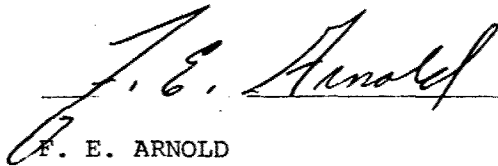
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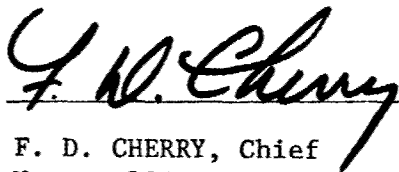


F. E. ARNOLD
Project Scientist



R. L. VAN DEUSEN
Chief, Polymer Branch

FOR THE COMMANDER



F. D. CHERRY, Chief
Nonmetallic Materials Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Additional cure effects on TMA experiments are investigated and the results are compared with those from TICA experiments. The penetration mode results are found to be more consistent and show similar behaviors between known Tg samples and isothermal cure samples. The expansion mode results may have been influenced by the physical aging effects and show different patterns between the two sets of samples. Because of the change in probe movement direction before and after the softening point in the penetration mode experiments, penetration mode results can highlight the additional cure effect more. Comparison with TICA results show, as		

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20. Abstract (Continued)

expected, influence due to scanning rate.

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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 the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the Materials Laboratory Project Scientist. Co-authors were Mr. E. J. Soloski, University of Dayton Research Institute and Dr. C. Y-C. Lee, Air Force Materials Laboratory (AFWAL/MLBP).

This report covers research conducted from March 1981 to December 1981.

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SECTION I

INTRODUCTION

Additional cure effects have been studied in this laboratory with Torsion Impregnated Cloth Analysis (TICA) techniques and methods of T_g measurements without these effects had been developed (Reference 1). However, these methods are time consuming in comparison to some of the thermal analysis techniques that are available.

DSC is not a good method of studying the T_g of partially cured specimens because the residual exotherms often obscure the heat capacity changes at the glass transition temperature. TMA, however, can be run in either the penetration or expansion mode. The changes due to additional cure are similar in magnitude to that attributing to the glass transition. This study is to investigate the influence of the additional cure on the TMA results. Attempts will be made to correlate the TMA data with the previous results from TICA experiments.

SECTION II

RESULTS AND DISCUSSION

All experiments were run using a DuPont 942 Thermomechanical Analyzer and with a constant heating rate of 10°C/min. The samples were precured under different conditions prior to the TMA experiments using a Perkin Elmer DSC-1B as the curing instrument.

1. PENETRATION MODE

The penetration mode was run with a standard penetration probe. A load of 10 gm was put on the loading tray. A typical run is shown in Figure 1. This particular run was using a sample that had been cured at 200°C for one hour. The features observed are typical to all the runs: an initial penetration followed by another region of expansion, and finally, the penetration at higher temperature.

The initial penetration is related to the softening of the material around the T_g of the partially cured sample. As the temperature is raised during the scan, additional curing occurs. Two factors could have contributed to the expansion observed in this region.

One is the expansion of the glassy state with temperature. If the additional cure is in Stage III (Reference 2) in this temperature region, the sample could have revitrified into the glassy state. This phenomenon has been well documented in TICA and TBA experiments (References 3 and 4). After revitrification, the sample should expand with increasing temperature much like the region before the initial softening.

The second factor can be due to the actual volume change due to the cure reaction. Unpublished data (Reference 5) indicates that when BADABBA is cured isothermally, its density increases initially but after vitrification the density decreases. This implies that the volume decreases before vitrification but expands after vitrification. The decrease before vitrification can be contributed to the system changing from the liquid state to the solid state. The increase after vitrification would imply volume expansion due to reaction. Similar observations

have been recorded in a recent density study of ATS-G (Reference 6). After vitrification, the density of ATS-G is found to decrease with increasing extent of cure. Further increase in the extent of cure causes the density to increase again but the data are insufficient to explain if the density increase is the result of different cure mechanisms or effects of physical aging due to annealing at the cure temperature.

The final softening at high temperature may or may not be related to the T_g of the fully cured system. With TICA experiments, the $2^\circ\text{C}/\text{min}$ scans of specimens with similar precure history indicated a final T_g above 400°C (Reference 2). The inflection point in Figure 1 is 368°C . This could either reflect the discrepancy between the TMA softening point and the dynamic mechanical T_g measurements, or at a $10^\circ\text{C}/\text{min}$ scan rate, the T_g increase rate due to additional cure is slower than the temperature scanning rate. If the latter case is true then the system was in Stage II and the softening may not reflect the final T_g of the system.

By using the cure phase diagram generated with the TICA experiments (Reference 2), samples with known T_g , as determined by a 10 rad/sec experimental frequency, can be prepared by curing at different cure temperatures using a predetermined period of time (Reference 1). The TMA results of these samples were recorded. One of these traces is shown in Figure 3. The three response inflection temperatures, labelled as T_a , T_b , and T_c as shown in Figure 1, are listed in Table 1. In Figure 2, these inflection temperatures are also plotted vs the T_g as determined by the precure history.

The dashed line in Figure 2 represents the equal temperature points between the two axes. It can be seen that between 200°C to 240°C , the T_a values are almost parallel to the dash line and are lower by about 10°C . The amount of difference can be due to the different experimental methods represented by the two axes. The y-axis in this plot represents results from a $10^\circ\text{C}/\text{min}$ scan TMA experiment, but the x-axis represents T_g measurements using dynamic deformation frequency of 10 rad/sec . The T_a line crosses the dash line at about 275°C . This deviation from the parallel situation is a reflection of the additional cure effect under

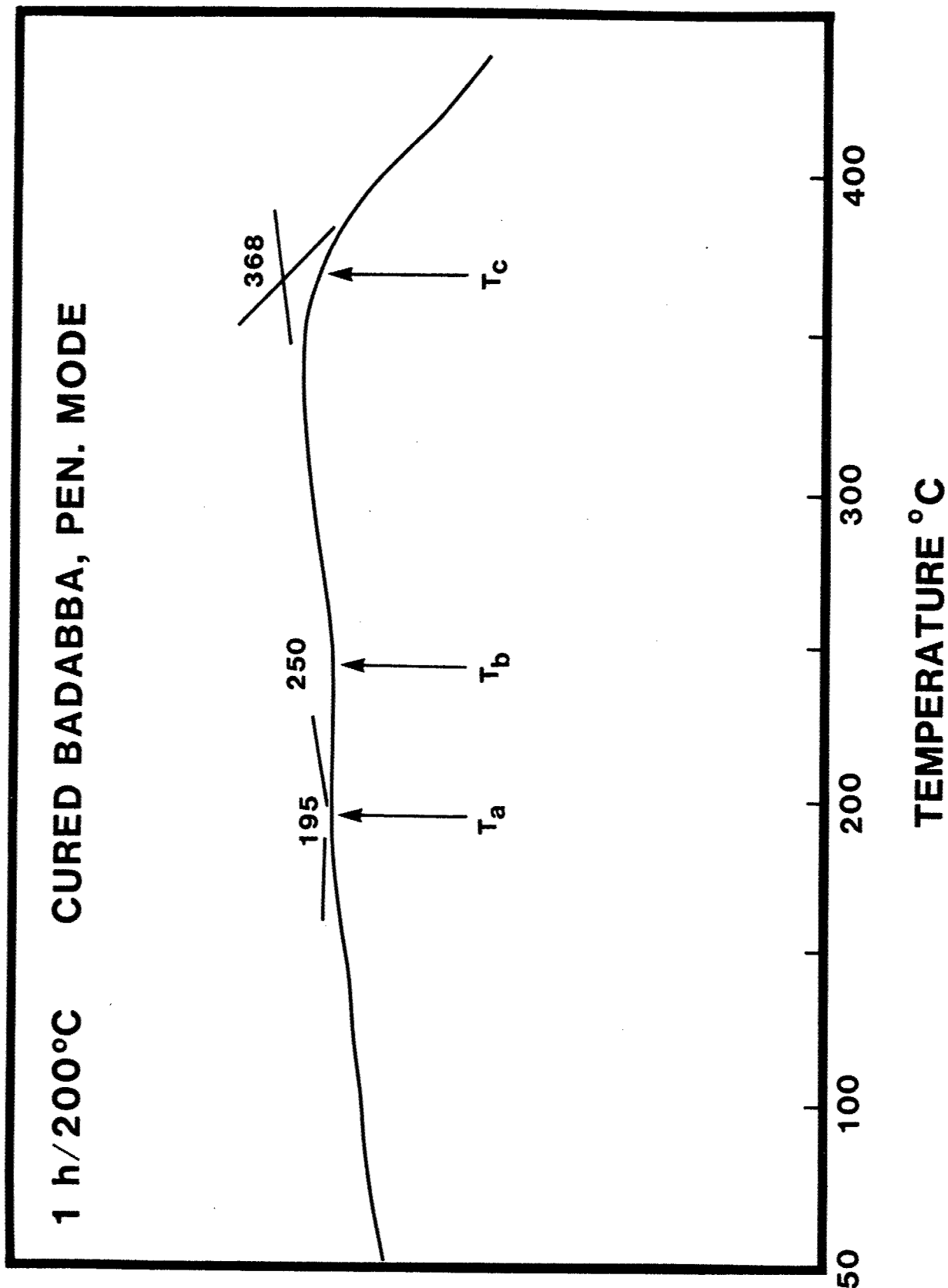


Figure 1. Penetration Trace of a Partially Cured Sample

TABLE 1
 BADABBA TMA RESULTS
 PENETRATION MODE - PREDETERMINED T_g SAMPLES

Cure Temperature = Predetermined T_g	Cure Time Sec	T_{σ_a} $^{\circ}\text{C}$	T_{σ_b} $^{\circ}\text{C}$	T_{σ_c} $^{\circ}\text{C}$
200 $^{\circ}\text{C}$	3000	189	245	366
220 $^{\circ}\text{C}$	1500	209	255	370
240 $^{\circ}\text{C}$	900	225	290	362
260 $^{\circ}\text{C}$	660	257	300	378
290 $^{\circ}\text{C}$	540	290	328	375

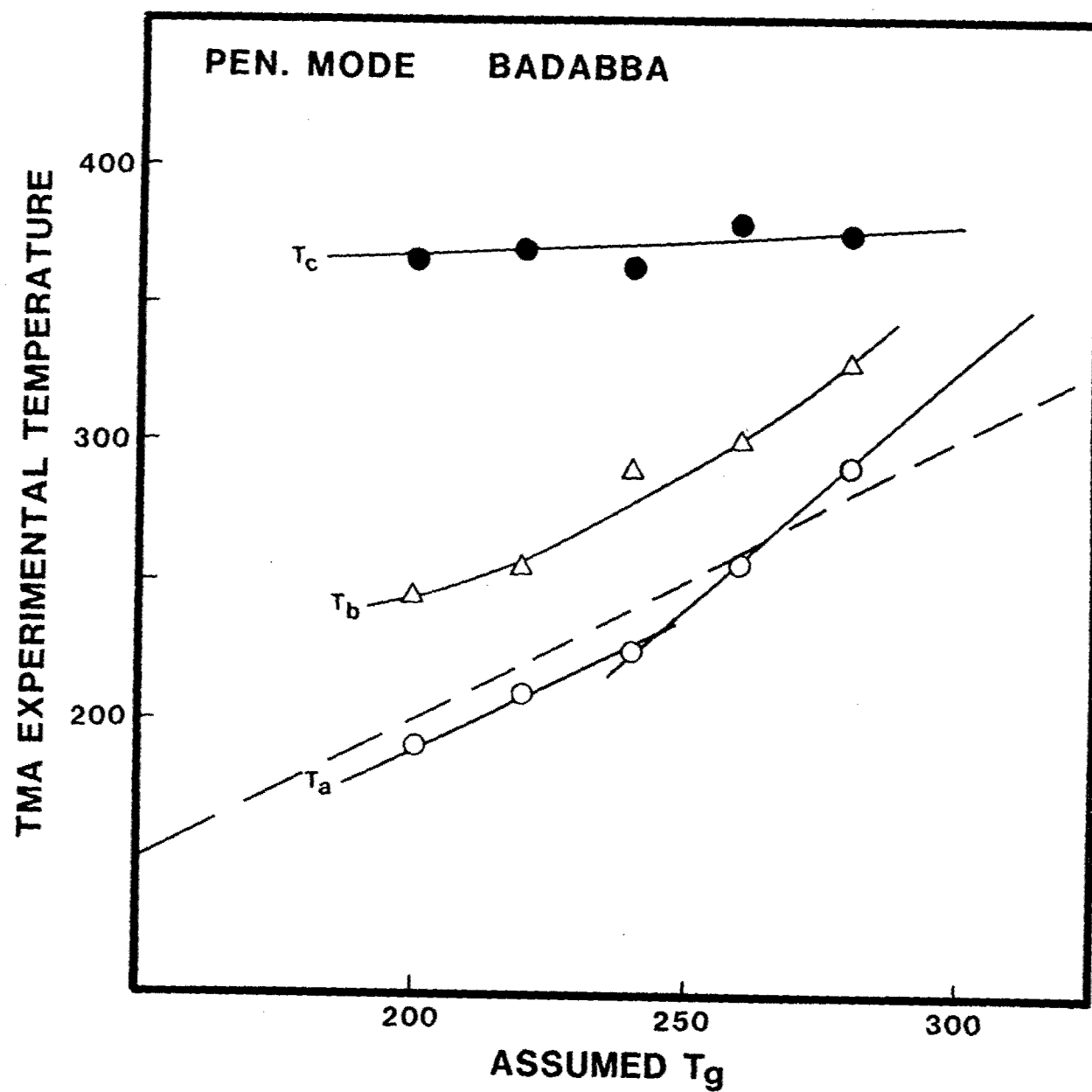


Figure 2. Plot of Penetration Inflection Points vs Assumed T_g

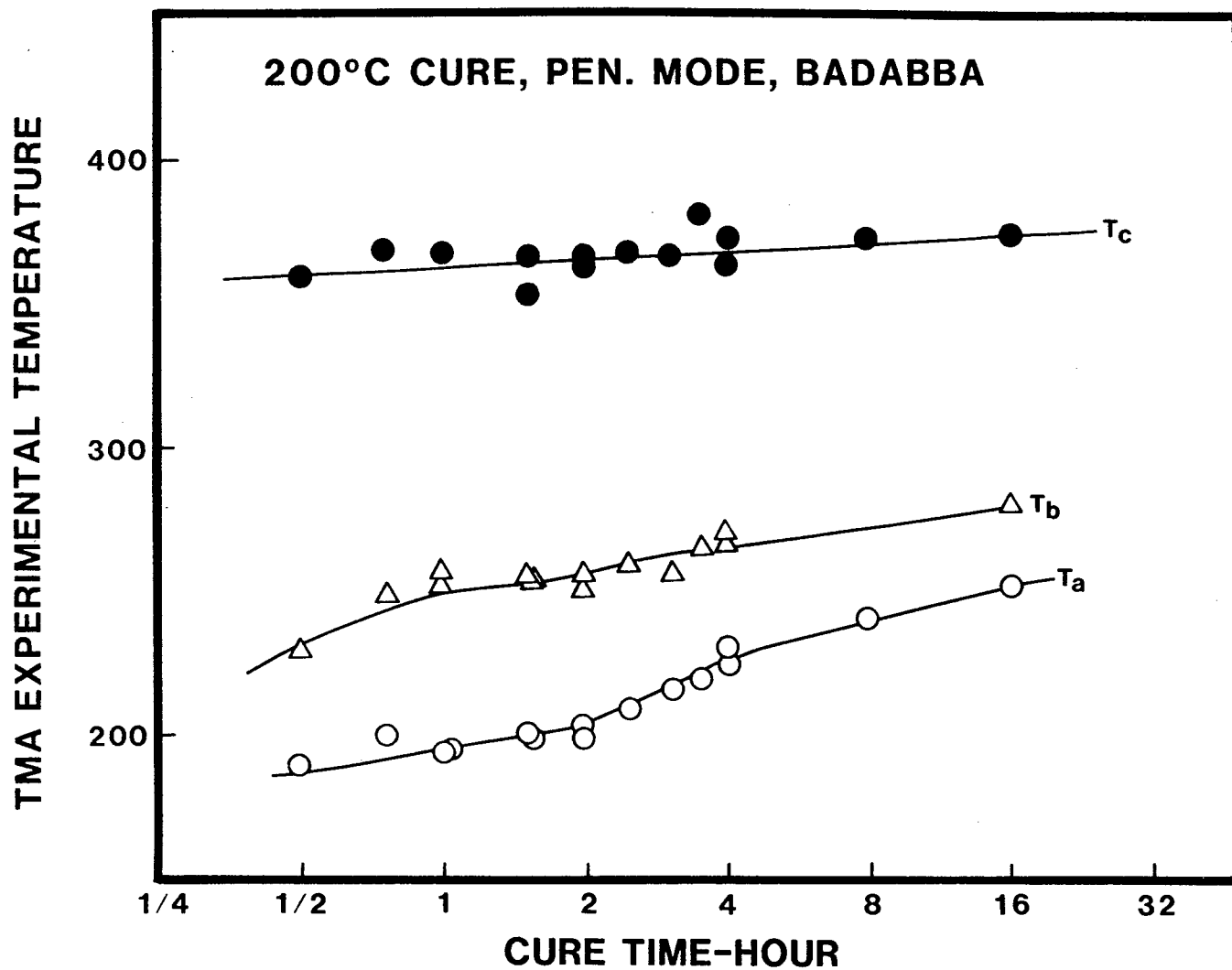


Figure 3. Plot of Penetration Inflection Points vs Cure Time.

a scan rate of 10°C/min. Previous TICA experiments using a 2°C/min scan rate showed the additional cure effect to occur at a lower temperature.

Figure 2 shows that T_b increases as the T_g increases with additional cure but T_c is only slightly affected by the cure state before the scans. These are in agreement with the earlier explanation of the origins of these inflection temperatures. T_b , being related to the additional cure during the scan, would be affected by the T_g before the scan. The fact that it is an increasing function implies that the additional cure kinetics in this region is not controlled by the activation energy term in the kinetic rate equation. The rate is controlled by the local viscosity, the concentration of the unreacted species or a combination of both. T_c , however, should be close to the final T_g of the system. The local viscosity should be similar regardless of the sample's cure state before the scan. Any difference in the extent of cure due to the precuring conditions would have been minimized. So T_c is not very sensitive to the precure conditions.

A series of samples were cured isothermally at 200°C for various lengths of time. The TMA results are listed in Table 2 and plotted in Figure 3. Again T_c shows only a small correlation with different cure times. T_a , which correlates best with the assumed T_g , shows a slight increase before two hours. The slope of the increase becomes sharper between two to four hours, and levels off after four hours.

By using Figure 2 as a calibration chart correlating T_a with T_g , a plot of T_g vs cure time can be constructed. Such a plot is shown in Figure 4. The T_g increase vs cure time curve from a previous study using TICA is also shown. The T_g after long time cure from both experiments agree well, but the short time results do not. It should be pointed out, however, that the short time data from Figure 3 can match both the T_a and T_b values from Figure 2 at the same assumed T_g reading but for long time data this is not the case. This can imply that the cure state reached at 200°C at long time may be different from the states reached at higher temperature. This possibility was pointed out in an earlier publication (Reference 7). This point is further supported by results of the cure study reported by McDonnell Douglas Research Laboratory (Reference 8).

TABLE 2

BADABBA RESULTS

PENETRATION - ISOTHERMAL CURE @ 200°C

Cure Time	T _a	T _b	T _c
½ h	191	230	360
¾ h	200	248	369
1 h	195	252	368
1½ h	202	255	367
2 h	200	255	362
2½ h	210	262	368
3 h	215	253	360
3½ h	220	265	372
4 h	225	267	373
8 h	240	-	375
16 h	252	280	374

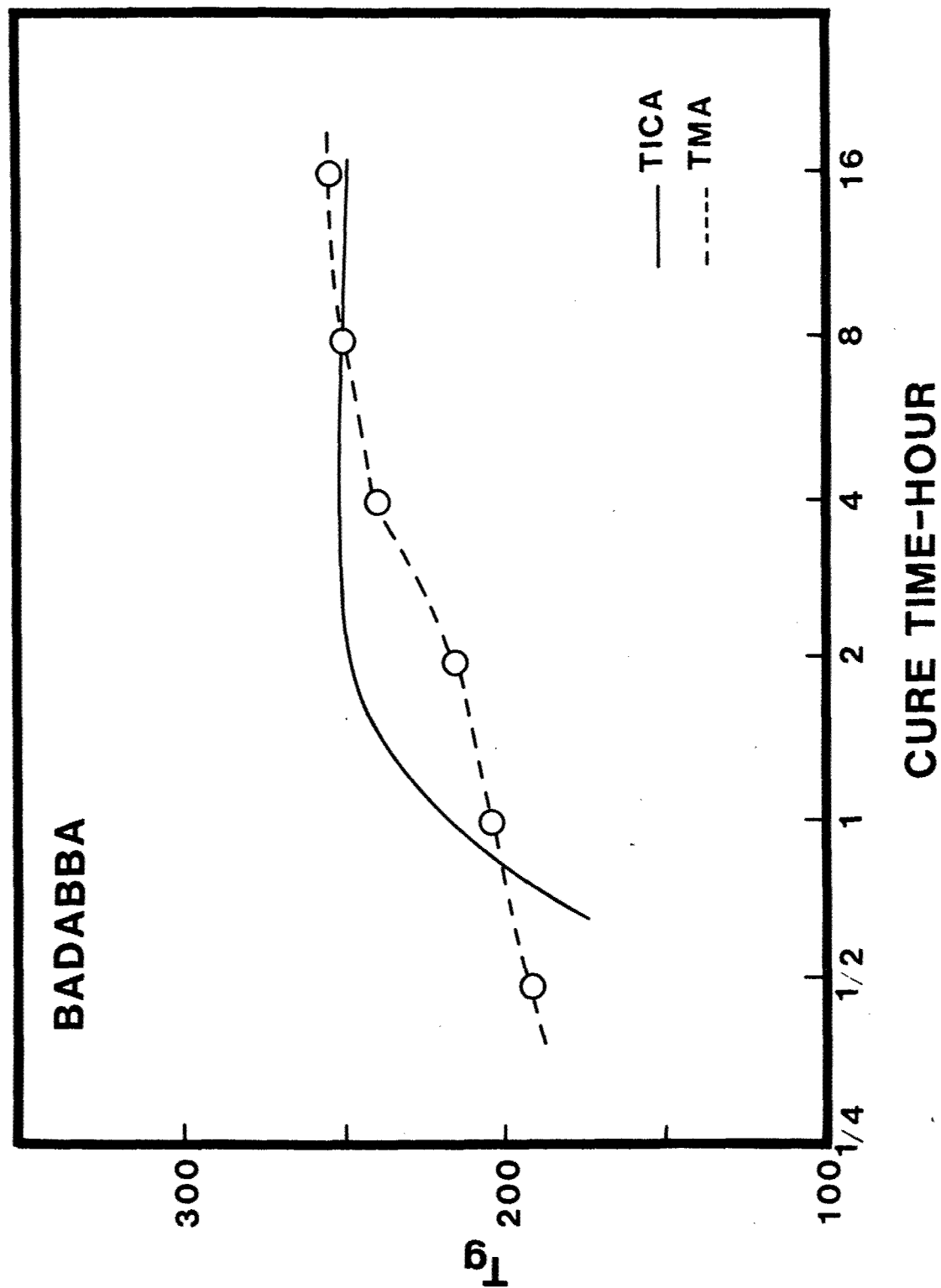


Figure 4. Comparison on TMA and TICA Calibrated T_g Results

2. EXPANSION EXPERIMENTS

The expansion mode experiments were run with a standard expansion probe with 1 gm weight on the tray. Two series of runs were initiated at different times. One series was with samples cured at 200°C for various lengths of time. Another series was with samples cured to known T_g values as in the penetration experiments. The expansion data from the two series of experiments are different.

When the sample was only slightly cured, the resin changed to a low viscosity liquid state soon after the T_g . The result of such a sample will show penetration instead of expansion because the liquid cannot hold the weight of the probe. Figure 5a shows such a result from a sample cured at 200°C for 15 minutes. A slight expansion was detected at 110°C as the T_g of the partially cured sample. At higher temperature, the probe penetrated into the specimen.

Figure 5b shows the result from a specimen that had been cured at 200°C for 45 minutes. An expansion was detected at 208°C. At 283°C, the TMA trace showed a decrease in expansion rate. Expansion resumed again at 355°C. The first expansion can be explained as the T_g of the partially cured sample. The decrease in expansion rate at 283°C can be due to additional cure during the scan. The final expansion is due to the sample being close to the completion of reaction. This TMA scan pattern persists even with a longer time of cure. The result of a sample that has been cured for 16 hours is shown in Figure 5c. Again by noting the successive temperature readings of the slope changes as T_a , T_b , and T_c , the pattern of changes from different cure histories can be compared. The results are tabulated in Table 3 and shown in Figure 6.

The expansion data from samples with assumed known T_g 's are quite different. Figure 7 shows the TMA traces of samples with T_g of 200°C, 240°C, and 260°C. The first slope change indicated a decrease in expansion rate and the successive changes are exactly the opposite of what were observed in Figure 5.

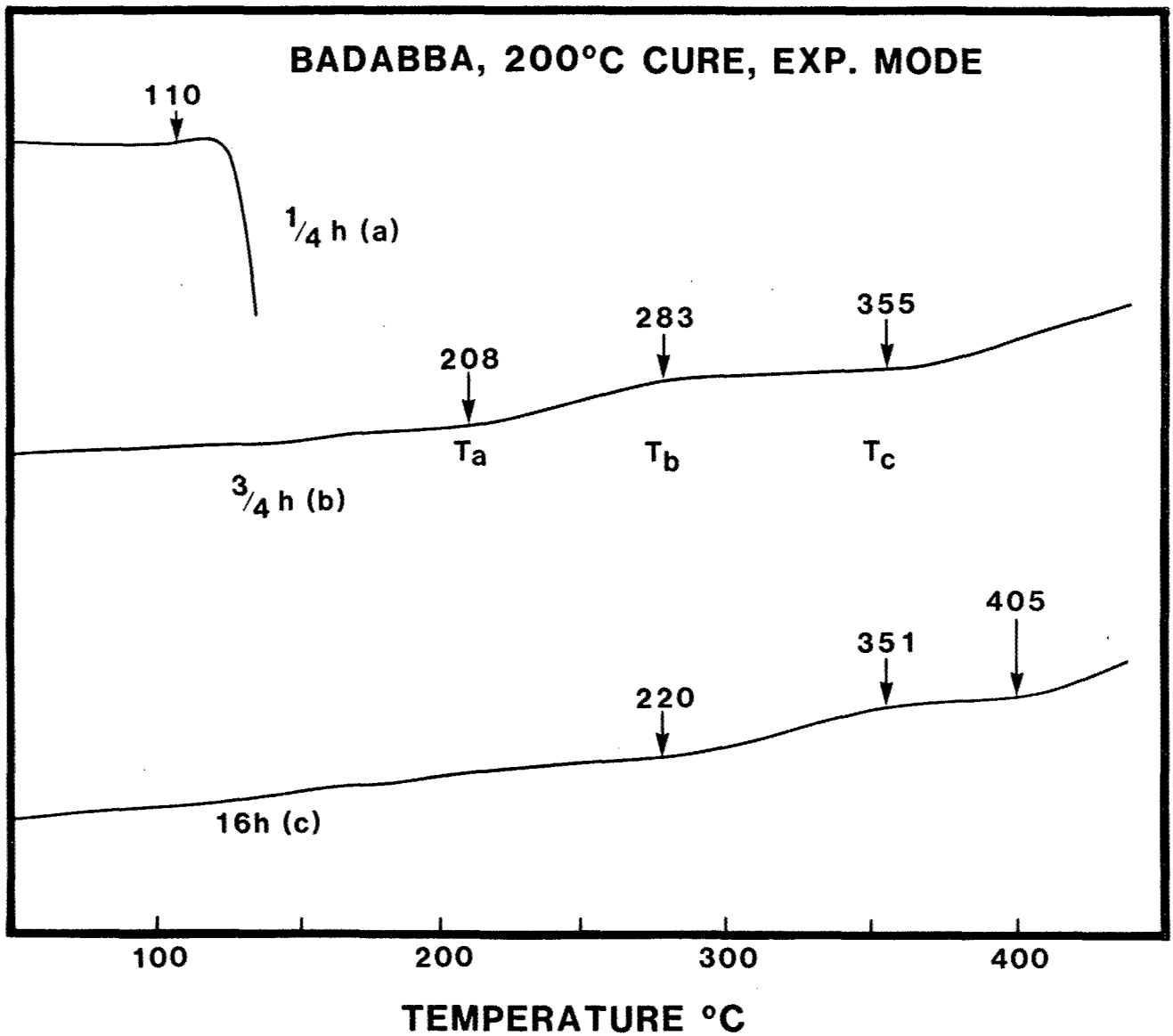


Figure 5. Expansion Traces of Partially Cured Samples

TABLE 3
EXPANSION MODE RESULTS
10°C/MIN TMA SCAN
200°C/N₂ CURE BADABBA SAMPLES

Cure Time	T _a (°C)	T _b (°C)	T _c (°C)
1/4 h	110	-	-
1/2 h	165	188	240
3/4 h	208	283	355
1 h	200	270	385
1 1/2 h	243	300	-
2 h	240	350	415
4 h	260	345	415
8 h	-	358	-
16 h	280	351	405

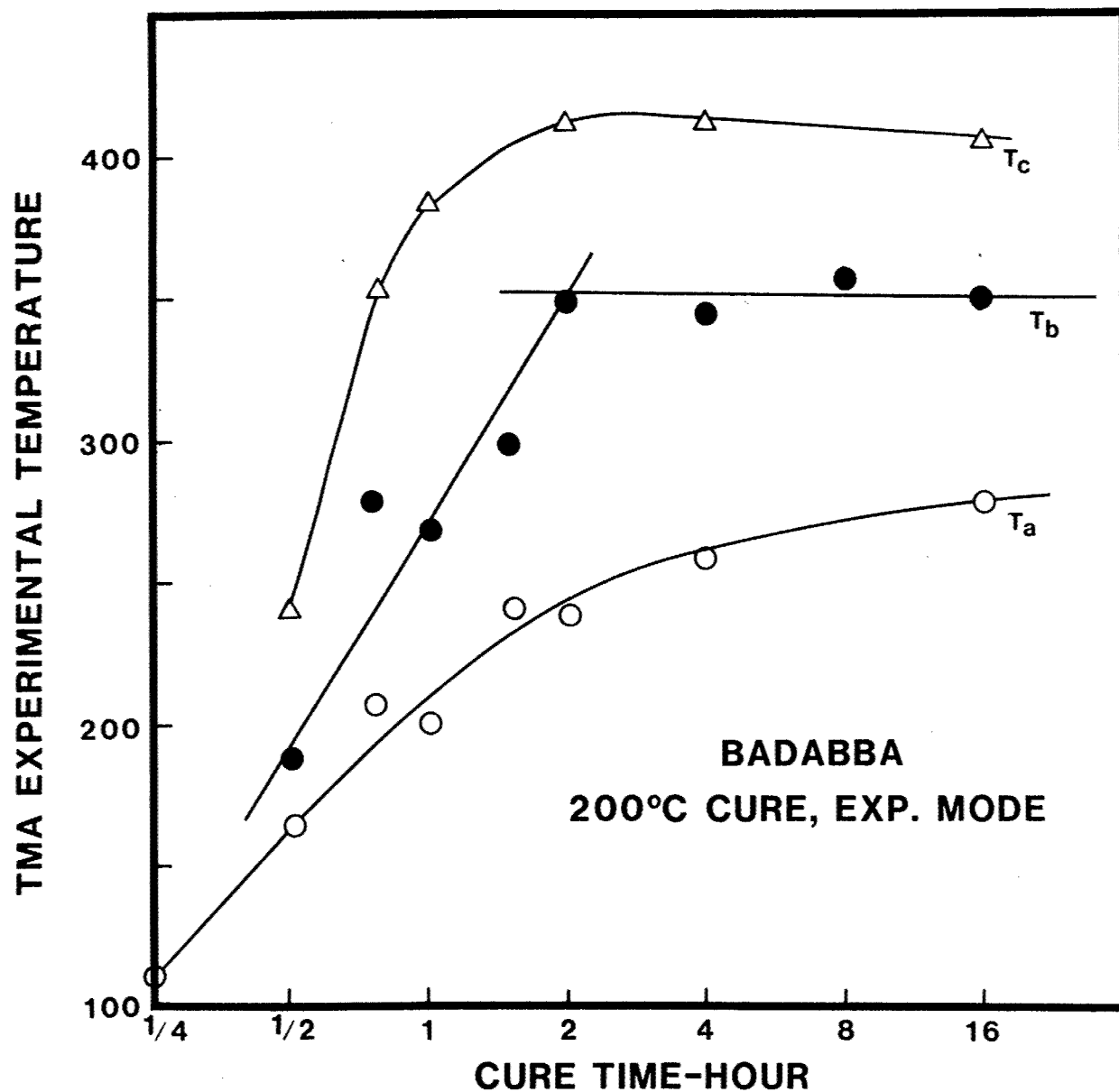


Figure 6. Plot of T_a , T_b , and T_c with Different Cure Time (@200°C)

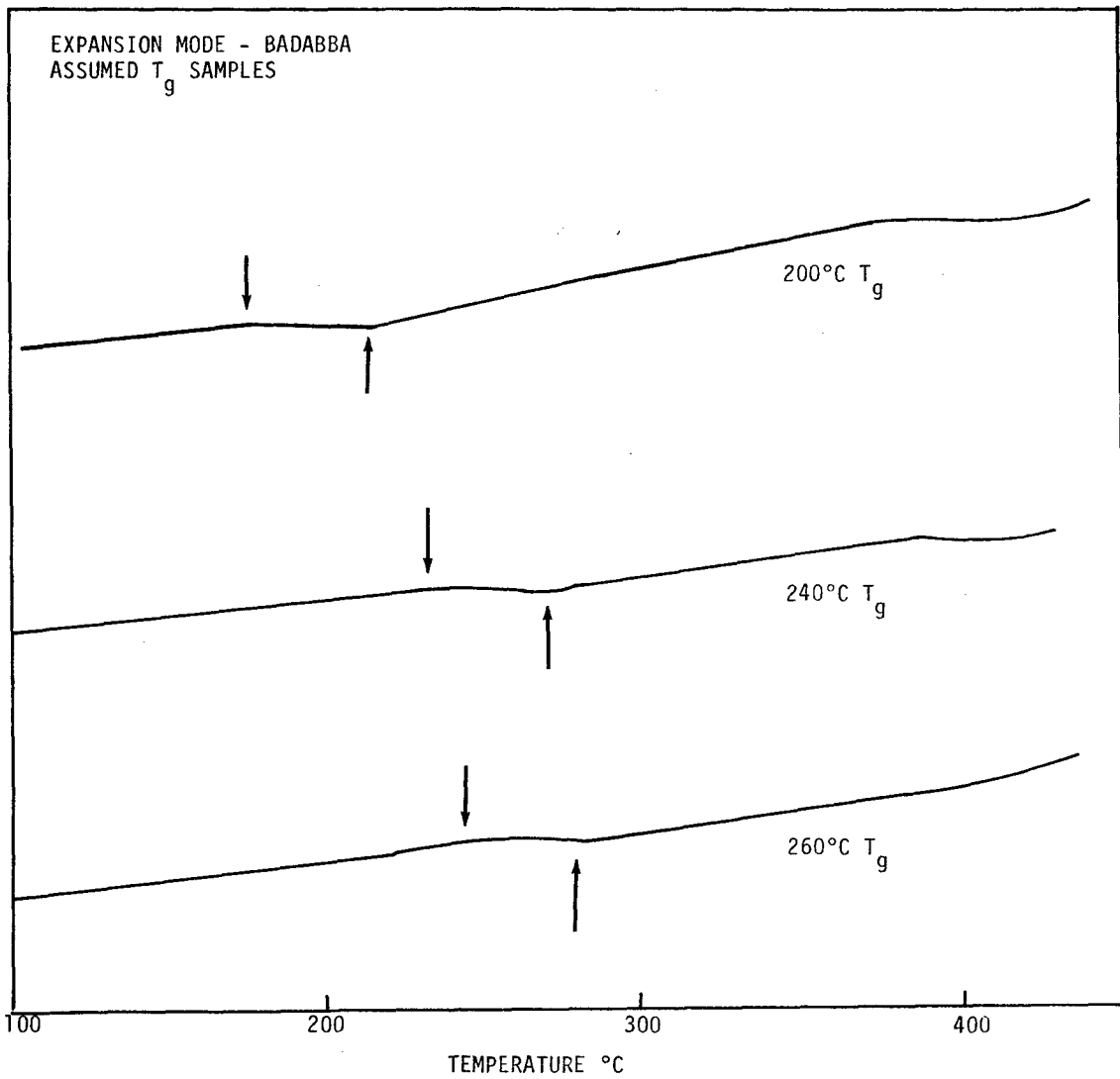


Figure 7. Expansion Traces of Samples with Assumed T_g

Since these two series of samples were run at different times, the cool down procedure after the initial cure may have been different. Those especially affected were the samples having known T_g 's. They were removed from the heating block of the DSC when their T_g 's were supposedly the same as the sample temperatures. Under this condition, the volume of the sample is most susceptible to relaxation effects which manifests itself in volume changes in the sample. This may have caused the different thermal expansion patterns observed during the subsequent temperature scans.

Because of the different behaviors between the known T_g samples and the isothermal data, comparison between these two sets of data cannot be made as in the penetration results.

CONCLUSIONS

From this study, the penetration results are more consistent with the TICA study than the expansion results. The penetration results from the known T_g samples show similar additional cure patterns as the isothermal cure samples. The expansion results between the two types of samples are not the same. This may be because in the penetration mode, the experiment is measuring the compressive modulus of the sample, while in the expansion mode, the volume of the sample is being monitored. Physical relaxation effects will influence the volume more dramatically. Therefore the behaviors observed during the subsequent rescan are more susceptible to difference in previous thermal history.

For the study of partially cured samples, where additional cure effects may be present during the scan, penetration mode should be better than expansion mode. Before the softening point, the weight of the probe is supported by the sample. So before the softening point, the probe will record the volume expansion of the sample due to thermal effects. After the softening point, the probe will move in the opposite direction indicating penetration into the sample. This reverse in probe movement direction will help to monitor the sample moving back and forth between the softening and hardening points during the scan. In the expansion mode, the volume changes before and after glass transition temperature are being monitored. In both instances, the volume increases with increasing temperature only the slope is changed.

From the penetration results, a good correlation was obtained between the known T_g 's and the softening points of the samples. At low temperature, the softening points are consistently lower than the known T_g 's by about 10°C. This is due to the experimental difference between the TMA and the dynamic mechanical measurements. At higher temperature, the TMA results become higher than the T_g 's. This is because the T_g values are obtained through isothermal results, where additional cure effects are eliminated. The TMA results, however, are measured during thermal scans. At high temperature, the additional cure effects become significant.

Additional cure effects of BADABBA are also present in thermal scans of dynamic mechanical measurements and have been reported. In those experiments, the additional cure effects occur at a lower temperature. This is because of the different scanning rates used. In TICA measurements a scanning rate of 2°C/min was used, but a 10°C/min rate was used in the TMA experiments. The rate conversion points R, where the sample changes from Stage II to Stage III or vice versa, are usually significant signs of the additional cure effect. The first R point of TMA, which is the transition from Stage II to Stage III occurs at a higher temperature than the TICA results. Similarly, the second R point, which is the transition from Stage III to Stage II, is lower in TMA than the TICA results. This is as expected because of the higher scanning rate of the TMA experiments.

In the penetration experiments, the isothermal results do not match the known T_g results. One can match the T_a or T_b , but not both at the same time for the long time cure samples. This fact underscores the importance of the need of a multi-parameter approach to identify the cure states. A single parameter approach will often lead to a misleading comparison between samples.

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