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# **The Development of the Dynamic Mechanical Analyzer Calibration and Testing Procedures**

September 2016

Final Report

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16. Abstract Dynamic mechanical analysis (DMA) is the most preferred and widely used thermal analysis technique for determining the glass transition temperature ( $T_g$ ) of polymer matrix composites because it is more sensitive to $T_g$ measurements than other thermal analysis techniques. An interlaboratory study was developed and conducted by the American Society for Testing and Materials (ASTM) for its D7028-07 test standard ( $T_g$ by DMA) in 2007. The results of the study indicated that reproducibility was poor between DMA instruments and laboratories. A reproducibility standard deviation of 15.09°F and 14.72°F was found for dry $T_g$ and wet $T_g$ measurements, respectively.  Poor reproducibility of $T_g$ measurements creates uncertainty in cases in which $T_g$ measurements are used. Service temperature and process control determinations may be difficult to establish if reproducibility of $T_g$ measurements remains poor.  The goal of this research was to improve laboratory-to-laboratory and instrument-to-instrument reproducibility. To accomplish this, several potential influencers of $T_g$ measurements, such as thermocouple (TC) positioning, dimensional variation of specimens, and temperature calibration configurations and methods were evaluated. These evaluations were the framework for the development of TC guidelines and temperature calibration procedures to aid test operators in areas in which the test and calibration standards were not specific.  To assess if this goal was achieved, a follow-on interlaboratory study was conducted. A reproducibility standard deviation of 7.86°F and 7.30°F was determined for dry $T_g$ and wet $T_g$ measurements, respectively. When compared with the interlaboratory study conducted by ASTM, the follow-on interlaboratory study indicated a 50% improvement in the reproducibility of $T_g$ measurements was achieved with the implementation of the developed TC guidelines and temperature calibration procedures.					
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## LIST OF ACRONYMS

ASTM	American Society for Testing and Materials
BIS	Bureau of Industry and Security
DMA	Dynamic Mechanical Analysis
DMTA	Dynamic Mechanical Thermal Analyzer
DSC	Differential scanning calorimetry
FAA	Federal Aviation Administration
NCAMP	National Center for Advanced Materials Performance
NIAR	National Institute for Aviation Research
NIST	National Institute of Standards and Technology
PEEK	Polyetheretherketone
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
RC	Resin content
SACMA	Suppliers of Advanced Composite Materials Association
SRM	SACMA Recommended Method
TC	Thermocouple
TMA	Thermomechanical analysis

## LIST OF SYMBOLS

$\delta$	Viscoelastic phase angle
$\lambda$	Thermal conductivity
$\rho$	Density
$c_p$	Specific heat capacity (at constant pressure)
$D$	Thermal diffusivity
$E^*$	Complex modulus
$E'$	Storage modulus
$E''$	Loss modulus
$S_r$	Repeatability standard deviation (per ASTM E691)
$S_R$	Reproducibility standard deviation (per ASTM E691)
$\overline{S}_r$	Mean repeatability standard deviation (per ASTM E691)
$\overline{S}_R$	Mean reproducibility standard deviation (per ASTM E691)
$\tan\delta$	Tangent of $\delta$
$T_g$	Glass transition temperature
$T_{gE'}$	$T_g$ determined from the $E'$ curve of the DMA test
$T_{gE''}$	$T_g$ determined from the $E''$ curve of the DMA test
$T_{g_{\text{eig}}}$	$T_g$ determined from the onset of the heat flow curve of the DSC test
$T_{g_{\text{exp}}}$	$T_g$ determined from the displacement measurement of the TMA expansion test
$T_{g_{\text{flex}}}$	$T_g$ determined from the deflection measurement of the TMA flexure test
$T_{g_{\text{mg}}}$	$T_g$ determined from the mid-height of the heat flow curve of the DSC test
$T_{g_{\text{tan}\delta}}$	$T_g$ determined from the $\tan\delta$ curve of the DMA test
$T_m$	Melting temperature
$T_m\Delta^*$	$T_m\Delta_i$ averaged for all melting standard and fixture combinations for a particular candidate material
$T_m\Delta_i$	Difference in melting temperatures between $T_{mPM_{\text{avg}}i}$ and $T_{mCM_i}$ ; $i$ th melting standard and fixture combination
$T_mCM_i$	Melting temperature of the calibration melting standard when using the candidate material as a calibration support beam; $i$ th melting standard and fixture combination
$T_mPM^*_i$	Melting temperature of the calibration melting standard when using the polymer matrix material as a calibration support beam; average of all polymer matrix materials for the $i$ th melting standard and fixture combination
$\overline{X}$	Mean

## EXECUTIVE SUMMARY

Dynamic mechanical analysis (DMA) is the most preferred and widely used thermal analysis technique for determining the glass transition temperature ( $T_g$ ) of polymer matrix composites because it is more sensitive to  $T_g$  measurements than other thermal analysis techniques. An interlaboratory study was developed and conducted by the American Society for Testing and Materials (ASTM) for its D7028-07 test standard ( $T_g$  by DMA) in 2007. The results of the study indicated that reproducibility was poor between DMA instruments and laboratories. A reproducibility standard deviation of 15.09°F and 14.72°F was found for dry  $T_g$  and wet  $T_g$  measurements, respectively.

Poor reproducibility of  $T_g$  measurements creates uncertainty in cases in which  $T_g$  measurements are used. Service temperature and process control determinations may be difficult to establish if reproducibility of  $T_g$  measurements remains poor.

The goal of this research was to improve laboratory-to-laboratory and instrument-to-instrument reproducibility. To accomplish this, several potential influencers of  $T_g$  measurements, such as thermocouple (TC) positioning, dimensional variation of specimens, and temperature calibration configurations and methods were evaluated. These evaluations were the framework for the development of TC guidelines and temperature calibration procedures to aid test operators in areas in which the test and calibration standards were not specific.

To assess if this goal was achieved, a follow-on interlaboratory study was conducted. A reproducibility standard deviation of 7.86°F and 7.30°F was determined for dry  $T_g$  and wet  $T_g$  measurements, respectively. When compared with the interlaboratory study conducted by ASTM, the follow-on interlaboratory study indicated a 50% improvement in the reproducibility of  $T_g$  measurements was achieved with the implementation of the developed TC guidelines and temperature calibration procedures.

## 1. INTRODUCTION

### 1.1 MOTIVATION AND KEY ISSUES

The general use of polymer matrix composites has increased significantly over the past 25 years. These materials are used primarily because of their superior specific strength and stiffness properties compared to metals. However, polymer matrix composites do not maintain integrity at temperatures as high as metals.

The glass transition temperature ( $T_g$ ) is the temperature associated with the transition from a glassy, solid state to a liquid or rubbery state in amorphous polymers (e.g. thermosets, thermoplastics, and semi-crystalline polymers). The service temperature of polymer matrix composites is most often defined by subtracting 50°F from the wet  $T_g$ . The wet  $T_g$  is found by subjecting a specimen to 85% relative humidity until effective equilibrium has been achieved.

The Bureau of Industry and Security (BIS) regulates polymer matrix composites within the Export Administration Regulations. The BIS sets higher restrictions on materials with higher service temperatures. Because of the lower working temperature of polymer matrix composites compared to metals, developers have examined ways to increase the service temperatures of these materials. As a response to potentially higher restrictions applied by BIS, acute emphasis and scrutiny will be placed on the methods of determining the service temperature of polymer matrix composites.

The  $T_g$  is often used as a process control tool. When a material system is developed, process controls are established and implemented for quality assurance. The  $T_g$  of a dried sample or a sample with minimal exposure to moisture is commonly referred to as the dry  $T_g$ , and is often used as a process inspection tool for the cure process. This is accomplished by establishing an allowable dry  $T_g$  that each cure process can be checked against.

Dynamic mechanical analysis (DMA) is the most widely used technique to determine  $T_g$  measurements. Other techniques, such as differential scanning calorimetry (DSC) and thermomechanical analysis (TMA), are also capable of determining  $T_g$ ; however, DMA is the preferred method because it is the most sensitive in defining the  $T_g$ . For example, the  $T_g$  of a highly cross-linked material (i.e. polymer matrix composites) can be difficult to determine by DSC because the change in heat capacity is very small. Similarly, when using TMA to determine the  $T_g$ , the change in CTE can be very small, which can make determining the  $T_g$  very difficult as well.

There are several companies worldwide that design and manufacture DMA instruments. The models vary in technology, accuracy, and precision, resulting in instrument-to-instrument reproducibility issues. Material suppliers, fabricators, and test laboratories are the primary users of DMA instruments.

Current DMA test standards were developed to aid in the reproducibility and repeatability of  $T_g$  measurements. However, differences in the test standards, some of which defer to either the instrument manufacturer or the test operator to select values and settings appropriate to the DMA

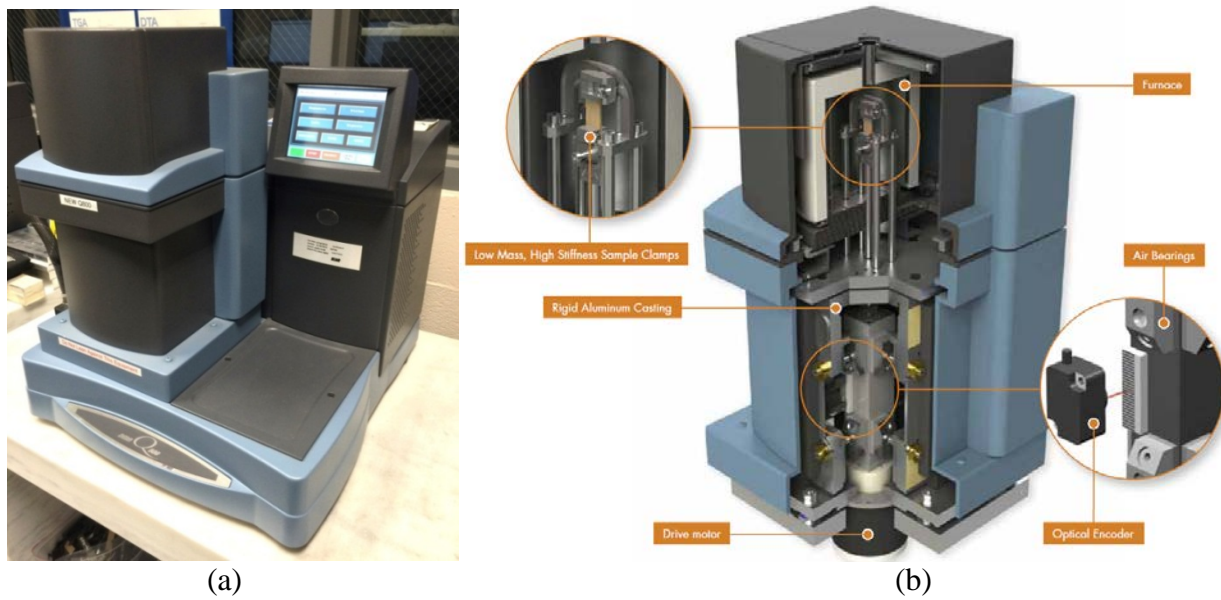
model used, have resulted in significant differences in  $T_g$  values in laboratory-to-laboratory results.

The American Society for Testing and Materials (ASTM) D30 committee conducted an interlaboratory study in 2007 to establish the precision statements of the ASTM D7028-07 test standard [1 and 2]. They found poor laboratory-to-laboratory and instrument-to-instrument reproducibility. Portions of the findings of this interlaboratory study are presented in this report. Additionally, significant differences in  $T_g$  measurements between material suppliers and test laboratories have been observed during material qualification test programs. These programs require the oversight and acceptance of the Federal Aviation Administration (FAA). In one extreme case, an aircraft manufacturer was nearly required to change materials midway through the material qualification process because of considerable differences between  $T_g$  values determined by the material supplier and test laboratory.

## 1.2 BACKGROUND

### 1.2.1 Definition of DMA

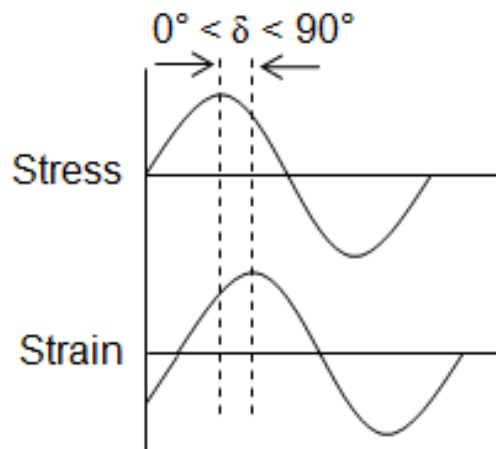
The DMA (figure 1) is the most sensitive thermal analysis technique for measuring the viscoelastic properties (e.g.,  $T_g$ ) of materials as they are deformed periodically under stress at a defined frequency [3]. The DMA instrument can determine the viscoelastic properties of a material by applying a variable sinusoidal stress, measuring the resulting sinusoidal strain, and determining the complex modulus. Most test standards require the user to input the displacement amplitude or strain. The user is also required to input a number of parameters. The span and type of fixture and the sample width and thickness are a few of the user defined parameters. The instrument software uses these parameters to calculate the stress/force required to achieve the desired amplitude or strain. The ASTM standard and manufacturer's operating manual describe this in detail.



**Figure 1. Typical design of a DMA, a) overview b) exploded view**

In brief, a test specimen is clamped and loaded (e.g., three-point flexural test) at a periodic sinusoidal frequency while enclosed in a thermal chamber. Various parameters are selected (e.g., frequency and amplitude) and the test specimen is exercised through a temperature range at the specified heating rate. Purge gas is introduced near the specimen to minimize the effect of products of decomposition. Typically, the strain is defined, the stress is measured, and the complex modulus is calculated from which the elastic (storage) modulus, the viscous (loss) modulus, and the tan delta are determined. The  $T_g$  can be determined from several measurements: the onset of the storage modulus curve ( $T_{gE'}$ ), the peak value of the loss modulus curve ( $T_{gE''}$ ), and the peak value of the tan delta curve ( $T_{g\tan\delta}$ ).

During loading a material that deforms in-phase with the application of stress is purely elastic, whereas a material that deforms  $90^\circ$  out-of-phase with the application of stress is purely viscous. However, most materials, including polymer matrix composites, are viscoelastic because they display both elastic and viscous behavior. Therefore, the phase angle for these materials is between  $0^\circ$  (in-phase) and  $90^\circ$ . The relationship of the phase angle to the stress-strain response is shown in figure 1.



**Figure 2. Viscoelastic stress-strain response and phase angle [3]**

The DMA instrument can separate this phenomenon because of its dynamic stress-strain application. The complex modulus, which is the measure of the overall resistance to deformation, can be determined from the stress-strain response.

The complex modulus is expressed by the following equation:

$$E^* = \text{stress/strain} \quad (1)$$

From the complex modulus, the elastic modulus ( $E'$ , also known as the storage modulus) can be determined by:

$$E' = E^* \cos \delta \quad (2)$$

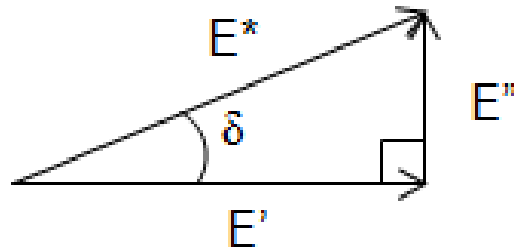
the viscous modulus ( $E''$ , also known as the loss modulus) can be determined by:

$$E'' = E^* \sin \delta \quad (3)$$

and  $\tan \delta$  can be determined by:

$$\tan \delta = E''/E' \quad (4)$$

The complex modulus vector is shown in figure 2.



**Figure 3. Complex modulus vector [3]**

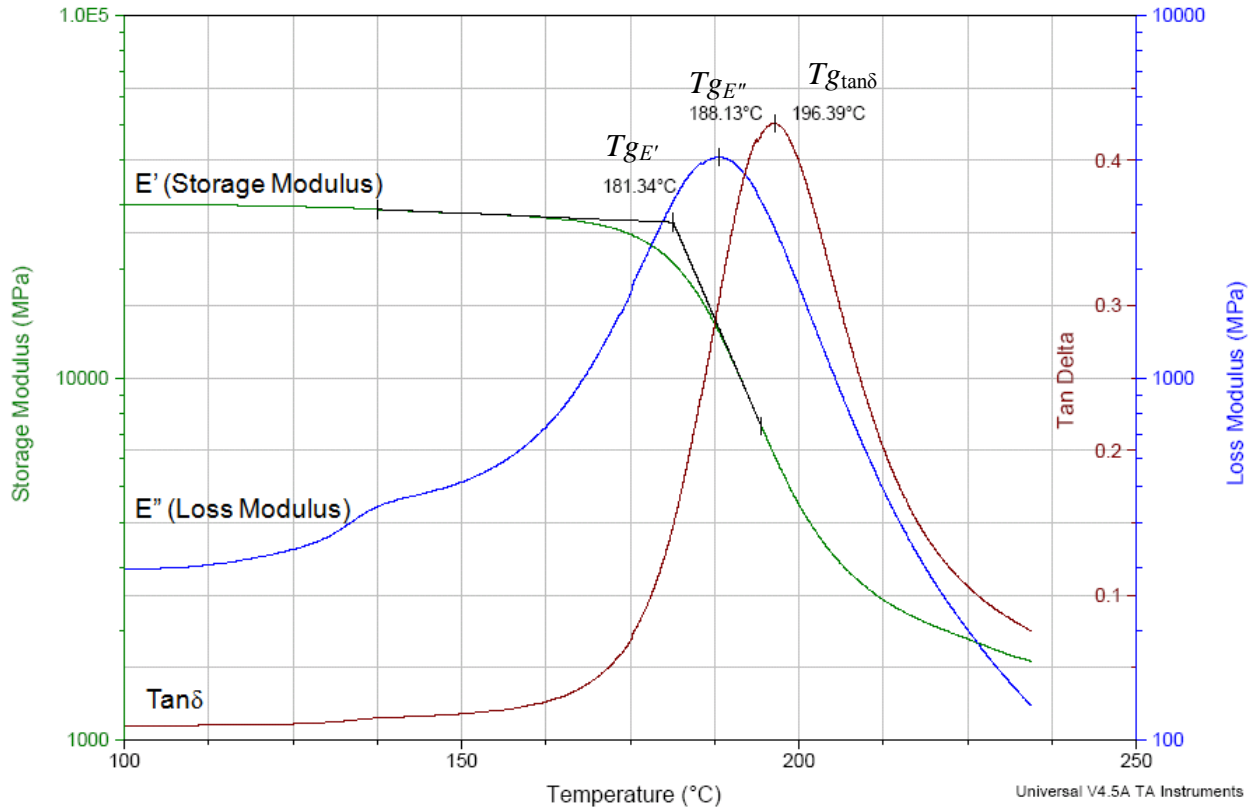
Data recorded by the DMA instrument can be plotted as a function of temperature for the determination of the  $T_g$ . A typical DMA plot for the determination of  $T_g$  is shown in figure 3.

The  $T_{gE'}$  is determined from the intersection of two tangent lines from the storage modulus ( $E'$ ) curve and is related to mechanical failure. The storage modulus is a measure of stress stored in the sample as mechanical energy, and is also known as the elastic modulus. The  $T_{gE'}$  occurs at the lowest temperature and is normally reported as DMA  $T_g$ . ASTM D7028 [2] and SACMA SRM 18R-94 [4] require the user to report the  $T_{gE'}$  as the DMA  $T_g$ .

The  $T_{gE''}$  is determined from the peak of the loss modulus ( $E''$ ) curve and is closely related to the physical property changes attributed to plastics. The loss modulus is a measure of stress dissipated as heat, and is also known as the viscous modulus. This is observed at the middle temperature and is normally used as means of comparison.

The  $T_{g_{\tan \delta}}$  is determined from the peak of the  $\tan \delta$  curve. The  $\tan \delta$  is the phase lag between stress and strain.  $T_{g_{\tan \delta}}$  relates to the damping properties and occurs at the highest temperature. It is normally used as means of comparison. [5].





**Figure 4. Typical DMA plot for the determination of  $T_g$**

### 1.2.2 ASTM D7028-07 Interlaboratory Study

During the development of the ASTM D7028-07 [2] standard for the determination of  $T_g$  by DMA for polymer matrix composites, the ASTM D30 committee conducted an interlaboratory study to determine precision statements for the standard. Precision statements are made in the precision and bias section of most ASTM standards. Precision statements were determined through statistical analysis of the  $T_g$  values reported from the interlaboratory study. Seven laboratories participated in the interlaboratory study. Participants included material suppliers, aircraft manufacturers, and test laboratories. Four polymer matrix composite materials (unitape and fabric reinforcement) were used to conduct dry and wet tests, in accordance with ASTM D7028-07 [2]. The chosen materials'  $T_g$  ranged from a high value of 503.6°F (average dry  $T_{gE'}$ ) to a low value of 174.2°F (average wet  $T_{gE'}$ ). Two specimens of each material were run for both dry and wet conditions by each laboratory.

Each laboratory was required to calibrate their instrument in accordance with ASTM D7028-07 [2]. However, according to appendix C of the report generated for the ASTM D7028-07 interlaboratory study [1], the laboratories used different calibration materials (polyvinyl chloride [PVC], polycarbonate, indium, tin, and zinc), heating rates (2°C/min, 3°C/min, 5°C/min, and 10°C/min), and procedures. The method of supporting or encapsulating the indium, tin, and zinc calibration melting standards was not reported. In some instances, the temperature calibration data was not used to modify the temperature readings, but only used as a temperature check.

Precision statements were produced by the ASTM committee and individual test data was reported in appendix C of the report generated for the ASTM D7028-07 interlaboratory study [1]. For the purposes of this report, the  $T_{gE'}$  statistics were calculated from the individual test data so that  $T_{gE'}$  statistics could be reported separately from  $T_{gE''}$  and  $T_{g_{\tan\delta}}$ . This was done because  $T_{gE'}$  is most commonly reported as the  $T_g$ .

From statistical analysis of the data, two important measurements can be determined: repeatability and reproducibility. According to ASTM E691-05 [5], repeatability is where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time. In contrast, reproducibility is where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment.

Using the  $T_{gE'}$  data, the repeatability and reproducibility standard deviations for the dry specimens were 2.36°F and 15.09°F, respectively, and 2.37°F and 14.72°F for the wet specimens, respectively. The  $T_{gE'}$  repeatability standard deviation indicates that these tests are highly repeatable within a particular laboratory; however, the large reproducibility standard deviation indicates that the laboratory-to-laboratory and instrument-to-instrument reproducibility is poor. Instrument-to-instrument reproducibility is the comparison of the results of two different DMA instruments within the same laboratory.

### 1.2.3 Ambiguity in Test and Calibration Standards

The most widely used test standards for the determination of  $T_g$  by DMA of polymer matrix composites are ASTM D7028-07 [2] and Suppliers of Advanced Composite Materials Association (SACMA) SACMA Recommended Method (SRM) 18R-94 [6]. These standards contain many of the same recommendations, such as a loading frequency of 1Hz and a heating rate of 5°C/min. However, many other parameters are taken from other standards, the instrument manufacturer, or are defined by the test user. Some of the undefined parameters include purge gas and flow rate, thermocouple (TC) location, specimen fiber orientation, calibration, specimen dimensions, type of bending fixture, and strain amplitude.

From a review of the ASTM D7028-07 interlaboratory study [1], it was evident that there were variations in the way the temperature calibration was conducted. This was believed to be primarily a result of ambiguity in the test and calibration standards. ASTM D7028-07 [2] requires users to follow ASTM E1867-13 [7] to temperature calibrate the DMA instrument, whereas SACMA SRM 18R-94 [6] requires input from the instrument manufacturer.

ASTM E1867-13 [7] requires the use of calibration melting standards and lists suitable materials and their melting points. Many of these melting standards are traceable by the National Institute of Standards and Technology (NIST). Among those listed in the standard, indium and tin apply to low-to-medium temperature polymer matrix materials. The nominal melting point of indium and tin are 156.60°C (313.88°F) and 231.93°C (449.57°F), respectively. However, indium and tin are insufficient in bounding the upper ranges of interest for bismaleimide and polyimide polymer matrix composites. Zinc has a nominal melting point of 419.47°C (787.05°F) and was listed in the standard prior to 2013, but removed in the most recent revision. ASTM E1867-13 [7] recommends the use of polytetrafluoroethylene (PTFE) or polyetheretherketone (PEEK)

tubing to encapsulate the calibration melting standards. However, PTFE has a maximum operating temperature of approximately 260°C (500°F), which prevents it from being used with high-temperature melting standards such as zinc. PEEK has a maximum operating temperature that is even lower than PTFE.

ASTM E1867-13 [7] does not recommend the use of polycarbonate or PVC as a calibration standard or calibration by an external TC; however, these calibration materials and techniques were all used in the ASTM D7028-07 interlaboratory study [1]. Currently, there is no recommended ASTM DMA procedure for use of high-temperature calibration standards, such as zinc.

In addition, the instrument manufacturers have not produced any viable calibration procedures or provided specific TC location recommendations beyond recommending that the TC be in close proximity to the sample. This has been identified as significant source of temperature variability. Before this research began, a check by the composites test laboratory at the National Institute for Aviation Research (NIAR) indicated that temperatures within the test furnace of their TA Instruments DMA Q800 varied by almost 30°F.

### 1.3 OBJECTIVE

The purpose of this research was to improve laboratory-to-laboratory and instrument-to-instrument reproducibility of DMA results. A literature review and input from DMA subject matter experts determined key variables that impacted the reproducibility of  $T_g$  measurements. They included TC positioning, dimensional variation of specimens, and temperature calibration configurations. These evaluations were used as the framework to develop guidelines and procedures for areas in which the test and calibration standards are not specific.

To assess whether reproducibility was improved through the developed guidelines and procedures, an interlaboratory study was conducted using many of the same participants from the ASTM D7028-07 interlaboratory study [1]. The findings of this interlaboratory study were compared with the ASTM D7028-07 interlaboratory study [1].

Multiple variables were evaluated throughout this research and many questions were answered about these variables; however, not all of the variables were able to be fully defined. Future research will be required to fully understand the implication of those undefined variables.

## 2. INVESTIGATIVE APPROACH

A multiphase approach was taken to address the laboratory-to-laboratory and instrument-to-instrument reproducibility issues of  $T_g$  measurements determined by DMA instruments. The basic research conducted under the first phase consisted of isolating specific variables that were deemed as potential influencers of  $T_g$  measurements. The targeted variables were the specimen TC location, specimen dimensions, and the calibration support beam dimensions, configurations, and materials. These variables, which were thought to affect repeatability and reproducibility of  $T_g$  measurements, were chosen from the findings of the literature review and discussion with subject matter experts. This basic research would prove beneficial to the subsequent phases.

The second phase consisted of the development of TC location guidelines and temperature calibration procedures by drawing upon the findings of the first phase. These guidelines and procedures were developed to address the reproducibility concerns and were also necessary to provide methods of producing accurate and reliable  $T_g$  measurements.

The third and final phase was developed to assess the significance and validity of the TC location guidelines and temperature calibration procedures. The laboratory-to-laboratory and instrument-to-instrument reproducibility was assessed through an interlaboratory study involving material suppliers, aircraft manufacturers, and test laboratories. Accuracy and reliability were evaluated by using other thermal analysis techniques (DSC and TMA). Four polymer matrix composite materials were used throughout the research. Each material was given a name for ease of referencing. The material identities were:

- 180F- $T_g$ -EPXY—Hysol EA9394, a two-part paste adhesive. The specimens were extracted from panels that were cured at room temperature for two days followed by a post-cure at 160°F for 20 minutes; 180°F was considered the nominal  $T_g$ .
- 350F- $T_g$ -EPXY—Cytec CYCOM<sup>®</sup> EP 2202 reinforced with IM7G unitape fiber (grade 190, resin content [RC] 33%). The specimens were extracted from panels fabricated with a cross-ply layup scheme. The 0.04"-thick panel consisted of a [0/90/0/90/0] ply orientation; the 0.08"-thick panel consisted of a [0/90/0/90/0/90/0/90/0/90/0] ply orientation; and the 0.12"-thick panel consisted of a [0/90]4s ply orientation. All panels were autoclave cured according to the National Center for Advanced Materials Performance (NCAMP) process specification NPS 82202 [8]; 350°F was considered the nominal  $T_g$ .
- 500F- $T_g$ -BMI—Cytec CYCOM 5250-5 reinforced with T650 6K-135 5-harness fabric (RC 35%). Specimens were extracted from panels fabricated of plies oriented at 0 degrees. All panels were autoclave cured according to the NCAMP process specification NPS 81226 [9]; 500°F was considered the nominal  $T_g$ .
- 600F- $T_g$ -EPXY—Renegade MVK-14 reinforced with T650 3K-135 8-harness fabric. Specimens were extracted from panels fabricated of plies oriented at 0 degrees. All panels were autoclave cured according to the NCAMP process specification NPS 81141 [10]; 600°F was considered the nominal  $T_g$ .

## 2.1 PHASE 1—BASIC RESEARCH

For purposes of conducting basic research, the TA Instruments DMA Q800 was used at the NIAR facility at Wichita State University. The DMA Q800 is the most commonly used DMA instrument in the aviation industry. Supplemental information on the DMA Q800 is provided in appendix A.

The mechanics and electronics of the DMA Q800 were calibrated according to the recommendations of TA Instruments; however, the temperature was not calibrated because the goal was to evaluate the data comparatively during the basic research phase.

All research was conducted with nitrogen purge gas with a flow rate of 50 mL/min per the recommendation of TA Instruments. All DMA tests were conducted at a heating rate of 5°C/min, consistent with the recommendations of ASTM D7028-07 [2] and SACMA SRM 18R-94 [6]. A 50mm 3-point bend and 35mm dual cantilever fixture were studied for each basic research evaluation.

### 2.1.1 Specimen TC Location Evaluation

The evaluation of TC location was conducted first because this information was used to determine the specimen TC location for the remaining research. These tests were conducted according to ASTM D7028-02(2) [2] under controlled strain and loading frequency of 1HZ.

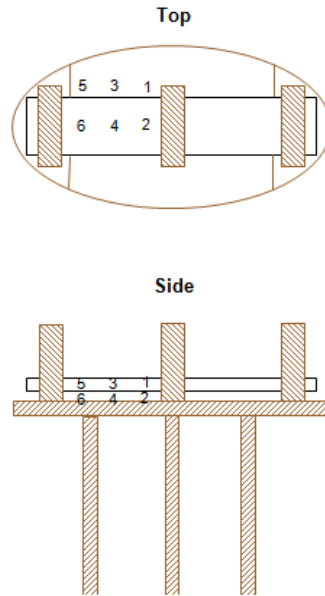
The location of the specimen TC was evaluated to assist in the determination of the recommended TC location for DMA calibration and testing. There are numerous variables in a DMA test that affect heat transfer to the sample. The primary variables are the fixture (mass, configuration, and material), furnace, and type and flow rate of purge gas. Because it would be difficult to mandate requirements for each of these variables across the industry, the specimen TC evaluation was conducted to determine the most appropriate location for determining accurate  $T_g$  measurements. Because the determination of  $T_g$  from the onset of the storage modulus is most often reported, it would be reasonable to associate this  $T_g$  measurement with the warmest region of the specimen because this would be the first region to lose its rigidity.

The specimen TC evaluation consisted of running DMA tests on numerous polymer matrix composite materials to determine the  $T_g$  at six different TC locations approximately 1mm–2mm from the test specimen. The locations were selected at several positions along the length of the specimen to assess the potential effects of the fixture and proximity to the furnace wall. These lengthwise locations were repeated, but moved laterally, underneath the specimen to examine the heat flow characteristics in this region. A 50mm 3-point bend and 35mm dual cantilever fixture were studied as part of this evaluation. Both fixtures were studied because their differences in mass and geometry were likely to affect the outcome of the evaluation. Four materials, with a wide spectrum of  $T_g$  values, were tested on both fixtures for each of the TC locations.

The test matrix for the specimen TC evaluation is shown in table 1. The TC locations are shown in figure 4. The DMA Q800 has a specimen and environment TC to control temperature. For all evaluations, only the specimen TC was considered.

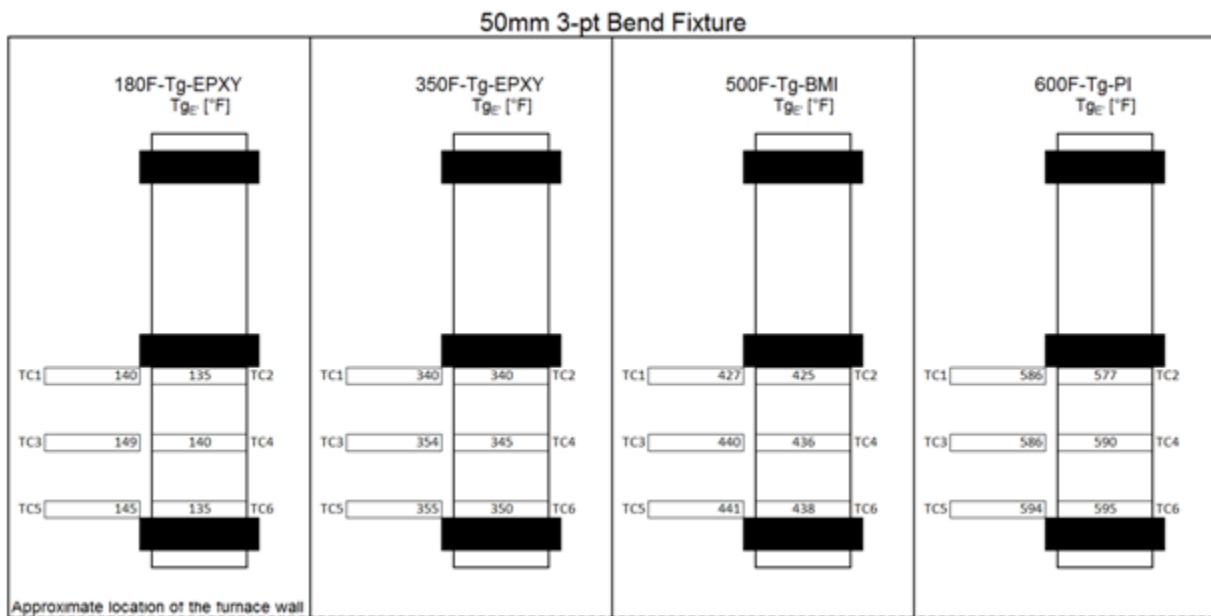
**Table 1. Test matrix for the specimen TC evaluation**

Property	Test Method	TC Location	Tests per Material x (Number of Materials)		Material ID
			50mm 3-pt Bend Fixture	35mm Dual Cantilever Fixture	
<i>T<sub>g</sub></i> , Dry, by DMA	ASTM D7028	1	1 x (4)	1 x (4)	180F- <i>T<sub>g</sub></i> -EPXY 350F- <i>T<sub>g</sub></i> -EPXY 500F- <i>T<sub>g</sub></i> -BMI 600F- <i>T<sub>g</sub></i> -PI
		2	1 x (4)	1 x (4)	180F- <i>T<sub>g</sub></i> -EPXY 350F- <i>T<sub>g</sub></i> -EPXY 500F- <i>T<sub>g</sub></i> -BMI 600F- <i>T<sub>g</sub></i> -PI
		3	1 x (4)	1 x (4)	180F- <i>T<sub>g</sub></i> -EPXY 350F- <i>T<sub>g</sub></i> -EPXY 500F- <i>T<sub>g</sub></i> -BMI 600F- <i>T<sub>g</sub></i> -PI
		4	1 x (4)	1 x (4)	180F- <i>T<sub>g</sub></i> -EPXY 350F- <i>T<sub>g</sub></i> -EPXY 500F- <i>T<sub>g</sub></i> -BMI 600F- <i>T<sub>g</sub></i> -PI
		5	1 x (4)	1 x (4)	180F- <i>T<sub>g</sub></i> -EPXY 350F- <i>T<sub>g</sub></i> -EPXY 500F- <i>T<sub>g</sub></i> -BMI 600F- <i>T<sub>g</sub></i> -PI
		6	1 x (4)	1 x (4)	180F- <i>T<sub>g</sub></i> -EPXY 350F- <i>T<sub>g</sub></i> -EPXY 500F- <i>T<sub>g</sub></i> -BMI 600F- <i>T<sub>g</sub></i> -PI

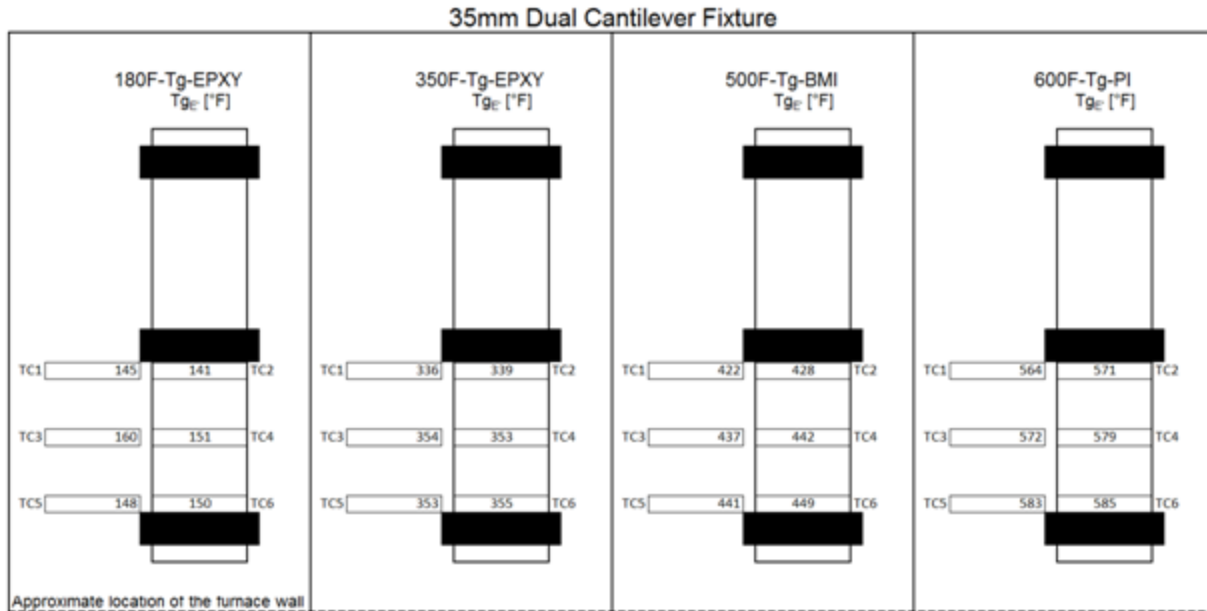


**Figure 5. Evaluation of specimen TC locations**

The  $Tg_{E'}$  measurements acquired from this evaluation are shown in figures 5 and 6 for the 50mm 3-point bend and 35mm dual cantilever fixtures, respectively.



**Figure 6. Findings of the specimen TC location evaluation for the 50mm 3-point bend fixture**



**Figure 7. Findings of the specimen TC location evaluation for the 35mm dual cantilever fixture**

As anticipated, temperatures near the fixture at the mid-span were consistently lower for all four materials that were tested (TC 1 and 2). However, the temperatures near the fixture end support (TC 5 and 6) became progressively higher than the other TC locations as the temperatures increased. Because the DMA Q800 instrument is heated through a bifilar coil along the furnace sidewall, the presumption was that the proximity of the specimen to the furnace sidewall was the cause of this behavior. The maximum gradient between TC locations was approximately 18°F for the 3-point bend fixture and 27°F for the dual cantilever fixture.

The TC locations underneath the specimen were ruled out as the optimal measurement location because of the concern that a highly deformable material could contact the TC, resulting in erroneous data and potentially damaging the TC. Ultimately, location 3 was selected because it was least affected by the heat sink effect of the fixture and the proximity to the furnace wall. This was important because these effects were likely to vary for each DMA model, which would negatively affect the laboratory-to-laboratory and instrument-to-instrument reproducibility. Additionally, the  $T_{gE}$  values measured at TC location 3 were consistently higher than most of the other locations. TC location 3 was used for the remaining evaluations. The proper specimen TC location may not be the same for all DMA instruments. It would be beneficial for test users to conduct a similar evaluation.

### 2.1.2 Specimen Dimensions Evaluation

Dimensional variation of specimens was considered primarily because of the concern of thermal lag within the specimen and the varying stiffness of the specimens. Because the standards allow for a range of specimen dimensions, this was seen as a possible cause for reproducibility issues. A test matrix was developed to test specimens within the range of the suggested specimen dimensions found in the ASTM [2] and SACMA [6] test standards. Only the 350F- $T_g$ -EPXY

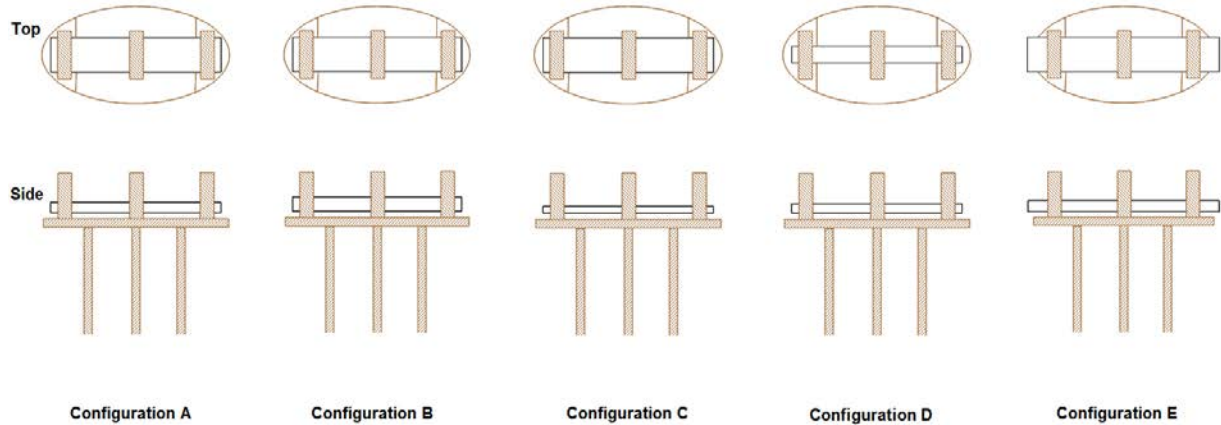


polymer matrix material was tested. It was assumed that most polymer matrix composite materials would be similarly affected by thermal lag and stiffness variation due to dimensional variation. Five configurations were evaluated; A was the baseline configuration. Only one dimensional variable was changed from the baseline configuration for each of the other configurations. These are noted as configurations B–E.

Table 2 defines the test plan for the specimen dimensions evaluation and figure 7 shows the various test configurations.

**Table 2. Test matrix for the specimen dimensions evaluation**

Property	Test Method	Configuration	Specimen Dimensions			Test per Material x (Number of Materials)		Material ID
			Thickness (in.)	Width (in.)	Length (in.)	50mm 3-pt Bend Fixture	35mm Dual Cantilever Fixture	
<i>T<sub>g</sub></i> , Dry, by DMA	ASTM D7028	A	0.08	0.5	2.5	1 x (1)	1 x (1)	350F- <i>T<sub>g</sub></i> -EPXY
		B	0.12	0.5	2.5	1 x (1)	1 x (1)	350F- <i>T<sub>g</sub></i> -EPXY
		C	0.04	0.5	2.5	1 x (1)	1 x (1)	350F- <i>T<sub>g</sub></i> -EPXY
		D	0.08	0.25	2.5	1 x (1)	1 x (1)	350F- <i>T<sub>g</sub></i> -EPXY
		E	0.08	0.5	2.25	1 x (1)	1 x (1)	350F- <i>T<sub>g</sub></i> -EPXY



**Figure 8. Evaluation of specimen dimensions and configurations**

These tests were conducted according to ASTM D7028-07 [2] under a controlled strain of 0.005% and 0.015% for the 3-point bend and dual cantilever, respectively, and a frequency of 1Hz. The  $T_{gE'}$  obtained from the evaluation are shown in table 3.

**Table 3. Findings of the specimen dimensions evaluation**

Property	Test Method	Configuration	Specimen Dimensions			$T_{gE}$ (°F)		Material ID
			Thickness (in.)	Width (in.)	Length (in.)	50mm 3-pt Bend Fixture	35mm Dual Cantilever Fixture	
$T_g$ , Dry, by DMA	ASTM D7028	A	0.06	0.5	2.5	371	374	350F- $T_g$ -EPXY
		B	0.12	0.5	2.5	365	375	350F- $T_g$ -EPXY
		C	0.04	0.5	2.5	385	384	350F- $T_g$ -EPXY
		D	0.08	0.25	2.5	381	385	350F- $T_g$ -EPXY
		E	0.08	0.5	2.25	372	373	350F- $T_g$ -EPXY

The evaluation showed that the  $T_g$  is dependent on specimen dimensions. However, the reason for this dependency was not revealed during the evaluation. The evaluation did provide insight for phase two, the development of temperature calibration procedures, which is found in section 2.2.

### 2.1.3 Calibration Support Beam Dimensions and Configurations Evaluation

Because ASTM E1867-13 [7] failed to specify a technique to support high-temperature calibration melting standards, various dimensions and configurations were evaluated with a rigid calibration support beam. This method was chosen because previous research had shown that sandwiching the melting standard between rigid beams was successful. The concern of heat transfer through the calibration support beam was similar to the concern of heat transfer through the specimen. Evaluating the calibration support beam at dimensions that represented the actual test sample seemed logical.

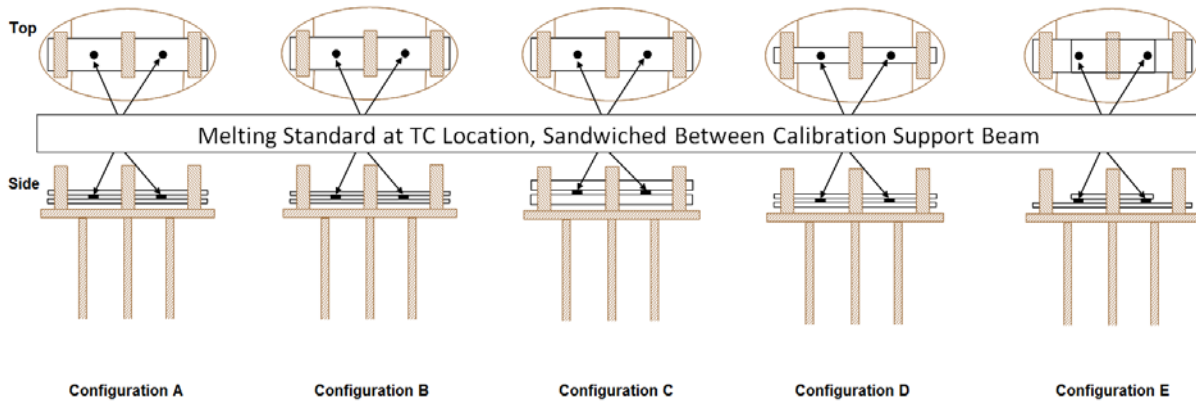
Evaluating the calibration support beam in this manner would help in understanding the thermal lag effect with actual test specimens. Because the calibration melting standard was sandwiched between support beams, the support beam thickness was chosen so that the overall thickness was comparable with the specimen dimensions from the dimensional evaluation of test specimens.

Only one support beam material was chosen for this evaluation. Because most polymer matrix composites considered in this research transfer heat similarly, it was assumed that most of these materials would similarly transfer heat to the calibration melting standard. The 500F- $T_g$ -BMI material was chosen because it could be used with indium and tin calibration melting standards because its dry  $T_g$  is sufficiently higher than both melting points.

The test matrix for the calibration support beam dimensions and configurations evaluation is shown in table 4. Figure 8 shows the various configurations. Because the TC was located midway from the fixture supports (TC location 3), two melting standards were required for each test: one to align with the TC and the other for symmetry with respect to the loading point. The melting standard was prepared to be between 2mg–5mg and 0.006”–0.01” thick to minimize the gap between the sandwich support beams.

**Table 4. Test matrix for the calibration support beam dimensions and configurations evaluation**

Property	Test Method	Configuration	Calibration Support Beam Dimensions			Test per Material x (Number of Materials)		Material ID
			Thickness (in.)	Width (in.)	Length (in.)	50mm 3-pt Bend Fixture	35mm Dual Cantilever Fixture	
Indium Melting Temperature	ASTM E1867	A	0.04	0.5	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F- $T_g$ -BMI
		B	0.02	0.5	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F- $T_g$ -BMI
		C	0.06	0.5	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F- $T_g$ -BMI
		D	0.04	0.25	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F- $T_g$ -BMI
		E	0.04	0.5	Bottom, 2.5 Top, 1.5	1 x (1)	1 x (1)	500F- $T_g$ -BMI
Tin Melting Temperature	ASTM E1867	A	0.04	0.5	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F- $T_g$ -BMI
		B	0.02	0.5	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F- $T_g$ -BMI
		C	0.06	0.5	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F- $T_g$ -BMI
		D	0.04	0.25	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F- $T_g$ -BMI
		E	0.04	0.5	Bottom, 2.5 Top, 1.5	1 x (1)	1 x (1)	500F- $T_g$ -BMI



**Figure 9. Evaluation of calibration support beam dimensions and configurations**

The melting temperature test was conducted under a constant force of 0.1N throughout the duration of the test. Displacement and temperature were recorded and plotted. The melting point was reported at the onset of melting, determined from the instantaneous increase in displacement. The melting temperature determined for each configuration is shown in table 5.

**Table 5. Findings of the calibration support beam dimensions and configurations evaluation**

Property	Test Method	Configuration	Calibration Support Beam Dimensions			T <sub>m</sub> (°F)		Material ID
			Thickness (in.)	Width (in.)	Length (in.)	50mm 3-pt Bend Fixture	35mm Dual Cantilever Fixture	
Indium Melting Temperature	ASTM E1867	A	0.04	0.5	Bottom, 2.5 Top, 2.5	323	335	500F-T <sub>g</sub> -BMI
		B	0.02	0.5	Bottom, 2.5 Top, 2.5	321	333	500F-T <sub>g</sub> -BMI
		C	0.06	0.5	Bottom, 2.5 Top, 2.5	323	334	500F-T <sub>g</sub> -BMI
		D	0.04	0.25	Bottom, 2.5 Top, 2.5	326	344	500F-T <sub>g</sub> -BMI
		E	0.04	0.5	Bottom, 2.5 Top, 1.5	321	334	500F-T <sub>g</sub> -BMI
Tin Melting Temperature	ASTM E1867	A	0.04	0.5	Bottom, 2.5 Top, 2.5	458	471	500F-T <sub>g</sub> -BMI
		B	0.02	0.5	Bottom, 2.5 Top, 2.5	455	467	500F-T <sub>g</sub> -BMI
		C	0.06	0.5	Bottom, 2.5 Top, 2.5	458	467	500F-T <sub>g</sub> -BMI
		D	0.04	0.25	Bottom, 2.5 Top, 2.5	458	472	500F-T <sub>g</sub> -BMI
		E	0.04	0.5	Bottom, 2.5 Top, 1.5	456	470	500F-T <sub>g</sub> -BMI

Most configurations had comparable melting temperatures. Configuration D, the narrow specimen, gave the highest melting temperatures for the conditions tested. Because the TC was not moved during any of the tests once it was positioned at location 3, the configuration D support beam was further from the TC, likely resulting in higher melting temperatures. A similar occurrence was observed during the specimen dimensions evaluation. This information was useful during the development of temperature calibration procedures.

#### 2.1.4 Calibration Support Beam Materials Evaluation

Materials were evaluated similarly to the calibration support beam configurations. For a two-point calibration that relies on interpolation rather than extrapolation, the ideal calibration support material would transfer heat comparably to the polymer matrix material to be tested, but maintain its rigidity above the melting temperatures of the calibration melting standards. For high-temperature materials, zinc is typically used because it melts at just under 800°F, exceeding the temperature range of interest for most tests.

An initial review process was undertaken to find several materials that maintain their rigidity up to 800°F and transfer heat similar to the materials to be tested. From this review, three materials were chosen: MACOR<sup>®</sup>, a machinable glass ceramic made by Corning Inc, lavastone, an

alumina silicate ceramic, and soda lime glass, a silica glass, commonly used for windows. Type 304 stainless steel was added to the candidate test matrix because it is a commonly used material and its properties are widely known.

A test matrix was developed to compare the polymer matrix composite materials already used in other parts of this research along with the candidate materials. To effectively evaluate and compare these materials for the purpose of the calibration support beam, melting temperature tests and thermal diffusivity tests were chosen.

The melting temperature tests for the polymer matrix composite materials and for the candidate materials are shown in tables 6 and 7, respectively.

**Table 6. Test matrix for the melting temperature tests of the polymer matrix composite materials**

Property	Test Method	Tests per Material x (Number of Materials)		Material ID
		50mm 3-pt Bend Fixture	35mm Dual Cantilever Fixture	
Indium Melting Temperature	ASTM E1867	3 x (3)	3 x (3)	350F- <i>Tg</i> -EPXY 500F- <i>Tg</i> -BMI 600F- <i>Tg</i> -PI
Tin Melting Temperature	ASTM E1867	3 x (2)	3 x (2)	500F- <i>Tg</i> -BMI 600F- <i>Tg</i> -PI

**Table 7. Test matrix for the melting temperature tests of the candidate materials**

Property	Test Method	Tests per Material x (Number of Materials)		Material ID
		50mm 3-pt Bend Fixture	35mm Dual Cantilever Fixture	
Indium Melting Temperature	ASTM E1867	3 x (4)	3 x (4)	MACOR Lavastone Soda Lime Glass Stainless Steel
Tin Melting Temperature	ASTM E1867	3 x (4)	3 x (4)	MACOR Lavastone Soda Lime Glass Stainless Steel

The melting temperature was determined in the same manner for the material evaluation as it was for the configuration evaluation. The polymer matrix composite materials evaluated were chosen for each calibration melting standard only if their dry *Tg* exceeded the melting temperature of the calibration standard.

The test matrix for the thermal diffusivity tests is shown in tables 8 and 9 for the polymer matrix composite materials and candidate materials, respectively.

**Table 8. Test matrix for the thermal diffusivity tests of the polymer matrix composite materials**

Property	Test Method	Temperature (°F)	Tests per Material x (Number of Materials)	Material ID
Specific Heat Capacity, Thermal Conductivity, and Thermal Diffusivity	ASTM E1461	77	1 x (4)	180F- <i>T<sub>g</sub></i> -EPXY 350F- <i>T<sub>g</sub></i> -EPXY 500F- <i>T<sub>g</sub></i> -BMI 600F- <i>T<sub>g</sub></i> -PI
		150	1 x (1)	180F- <i>T<sub>g</sub></i> -EPXY
		300	1 x (3)	350F- <i>T<sub>g</sub></i> -EPXY 500F- <i>T<sub>g</sub></i> -BMI 600F- <i>T<sub>g</sub></i> -PI
		450	1 x (2)	500F- <i>T<sub>g</sub></i> -BMI 600F- <i>T<sub>g</sub></i> -PI

**Table 9. Test matrix for the thermal diffusivity tests of the candidate materials**

Property	Test Method	Temperature (°F)	Tests per Material x (Number of Materials)	Material ID
Specific Heat Capacity, Thermal Conductivity, and Thermal Diffusivity	ASTM E1461	77	1 x (4)	MACOR Lavastone Soda Lime Glass Stainless Steel
		300	1 x (4)	MACOR Lavastone Soda Lime Glass Stainless Steel
		450	1 x (4)	MACOR Lavastone Soda Lime Glass Stainless Steel

The thermal diffusivity tests were conducted at temperatures close to the melting temperatures of indium and tin so that the melting temperature tests and diffusivity tests could be directly compared. However, in the case of the polymer matrix composite materials, the materials were only tested if the dry *T<sub>g</sub>* was above the desired test temperature. At least two temperatures were evaluated for thermal diffusivity so that a curve could be plotted over a temperature range. The curve was used to estimate the trend with respect to temperature so that behavior of the material could be predicted at temperatures as high as the melting point of zinc.

The specimens were machined at the NIAR facility but were sent to the Netzsch Instruments applications laboratory for thermal diffusivity testing. The specimens were tested following ASTM E1461-01 [11], using a NETZSCH LFA 447 Nanoflash™ instrument. The instrument follows the thermal diffusivity model of:

$$D = \frac{\lambda}{c_p \rho} \quad (5)$$

where  $D$  is the thermal diffusivity,  $\lambda$  is the thermal conductivity,  $c_p$  is the specific heat capacity, and  $\rho$  is the density.

The melting temperatures obtained from the tests of indium and zinc for both the polymer matrix composite materials and candidate materials are shown in table 10.

**Table 10. Findings of the melting temperature tests**

Property	Test Method	Material ID	Average $T_m$ (°F)	
			50mm 3-pt Bend Fixture	35mm Dual Cantilever Fixture
Indium Melting Temperature	ASTM E1867	350F- $T_g$ -EPXY	320	330
		500F- $T_g$ -BMI	320	330
		600F- $T_g$ -PI	318	328
		MACOR	317	328
		Lavastone	323	330
		Soda Lime Glass	318	328
		Stainless Steel	331	337
Tin Melting Temperature	ASTM E1867	500F- $T_g$ -BMI	454	464
		600F- $T_g$ -PI	453	463
		MACOR	453	460
		Lavastone	456	464
		Soda Lime Glass	454	461
		Stainless Steel	462	467

The melting temperatures obtained with the MACOR, lavastone, and soda lime glass support beams were very similar to the polymer matrix composite materials. To compare the data, an average of differences was calculated between the candidate materials and the average of the polymer matrix composite materials for all combinations of melting standards and fixtures. The average of differences was calculated by:

$$T_m \Delta^* = \frac{\sum_{i=1}^n T_m \Delta_i}{n} \quad (6)$$

where  $T_m\Delta_i$  is defined by:

$$T_m\Delta_i = T_mPM^*_i - T_mCM_i \quad (7)$$

and  $T_m\Delta^*$  is the average of differences of melting temperatures,  $T_mPM^*_i$  is the melting temperature determined when using the polymer matrix composite calibration support beam; averaged for all polymer matrix materials,  $T_mCM_i$  is the melting temperature of the candidate material calibration support beam,  $i$  is the  $i$ th combination of melting standards and fixtures, and  $n$  is the number of combinations.

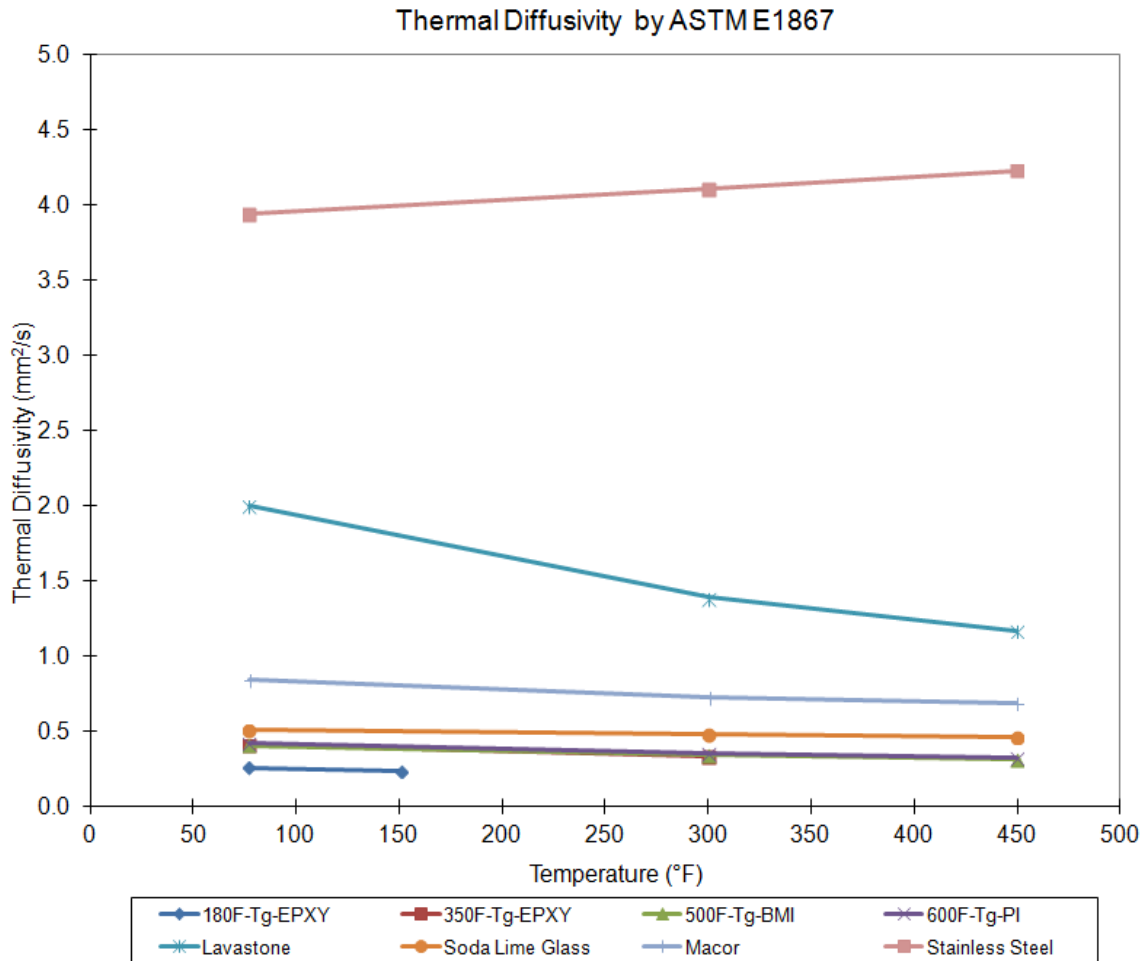
Using equation 6, the calculated  $T_m\Delta^*$  values are  $-1.73^\circ\text{F}$ ,  $1.77^\circ\text{F}$ ,  $-1.34^\circ\text{F}$ , and  $7.34^\circ\text{F}$  for MACOR, lavastone, soda lime glass, and stainless steel, respectively. These values indicate that the MACOR, lavastone, and soda lime glass support beams resulted in melting temperatures that were less than  $2^\circ\text{F}$  different than the average melting temperature of the polymer matrix composite materials for all combinations. Melting temperatures obtained when using the stainless steel support beam were significantly higher.

A summary of the thermal diffusivities determined for the polymer matrix and candidate materials is shown in table 11. The diffusivities are plotted as a function of temperature for each material in figure 9.



**Table 11. Findings of the thermal diffusivity tests**

Property	Test Method	Temperature (°F)	Material ID	Thermal Diffusivity (mm <sup>2</sup> /s)
Specific Heat Capacity, Thermal Conductivity, and Thermal Diffusivity	ASTM E1461	77	180F- <i>Tg</i> -EPXY	0.255
			350F- <i>Tg</i> -EPXY	0.407
			500F- <i>Tg</i> -BMI	0.404
			600F- <i>Tg</i> -PI	0.418
			MACOR	0.844
			Lavastone	2.00
			Soda Lime Glass	0.505
			Stainless Steel	3.94
		150	180F- <i>Tg</i> -EPXY	0.231
		300	350F- <i>Tg</i> -EPXY	0.331
			500F- <i>Tg</i> -BMI	0.341
			600F- <i>Tg</i> -PI	0.348
			MACOR	0.727
			Lavastone	1.39
			Soda Lime Glass	0.477
		450	Stainless Steel	4.11
			500F- <i>Tg</i> -BMI	0.310
			600F- <i>Tg</i> -PI	0.319
			MACOR	0.684
			Lavastone	1.17
			Soda Lime Glass	0.461
Stainless Steel	4.23			



**Figure 10. Findings of the thermal diffusivity tests**

MACOR and soda lime glass were thermally similar to the polymer matrix composite materials when using thermal diffusivity as a gauge. Stainless steel did not transfer heat similarly to polymer matrix composite materials. The thermal diffusivity data correlates well with the melting temperature tests. This was expected because the ability of heat to transfer through the calibration support beam directly affects the occurrence of the melting temperature. MACOR is recommended because it meets the criteria of a calibration support beam, it is easily machinable, and it is readily available. The findings of this evaluation were important in the process of developing temperature calibration procedures.

## 2.2 PHASE 2—DEVELOPMENT OF TC LOCATION GUIDELINES AND TEMPERATURE CALIBRATION PROCEDURES

The basic research conducted at the onset was crucial to the development of the TC location guidelines and temperature calibration procedures. The evaluations were reviewed and recommendations, guidelines, and calibration procedures were made from those findings.

TC location 3 was recommended because it was least affected by the fixture (heat sink effects) and the proximity of the furnace sidewall (heat generated through the furnace sidewall). This consideration was made because these effects are likely to be different for each DMA model, which would negatively affect the laboratory-to-laboratory and instrument-to-instrument reproducibility. Additionally,  $T_g$  values from TC location 3 were consistently at or near the highest of the other locations.

With the TC at location 3, there were not any significant differences seen in the measured melting temperature when calibration support beams of variable dimensions were evaluated. Therefore, a specific size requirement was not given in the developed temperature calibration procedures. However, a recommendation was made to use a calibration support beam that was similar in size to the intended test specimen.

The thermal evaluation of candidate calibration support beam materials suggests that materials with similar heat transfer abilities as those of the intended test materials should serve as a valid material for the purpose of supporting the calibration melting standard. The recommendation included in the developed temperature calibration procedures was for the calibration support beam to have a similar thermal diffusivity as the intended test specimen.

Details of the recommended specimen TC location guidelines and temperature calibration procedures are provided in appendix E and summarized in table 12.

**Table 12. Recommendations for TC location guidelines and temperature calibration procedures**

Description	Recommendation
Thermocouple - Position	Position the thermocouple to the side of the specimen (within 1mm–2mm) and mid-way between the fixture points.
Temperature Calibration - Calibration Support Beam - Configuration	Use a two-piece calibration support beam configuration to sandwich the calibration melting standard.
Temperature Calibration - Calibration Support Beam - Size	Use a calibration support beam that is similar in size to the intended test specimen.
Temperature Calibration - Calibration Support Beam - Material Selection	Select a material for the calibration support beam that has a similar thermal diffusivity to the intended test specimen and that can maintain rigidity beyond the melting temperature of the calibration melting standards to be used.
Temperature Calibration - Calibration Melting Standard - Position	Position the calibration melting standard at the same location along the length as the thermocouple.

### 2.3 PHASE 3—ASSESSING THE SIGNIFICANCE AND VALIDITY OF THE DEVELOPED TC GUIDELINES AND CALIBRATION PROCEDURES

The evaluation of the significance and validity of the developed TC guidelines and calibration procedures was completed in two ways. First, an interlaboratory study was designed; the ASTM D7028-07 interlaboratory study from 2007 [1] was used as a baseline for a comparative analysis. The second evaluation was conducted by comparing the  $T_g$  values achieved from the interlaboratory study with other thermal analysis techniques. The methodology of determining significance and validity is described in sections 2.3.1 and 2.3.2.

#### 2.3.1 Interlaboratory Study

The interlaboratory study was designed to test the developed TC guidelines and calibration procedures over a large range of temperatures. Materials with  $T_{gE'}$  values ranging from 180°F–600°F (nominally) were tested. Polycarbonate was added to the test matrix because it is known to be used as a calibration standard. The  $T_g$  values from the polycarbonate, determined through the interlaboratory study, can be compared to the defined  $T_g$  of polycarbonate. The difference between  $T_g$  values from the interlaboratory study and defined values would serve as a comparison for the two calibration methods.

Each laboratory from the ASTM D7028-07 interlaboratory study [1] was asked to participate in this study. One laboratory declined because their DMA instrument was in the process of relocation and another laboratory had previous commitments. Five laboratories participated: The Boeing Company, Cyttec, Hexcel, Intec, and NIAR.

Each laboratory was required to perform the developed calibration procedures using indium and zinc prior to testing. Testing was conducted in accordance with ASTM D7028-07 [2] on five materials in the dry condition and four materials in the wet condition. Three replicates of each material were tested for each test condition. Each laboratory followed the test requirements in table 13.

**Table 13. Test matrix for the interlaboratory study**

Property	Test Method	Tests per Material x (Number of Materials)		Material ID
		50mm 3-pt Bend Fixture	35mm Dual Cantilever Fixture	
		Interlaboratory Study	Interlaboratory Study	
DMA Temperature Calibration	ASTM E1867	1 x (2)	1 x (2)	Indium Zinc
DMA Temperature Verification	ASTM E1867	1 x (2)	1 x (2)	Indium Zinc
$T_g$ , Dry, by DMA	ASTM D7028	3 x (5)	3 x (5)	180F- $T_g$ -EPXY 350F- $T_g$ -EPXY 500F- $T_g$ -BMI 600F- $T_g$ -PI Polycarbonate
$T_g$ , Wet, by DMA	ASTM D7028	3 x (4)	3 x (4)	180F- $T_g$ -EPXY 350F- $T_g$ -EPXY 500F- $T_g$ -BMI 600F- $T_g$ -PI

Calibration and test materials were provided for each test laboratory. Each laboratory was provided with MACOR calibration support beams and NIST traceable indium and zinc calibration melting standards. The dry  $T_g$  specimens were dried at 160°F until equilibrium (except the 180F- $T_g$ -EPXY specimens) and stored in a sealed polyethylene bag with desiccant. Since the 180F- $T_g$ -EPXY specimens were cured at 160°F, it was not feasible to dry them at elevated temperature due to concerns of additional curing at elevated temperature. The as-fabricated specimens were stored in a sealed polyethylene bag with desiccant.

The wet  $T_g$  specimens were conditioned at 160°F and 85% relative humidity (except the 180F- $T_g$ -EPXY specimens) until effective equilibrium was reached. The 180F- $T_g$ -EPXY specimens were conditioned in a 100°F water bath until effective equilibrium was reached. The 180F- $T_g$ -EPXY specimens required a lower conditioning temperature so that the specimens were not post-cured during the conditioning process. Effective equilibrium was defined as less than 0.02% weight change over two periods of seven days. After conditioning, the wet specimens were stored in a sealed polyethylene bag with a damp cloth. All dry and wet specimens were sent to the respective laboratories within two weeks of conditioning. However, specimens were not tested during the same time period because of instrument availability.

DMA instruments from three different manufacturers, including four different models, were used. Pictures of each DMA instrument model are presented in appendices A–D. Not all of the pictures are from the interlaboratory study, as such, they should be viewed for reference only. The use of thicker specimens was preferred because of moisture retention considerations of the wet specimens during the DMA test. However, force limitations required thinner specimens for two instrument models. The length of the specimens was determined by the span length of the fixture and the width was adjusted with length-to-width and thickness-to-width ratios in mind. Both nitrogen and air were used as purge gases. Eleven configurations were tested. The test configurations of each test laboratory are shown in table 14.

**Table 14. Test configurations of each test laboratory**

Laboratory	Instrument	Purge Gas Type	Fixture	Specimen Dimensions (Nominal) Length x Width x Thickness (in.)
1	TA DMA 2980	Air	3-pt Bend	2.5" x 0.5" x 0.12"
			Dual Cantilever	
2	TA DMA 2980	Nitrogen	3-pt Bend	2.5" x 0.5" x 0.12"
			Dual Cantilever	
3	RS DMTA Mk V	Nitrogen	3-pt Bend	2" x 0.315" x 0.06"
			Dual Cantilever	
4	TA DMA Q800	Air	3-pt Bend	2.5" x 0.5" x 0.12"
			Dual Cantilever	
	PE DMA 7e	Helium	3-pt Bend	1" x 0.2" x 0.05"
5	TA DMA Q800	Nitrogen	3-pt Bend	2.5" x 0.5" x 0.12"
			Dual Cantilever	

### 2.3.2 Accuracy and Reliability of Developed TC Guidelines and Temperature Calibration Procedures

Several other thermal analysis techniques were used as a means to validate the accuracy and reliability of the  $T_g$  values obtained through the use of the developed TC guidelines and temperature calibration procedures. DSC and thermomechanical techniques were used to determine the dry  $T_g$  of the same materials tested in the interlaboratory study.

The DSC instrument operates by measuring heat flow through a sample as a function of temperature. The  $T_g$  is identified by a shift in the heat flow curve, which occurs because of a change in the heat capacity of the material. The heat capacity change is a phenomenon that occurs at the  $T_g$ . A TA Instruments DSC Q1000 was used to perform these tests. The instrument was calibrated and tested according to ASTM D3418-08 [12] and recommendations from TA Instruments. Three replicates of each material were tested in the dry condition.

The TMA instrument operates by measuring the displacement of a sample through contact with a probe over a temperature range of interest. The  $T_g$  can be identified by two methods. The first method is through thermal expansion. The  $T_g$  is known to cause a change in a material's thermal expansion rate. This rate change is observable from a graph of the displacement plotted as a function of temperature. The second method is a modified version of the first method that involves using a knife edge probe and support platform to conduct a 3-point flexure test. The deflection of the sample is plotted against temperature and the  $T_g$  is determined at the onset of deflection. The onset of deflection is determined from the intersection of lines drawn tangent to the slope of the curve prior to the transition and the slope of the curve during the transition.

A TA Instruments TMA Q400 was used to perform these tests. The instrument was calibrated and tested according to ASTM E1545-11 [13] and recommendations from TA Instruments. Three replicates of each material were tested in the dry condition.

Table 15 lists the test matrix for the accuracy and reliability evaluation.

**Table 15. Test matrix for the accuracy and reliability evaluation**

Property	Test Method	Tests per Material x (Number of Materials)	Material ID
<i>T<sub>g</sub></i> , Dry, by DSC	ASTM D3418	3 x (5)	180F- <i>T<sub>g</sub></i> -EPXY 350F- <i>T<sub>g</sub></i> -EPXY 500F- <i>T<sub>g</sub></i> -BMI 600F- <i>T<sub>g</sub></i> -PI Polycarbonate
<i>T<sub>g</sub></i> , Dry, by TMA Expansion	ASTM E1545, Procedure A	3 x (5)	180F- <i>T<sub>g</sub></i> -EPXY 350F- <i>T<sub>g</sub></i> -EPXY 500F- <i>T<sub>g</sub></i> -BMI 600F- <i>T<sub>g</sub></i> -PI Polycarbonate
<i>T<sub>g</sub></i> , Dry, by TMA Flex	ASTM E1545, Modified, Procedure B	3 x (5)	180F- <i>T<sub>g</sub></i> -EPXY 350F- <i>T<sub>g</sub></i> -EPXY 500F- <i>T<sub>g</sub></i> -BMI 600F- <i>T<sub>g</sub></i> -PI Polycarbonate

### 3. FINDINGS

#### 3.1 INTERLABORATORY TEST RESULTS

In this section, the results of the interlaboratory study and the accuracy and reliability evaluation of the developed TC guidelines and calibration procedures are provided. The averaged *T<sub>g</sub>* values ( $\bar{X}$ ) obtained from each laboratory are presented for each material. The repeatability standard deviation ( $S_r$ ) and reproducibility standard deviation ( $S_R$ ) for the  $T_{gE'}$  was determined according to ASTM E691-05 [5] and is also provided in the tables.  $T_{gE'}$  was chosen because it is commonly reported as the *T<sub>g</sub>*. Cells contain the letters NDR if no data was reported. A hyphen (-) was input in a cell if the test was conducted and a plot was generated, but the *T<sub>g</sub>* was not determinable. Cells containing an asterisk (\*) after the *T<sub>g</sub>* value indicate that there was only one determinable *T<sub>g</sub>* value; the value presented is not actually an average.

##### 3.1.1 Interlaboratory Test Results for 180F-*T<sub>g</sub>*-EPXY

Data from 27 dry and 26 wet 180F-*T<sub>g</sub>*-EPXY specimens were analyzed to determine the repeatability and reproducibility standard deviations. The results are shown in table 16. Reproducibility standard deviations of 7.084°F and 5.341°F were determined for the dry and wet test specimens, respectively.

**Table 16. Interlaboratory test results for 180F- $T_g$ -EPXY**

Instrument	Purge Gas Type	Specimen Dimensions (Nominal) Length x Width x Thickness (in.)	Fixture	Average $T_g$ of 180F- $T_g$ -EPXY					
				(°F)					
				Dry $T_{gE'}$	Dry $T_{gE''}$	Dry $T_{g\tan\delta}$	Wet $T_{gE'}$	Wet $T_{gE''}$	Wet $T_{g\tan\delta}$
TA DMA 2980	Air	2.5" x 0.5" x 0.12"	3-pt Bend	NDR	NDR	NDR	-	177	232
			Dual Cantilever	147	205	218	110	169	241
TA DMA 2980	Nitrogen	2.5" x 0.5" x 0.12"	3-pt Bend	150	213	224	116	173	241
			Dual Cantilever	151	220	235	114	181	246
TA DMA Q800	Air	2.5" x 0.5" x 0.12"	3-pt Bend	145	210	219	113	175	-
			Dual Cantilever	151	216	226	118	176	-
TA DMA Q800	Nitrogen	2.5" x 0.5" x 0.12"	3-pt Bend	141	207	217	116	173	244
			Dual Cantilever	146	213	222	124	182	255
RS DMTA Mk V	Nitrogen	2" x 0.315" x 0.06"	3-pt Bend	138*	201*	202*	111	-	-
			Dual Cantilever	135	207	-	-	-	-
PE DMA 7e	Helium	1" x 0.2" x 0.05"	3-pt Bend	150	199	211	112	-	136*
Statistical Analysis of Interlaboratory Test Results—ASTM E691				180F- $T_g$ -EPXY Interlaboratory Statistics					
				Dry $T_{gE'}$ (°F)			Wet $T_{gE'}$ (°F)		
				$\bar{X}$	$S_r$	$S_R$	$\bar{X}$	$S_r$	$S_R$
				146.380	5.314	7.084	115.197	3.777	5.341

NDR = No data reported

\* = Only one determinable  $T_g$  value was reported; not an average

- =  $T_g$  was not determinable

### 3.1.2 Interlaboratory Test Results for 350F- $T_g$ -EPXY

Data from 30 dry and 31 wet 350F- $T_g$ -EPXY specimens were analyzed to determine the repeatability and reproducibility standard deviations. The results are shown in table 17. Reproducibility standard deviations of 6.422°F and 5.657°F were determined for the dry and wet test specimens, respectively.



**Table 17. Interlaboratory test results for 350F-*T<sub>g</sub>*-EPXY**

Instrument	Purge Gas Type	Specimen Dimensions (Nominal) Length x Width x Thickness (in.)	Fixture	Average <i>T<sub>g</sub></i> of 350F- <i>T<sub>g</sub></i> -EPXY					
				(°F)					
				Dry <i>T<sub>gE'</sub></i>	Dry <i>T<sub>gE''</sub></i>	Dry <i>T<sub>g<sub>tanδ</sub></sub></i>	Wet <i>T<sub>gE'</sub></i>	Wet <i>T<sub>gE''</sub></i>	Wet <i>T<sub>g<sub>tanδ</sub></sub></i>
TA DMA 2980	Air	2.5" x 0.5" x 0.12"	3-pt Bend	357*	369*	381*	271	284	295
			Dual Cantilever	359	371	386	268	286	299
TA DMA 2980	Nitrogen	2.5" x 0.5" x 0.12"	3-pt Bend	365	378	389	275	292	302
			Dual Cantilever	358	370	384	269	286	301
TA DMA Q800	Air	2.5" x 0.5" x 0.12"	3-pt Bend	367	380	391	280	297	306
			Dual Cantilever	362	375	390	268	285	298
TA DMA Q800	Nitrogen	2.5" x 0.5" x 0.12"	3-pt Bend	362	370	386	272	285	302
			Dual Cantilever	363	375	388	276	292	305
RS DMTA Mk V	Nitrogen	2" x 0.315" x 0.06"	3-pt Bend	378	391	399	282	301	309
			Dual Cantilever	361	376	387	271	287	299
PE DMA 7e	Helium	1" x 0.2" x 0.05"	3-pt Bend	355	370	382	265	282	290
Statistical Analysis of Interlaboratory Test Results—ASTM E691				350F- <i>T<sub>g</sub></i> -EPXY Interlaboratory Statistics					
				Dry <i>T<sub>gE'</sub></i> (°F)			Wet <i>T<sub>gE'</sub></i> (°F)		
				$\bar{X}$	$S_r$	$S_R$	$\bar{X}$	$S_r$	$S_R$
				362.248	1.795	6.422	272.428	2.127	5.657

\* = Only one determinable *T<sub>g</sub>* value was reported; not an average

### 3.1.3 Interlaboratory Test Results for 500F-*T<sub>g</sub>*-BMI

Data from 30 dry and 26 wet 500F-*T<sub>g</sub>*-BMI specimens were analyzed to determine the repeatability and reproducibility standard deviations. The results are shown in table 18. Reproducibility standard deviations of 9.490°F and 8.194°F were determined for the dry and wet test specimens, respectively.

**Table 18. Interlaboratory test results for 500F- $T_g$ -BMI**

Instrument	Purge Gas Type	Specimen Dimensions (Nominal) Length x Width x Thickness (in.)	Fixture	Average $T_g$ of 500F- $T_g$ -BMI					
				(°F)					
				Dry $T_{gE'}$	Dry $T_{gE''}$	Dry $T_{g\tan\delta}$	Wet $T_{gE'}$	Wet $T_{gE''}$	Wet $T_{g\tan\delta}$
TA DMA 2980	Air	2.5" x 0.5" x 0.12"	3-pt Bend	NDR	NDR	NDR	344	388	396
			Dual Cantilever	504	528	542	342	379	397
TA DMA 2980	Nitrogen	2.5" x 0.5" x 0.12"	3-pt Bend	508	539	548	354	394	405
			Dual Cantilever	505	530	544	339	377	394
TA DMA Q800	Air	2.5" x 0.5" x 0.12"	3-pt Bend	505	537	547	364	398	409
			Dual Cantilever	505	529	541	352	387	403
TA DMA Q800	Nitrogen	2.5" x 0.5" x 0.12"	3-pt Bend	521	545	558	353	385	403
			Dual Cantilever	521	547	559	349	382	401
RS DMTA Mk V	Nitrogen	2" x 0.315" x 0.06"	3-pt Bend	523	557	564	-	411	-
			Dual Cantilever	510	544	556	340	391	410
PE DMA 7e	Helium	1" x 0.2" x 0.05"	3-pt Bend	495	538	550	-	-	-
Statistical Analysis of Interlaboratory Test Results—ASTM E691				500F- $T_g$ -BMI Interlaboratory Statistics					
				Dry $T_{gE'}$ (°F)			Wet $T_{gE'}$ (°F)		
				$\bar{X}$	$S_r$	$S_R$	$\bar{X}$	$S_r$	$S_R$
				509.727	3.359	9.490	348.837	1.736	8.194

NDR = No data reported  
 - =  $T_g$  was not determinable

**3.1.4 Interlaboratory Test Results for 600F- $T_g$ -PI**

Data from 30 dry and 21 wet 600F- $T_g$ -PI specimens were analyzed to determine the repeatability and reproducibility standard deviations. The results are shown in table 19. The wet  $T_g$  data with grey shaded cells were omitted from the statistical analysis because the data were significantly higher than the average of the other data, likely due to dry-out of the specimens during the DMA test. Because these specimens were significantly thinner, less moisture was likely in the specimens at the  $T_g$ . The small difference between the dry and wet  $T_g$  values further illustrates the likeliness of dry-out. Further explanation of the phenomenon is provided in section 4.3. The statistical values are listed in the table with a caret (^) after their value to indicate that data in the grey-shaded cells were omitted. Resulting reproducibility standard deviations of 12.947°F and 9.992°F were determined for the dry and wet test specimens, respectively.

**Table 19. Interlaboratory test results for 600F-*T<sub>g</sub>*-PI**

Instrument	Purge Gas Type	Specimen Dimensions (Nominal) Length x Width x Thickness (in.)	Fixture	Average <i>T<sub>g</sub></i> of 600F- <i>T<sub>g</sub></i> -PI					
				(°F)					
				Dry <i>T<sub>gE'</sub></i>	Dry <i>T<sub>gE''</sub></i>	Dry <i>T<sub>g tan δ</sub></i>	Wet <i>T<sub>gE'</sub></i>	Wet <i>T<sub>gE''</sub></i>	Wet <i>T<sub>g tan δ</sub></i>
TA DMA 2980	Air	2.5" x 0.5" x 0.12"	3-pt Bend	NDR	NDR	NDR	-	-	-
			Dual Cantilever	584	614	636	422	455	471
TA DMA 2980	Nitrogen	2.5" x 0.5" x 0.12"	3-pt Bend	605	630	645	434	474	487
			Dual Cantilever	595	626	647	421	455	469
TA DMA Q800	Air	2.5" x 0.5" x 0.12"	3-pt Bend	601	630	648	442	480	496*
			Dual Cantilever	587	613	637	432	467	480
TA DMA Q800	Nitrogen	2.5" x 0.5" x 0.12"	3-pt Bend	615	636	653	445	474	489
			Dual Cantilever	612	638	659	423	457	471
RS DMTA Mk V	Nitrogen	2" x 0.315" x 0.06"	3-pt Bend	625	656	668	600	625	643
			Dual Cantilever	604	633	649	588	609	626
PE DMA 7e	Helium	1" x 0.2" x 0.05"	3-pt Bend	604	631	648	592	613	633
Statistical Analysis of Interlaboratory Test Results—ASTM E691				600F- <i>T<sub>g</sub></i> -PI Interlaboratory Statistics					
				Dry <i>T<sub>gE'</sub></i> (°F)			Wet <i>T<sub>gE'</sub></i> (°F)		
				$\bar{X}$	$S_r$	$S_R$	$\bar{X}$	$S_r$	$S_R$
				603.175	4.631	12.947	431.260^	2.977^	9.992^

NDR = No data reported

\* = Only one determinable *T<sub>g</sub>* value was reported; not an average

^ = data in the grey-shaded boxes was omitted from the result

### 3.1.5 Interlaboratory Test Results for Polycarbonate

Data from 22 dry polycarbonate specimens were analyzed to determine the repeatability and reproducibility standard deviations. The results are shown in table 20. A reproducibility standard deviation of 3.341°F was determined for the dry test specimens. Nearly all of the data generated from the 3-point bend test fixture resulted in undeterminable *T<sub>g</sub>* values. This is because polycarbonate becomes deformable at the *T<sub>g</sub>* (plastically deforming). Because the 3-point bend fixture does not mechanically clamp the specimen, the load/displacement bar was thought to have lost contact with the specimen, resulting in erroneous data. Because the dual cantilever fixture mechanically clamps the specimen, the load bearing member maintains contact with the specimen throughout the test. Materials that behave in this manner are better suited for the dual cantilever fixture.

**Table 20. Interlaboratory test results for polycarbonate**

Instrument	Purge Gas Type	Specimen Dimensions (Nominal) Length x Width x Thickness (in.)	Fixture	Average $T_g$ of Polycarbonate		
				(°F)		
				Dry $T_{gE'}$	Dry $T_{gE''}$	Dry $T_{g\tan\delta}$
TA DMA 2980	Air	2.5" x 0.5" x 0.12"	3-pt Bend	NDR	NDR	NDR
			Dual Cantilever	301	304	312*
TA DMA 2980	Nitrogen	2.5" x 0.5" x 0.12"	3-pt Bend	-	296	304
			Dual Cantilever	296	298	307
TA DMA Q800	Air	2.5" x 0.5" x 0.12"	3-pt Bend	293	-	-
			Dual Cantilever	293	295	304
TA DMA Q800	Nitrogen	2.5" x 0.5" x 0.12"	3-pt Bend	-	-	-
			Dual Cantilever	299	301	310
RS DMTA Mk V	Nitrogen	2" x 0.315" x 0.06"	3-pt Bend	296	298	309
			Dual Cantilever	295	295	315
PE DMA T	Helium	1" x 0.2" x 0.05"	3-pt Bend	295	298	-
Statistical Analysis of Interlaboratory Test Results—ASTM E691				Polycarbonate Interlaboratory Statistics		
				Dry $T_{gE'}$ (°F)		
				$\bar{X}$	$S_r$	$S_R$
				296.110	1.790	3.341

\* = Only one determinable  $T_g$  value was reported; not an average  
 - =  $T_g$  was not determinable

**3.1.6 Comparison of Repeatability And Reproducibility Standard Deviations With the ASTM D7028-07 Interlaboratory Study**

To determine the significance and validity of the developed TC guidelines and temperature calibration procedures, the ASTM D7028 interlaboratory [1] results were subjected to the same statistical analysis for  $T_{gE'}$ . The repeatability and reproducibility standard deviations for each material were combined into an average for both interlaboratory studies and are shown in table 21.

The reproducibility standard deviation was essentially halved with the implementation of the developed TC guidelines and temperature calibration procedures. Reductions of 47.93% and 50.43% were observed for the dry and wet specimens, respectively.

**Table 21. Comparison of repeatability and reproducibility standard deviations with the ASTM D7028-07 interlaboratory study [1]**

Interlaboratory Study	Average Repeatability and Reproducibility Standard Deviations			
	Dry $Tg_{E'}$ (°F)		Wet $Tg_{E'}$ (°F)	
	$\bar{S}_r$	$\bar{S}_R$	$\bar{S}_r$	$\bar{S}_R$
ASTM D7028 Interlaboratory Study (2007)	2.36	15.09	2.37	14.72
Interlaboratory study with implementation of developed thermocouple guidelines and temperature calibration procedures	3.38	7.86	2.65	7.30
Change in reproducibility standard deviation with implementation of developed thermocouple guidelines and temperature calibration procedures	-	-47.93%	-	-50.43%

### 3.2 COMPARISON OF INTERLABORATORY TEST RESULTS WITH OTHER THERMAL ANALYSIS TECHNIQUES

The dry  $Tg$  values determined from this DMA interlaboratory study and the DSC and TMA thermal analysis techniques were averaged for each material and are shown in table 22. These techniques are presented in section 2.3.2.

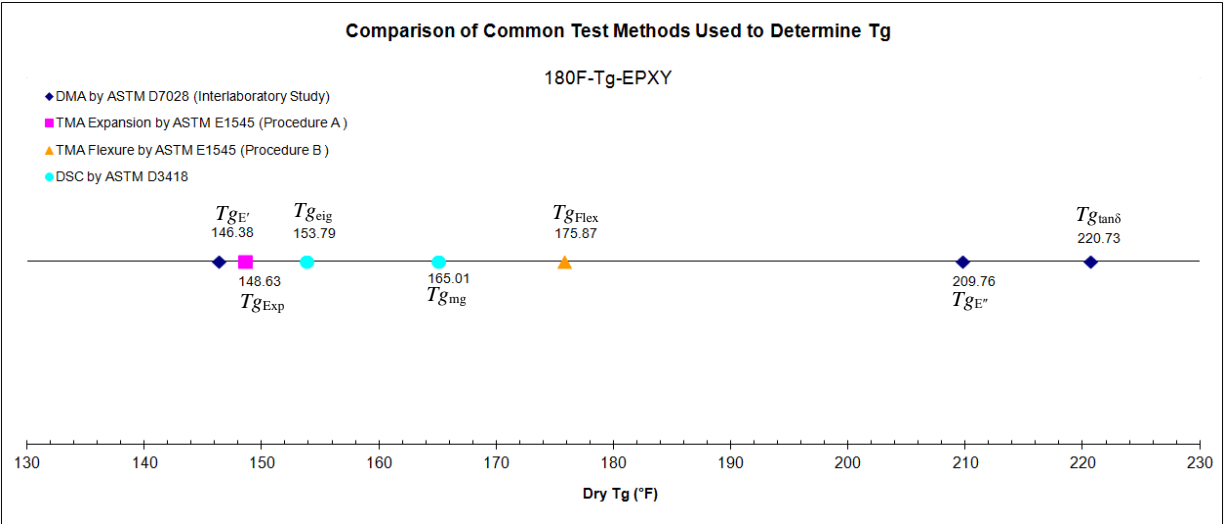
**Table 22. Comparison of thermal analysis techniques to measure  $Tg$**

Material ID	Average $Tg$ (°F)						
	DMA by ASTM D7028 (Interlaboratory Study)			TMA Expansion by ASTM E1545 (Procedure A)	TMA Flexure by ASTM E1545 (Procedure B)	DSC by ASTM D3418	
	Dry $Tg_{E'}$	Dry $Tg_{E''}$	Dry $Tg_{\tan\delta}$	Dry $Tg_{Exp}$	Dry $Tg_{Flex}$	Dry $Tg_{eig}$	Dry $Tg_{mg}$
180F- $Tg$ -EPXY	146.38	209.76	220.73	148.63	175.87	153.79	165.01
350F- $Tg$ -EPXY	362.25	374.94	387.57	364.22	361.28	362.74	375.07
500F- $Tg$ -BMI	509.73	539.49	550.85	520.07	503.42	506.35	527.13
600F- $Tg$ -PI	603.18	630.69	649.08	608.61	609.40	601.41	618.43
Polycarbonate	296.11	298.05	308.44	301.41	296.90	290.50	301.15

The average  $Tg$  values were plotted on a temperature graph for each material as shown in the figures in sections 3.2.1–3.3.2. There are multiple  $Tg$  measurements presented for the DMA:  $Tg_{E'}$ ,  $Tg_{E''}$ , and  $Tg_{\tan\delta}$ . There is a single  $Tg$  measurement for TMA  $Tg$  by expansion ( $Tg_{Exp}$ ) and for TMA  $Tg$  by flexure ( $Tg_{Flex}$ ). Both the onset  $Tg$  ( $Tg_{eig}$ ) and mid-height  $Tg$  ( $Tg_{mg}$ ) from the DSC heat flow curve are presented as well.

#### 3.2.1 Comparison of Thermal Analysis Techniques to Measure $Tg$ for 180F- $Tg$ -EPXY

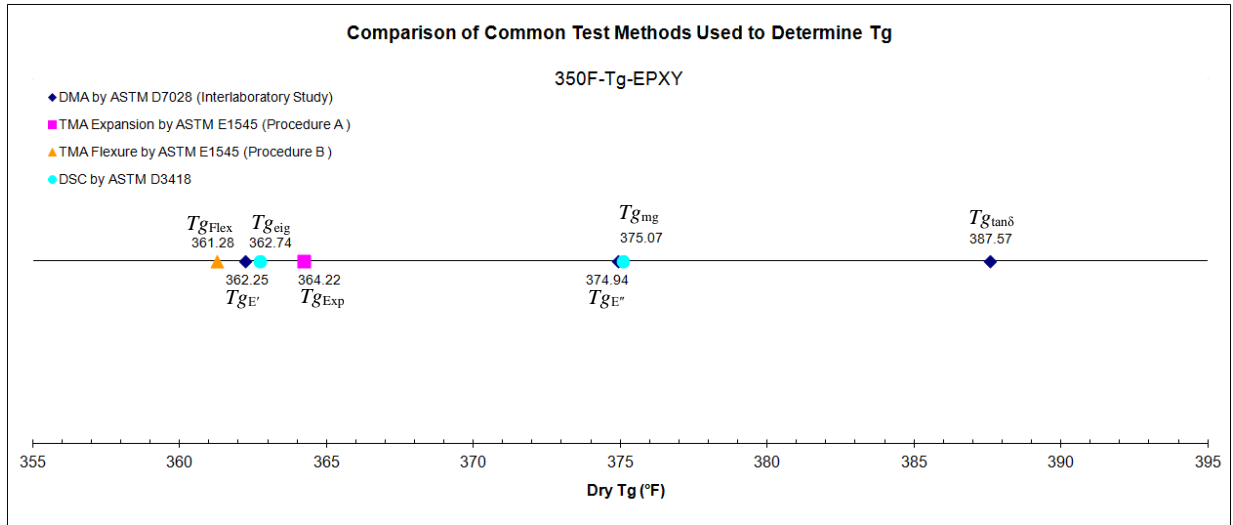
For the 180F- $Tg$ -EPXY material (see figure 10), the  $Tg_{E'}$  was the lowest  $Tg$  value, but only by a few degrees. The  $Tg_{E''}$  and  $Tg_{\tan\delta}$  are much higher than the other  $Tg$  values.



**Figure 11. Comparison of thermal analysis techniques to measure  $T_g$  for 180F-Tg-EPXY**

### 3.2.2 Comparison of Thermal Analysis Techniques to Measure $T_g$ for 350F-Tg-EPXY

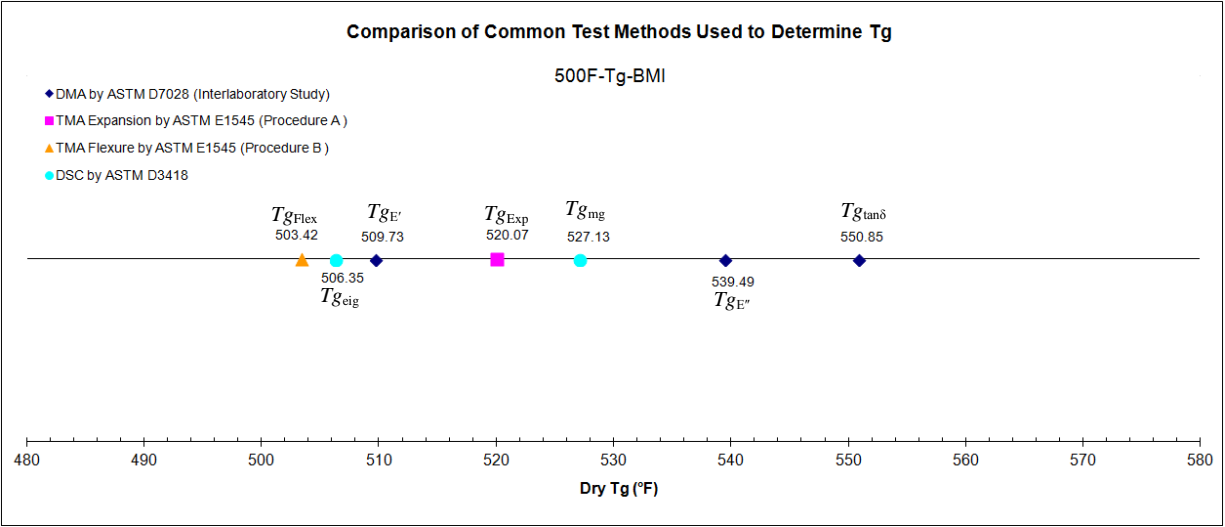
For the 350F-Tg-EPXY material (see figure 11), the  $T_{gE'}$  was one of the lower  $T_g$  values and the  $T_{gE''}$  and  $T_{gtan\delta}$  were two of the higher  $T_g$  values.



**Figure 12. Comparison of thermal analysis techniques to measure  $T_g$  for 350F-Tg-EPXY**

### 3.3 COMPARISON OF THERMAL ANALYSIS TECHNIQUES TO MEASURE $T_g$ FOR 500F-Tg-BMI

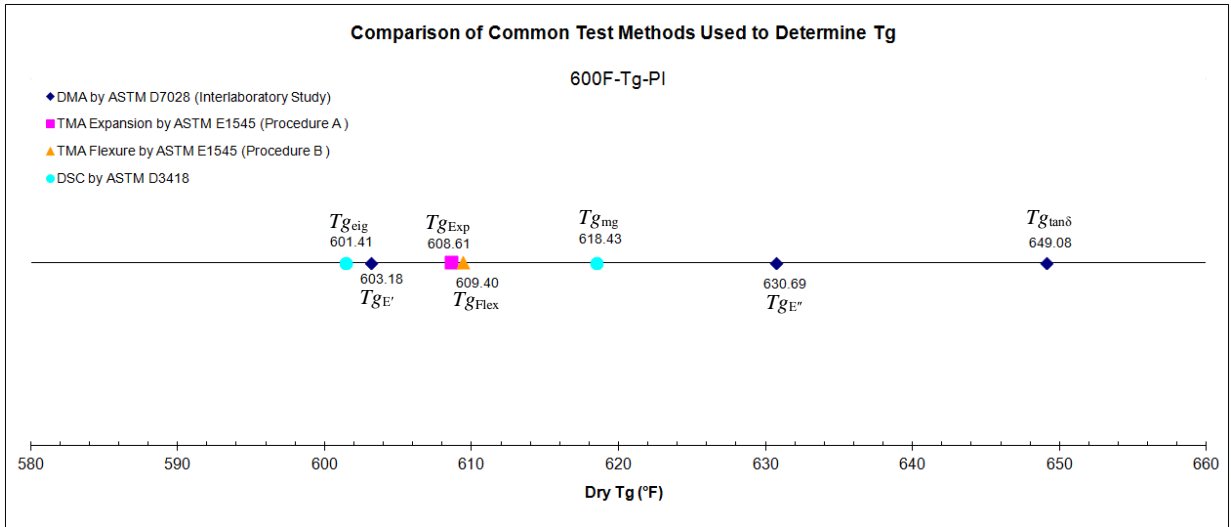
For the 500F-Tg-BMI material (see figure 12), the  $T_{gE'}$  was near the lower end of the  $T_g$  spectrum; however, the  $T_{gflex}$  and  $T_{geig}$  were even lower. The  $T_{gE''}$  and  $T_{gtan\delta}$  were much higher than the other  $T_g$  values.



**Figure 13. Comparison of thermal analysis techniques to measure  $T_g$  for 500F-Tg-BMI**

### 3.3.1 Comparison of Thermal Analysis Techniques to Measure $T_g$ for 600F-Tg-PI

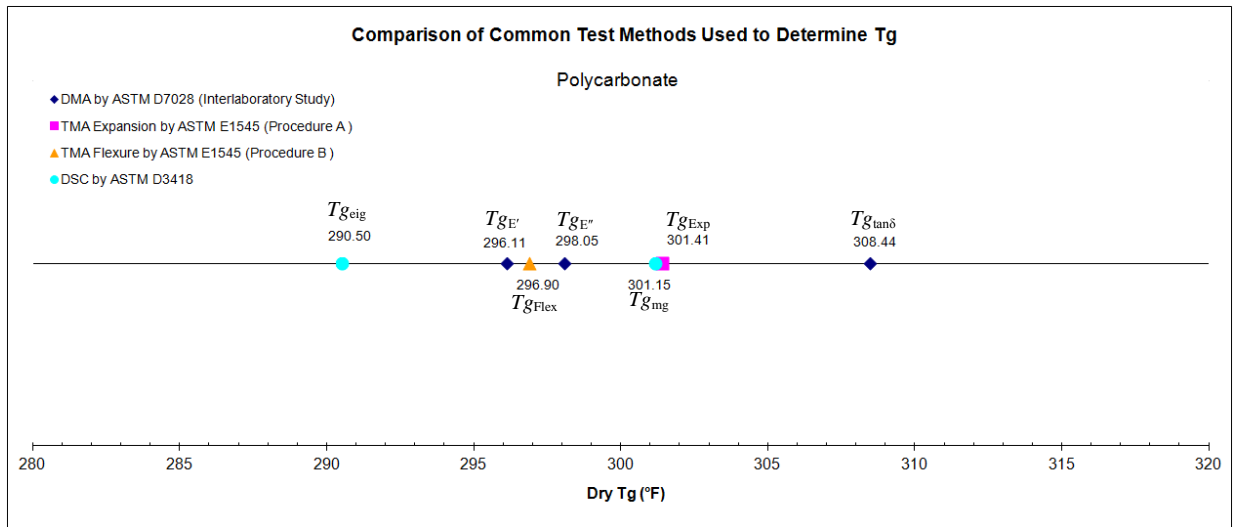
For the 600F-Tg-PI material (see figure 13), the  $T_{gE'}$  was one of the lower  $T_g$  values and the  $T_{gE''}$  and  $T_{g\tan\delta}$  were two of the higher  $T_g$  values.



**Figure 14. Comparison of thermal analysis techniques to measure  $T_g$  for 600F-Tg-PI**

### 3.3.2 Comparison of Thermal Analysis Techniques to Measure $T_g$ for Polycarbonate

For the polycarbonate material (see figure 14), the  $T_{gE'}$  was one of the lower  $T_g$  values,  $T_{g\tan\delta}$  was the highest  $T_g$  value, and  $T_{gE''}$  was in the middle.



**Figure 15. Comparison of thermal analysis techniques to measure  $Tg$  for polycarbonate**

### 3.3.3 Discussion on Thermal Analysis Techniques to Measure $Tg$

The  $Tg_{E'}$  was consistently one of the lower  $Tg$  values, and the  $Tg_{E''}$  and  $Tg_{tan\delta}$  were consistently two of the higher  $Tg$  values. This indicated that the  $Tg$  values determined when implementing the developed TC guidelines and temperature calibration procedures tended to bound the other  $Tg$  values. The  $Tg_{E'}$  can be described as a conservative measurement, whereas the  $Tg_{E''}$  and  $Tg_{tan\delta}$  are shown to be aggressive measurements of the  $Tg$ .

Table 23 shows the low, mean, and high values for all of the thermal analysis techniques and how they relate to the dry  $Tg_{E'}$  in order of increasing value.

**Table 23. Comparison of thermal analysis techniques to measure  $Tg_{E'}$**

Material ID	Average $Tg$ for All Techniques (°F)			
	Low to High $\longrightarrow$			
	Low	Dry $Tg_{E'}$	Mean	High
180F- $Tg$ -EPXY	146.38	146.38	174.31	220.73
350f- $Tg$ -EPXY	361.28	362.25	369.72	387.57
500F- $Tg$ -BMI	503.42	509.73	522.43	550.85
600F- $Tg$ -PI	601.41	603.18	617.25	649.08
Polycarbonate	290.50	296.11	298.94	308.44

## 4. DISCUSSION

The primary goal of this research was to improve the laboratory-to-laboratory and instrument-to-instrument reproducibility. A research plan was designed to address the ambiguity of the current TC location and temperature calibration recommendations. From comparing the



reproducibility standard deviation of the ASTM D7028-07 interlaboratory study [1] with the interlaboratory study conducted as part of this research, it is evident that this was accomplished.

However, it is also evident that there were variables within the interlaboratory study that prevented greater improvement. These variables and their potential effects are discussed in sections 4.1–4.3.

#### 4.1 PURGE GAS

Purge gas is used in a DMA to remove products of decomposition near the sample to minimize their effect on the measured temperature and act as a gas bearing for the moveable clamp that applies force to the specimen. For use in a DMA, helium, argon, and nitrogen are functionally equivalent and are referred to as inert gases. ASTM D7028-07 [2] does not require a specific gas to be purged during the DMA test. Nitrogen, helium, and air are all commonly used purge gases; each was used in at least one instrument from the interlaboratory study. The purge gas affects the heat flow from the furnace to the specimen and the thermal stability of the specimen. Inert gases aid in minimizing the potential oxidation of the specimen as compared to air, while air is convenient and readily available. Unless dry air is specified (which it is not), air is more prone to carry moisture, resulting in a wetter environment than when purged with an inert gas.

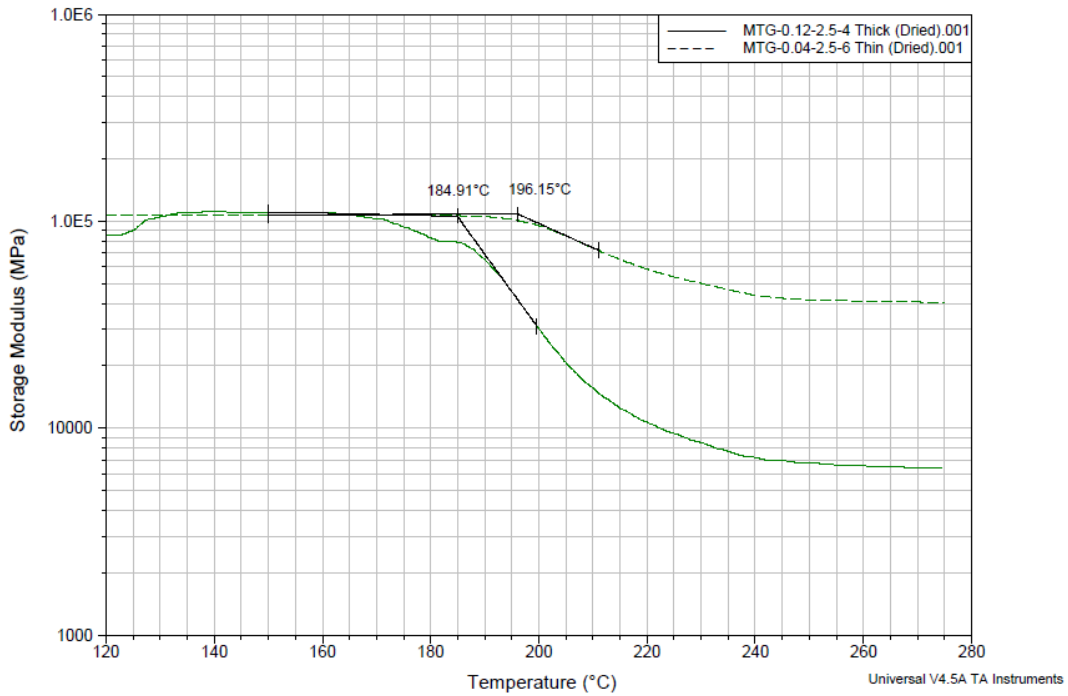
The dry  $Tg$  results from the instruments purged with air (as compared to inert gas), when averaged, are about 7°F lower than the mean for the 500F- $Tg$ -BMI material wh  $Tg_{E'}$ ,  $Tg_{E''}$ , and  $Tg_{\tan\delta}$  are considered. However, the wet  $Tg$  results are equivalent.

An even greater difference was observed for the 600F- $Tg$ -PI material. The dry  $Tg$  results from the instruments purged with air (as compared to inert gas), when averaged, are about 11°F lower than the mean for the 600F- $Tg$ -PI material when  $Tg_{E'}$ ,  $Tg_{E''}$ , and  $Tg_{\tan\delta}$  are considered. However, the wet  $Tg$  results are equivalent.

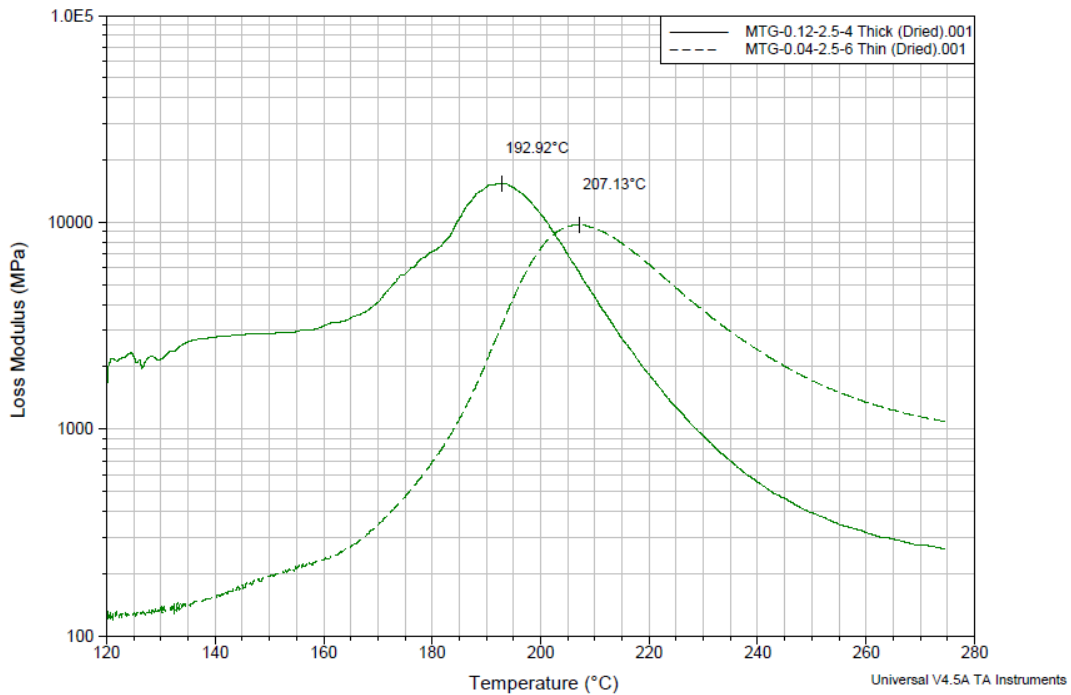
These differences between the air and inert gas environments were negligible for the other materials tested in the interlaboratory study.

#### 4.2 VISCOELASTIC BEHAVIOR

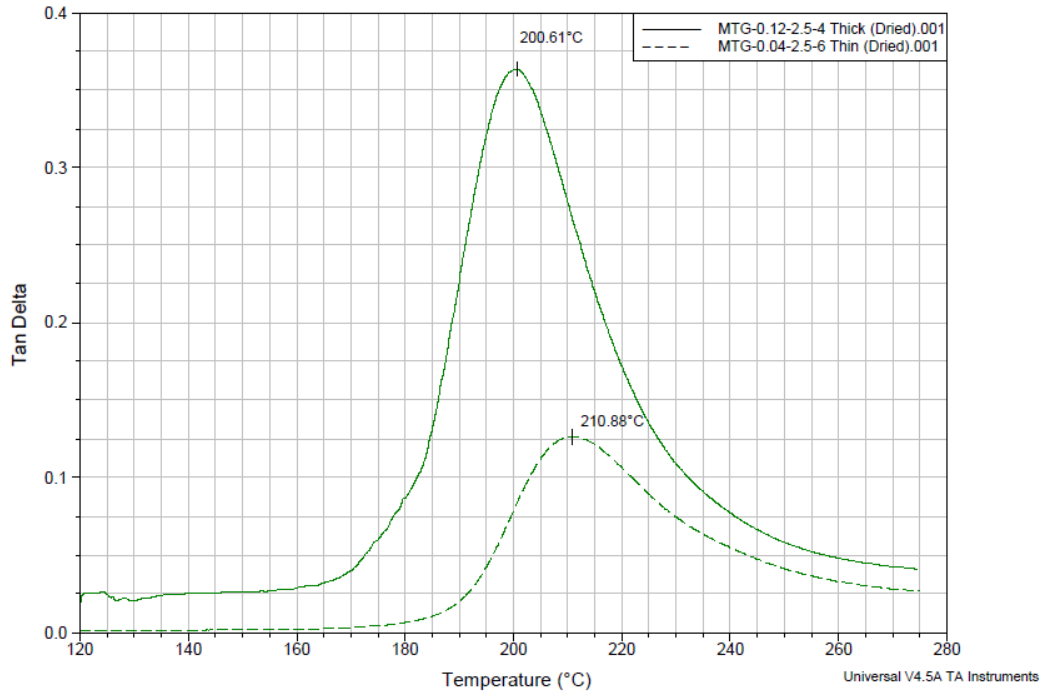
In section 2.1.2, data were presented from the specimen dimensions evaluation. These data indicated that the specimen thickness was influential on the  $Tg$  measurements. The DMA plots of the 0.04" and 0.12" thick specimens from the 3-point bend test are plotted for the  $Tg_{E'}$ ,  $Tg_{E''}$ , and  $Tg_{\tan\delta}$  in figures 15–17, respectively. The 0.04" thick specimen is represented by a dashed line and the 0.12" thick specimen is represented by a solid line.



**Figure 16. Plot of  $T_{gE'}$  for 0.04" and 0.12" thick specimens for 50mm 3-point bend fixture tests**

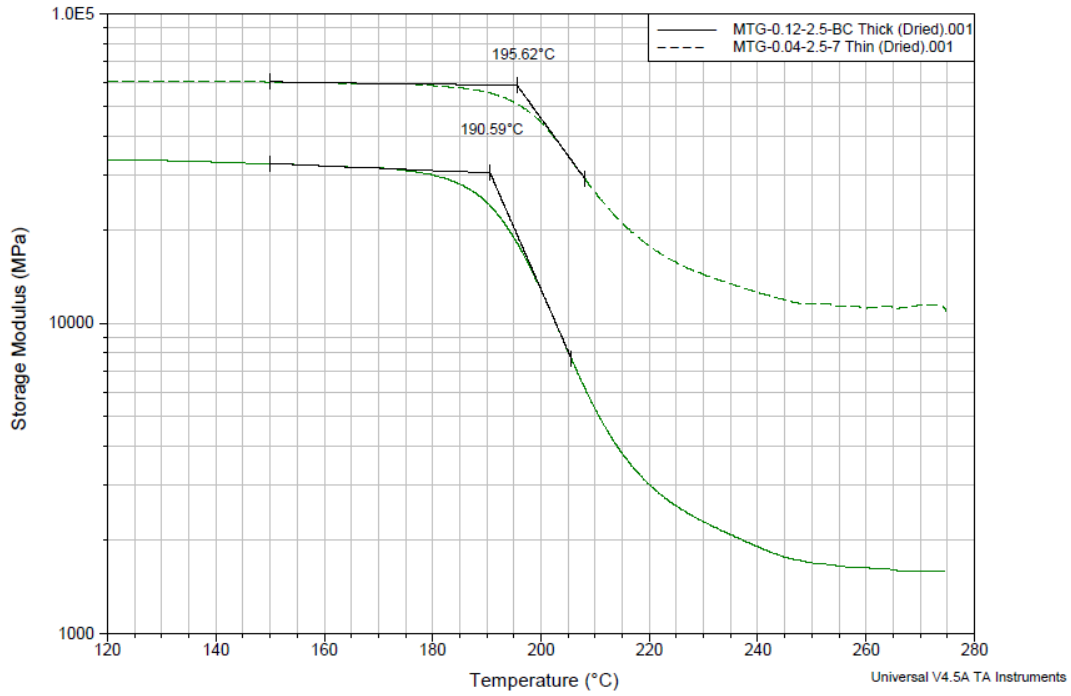


**Figure 17. Plot of  $T_{gE''}$  for 0.04" and 0.12" thick specimens for 50mm 3-point bend fixture tests**

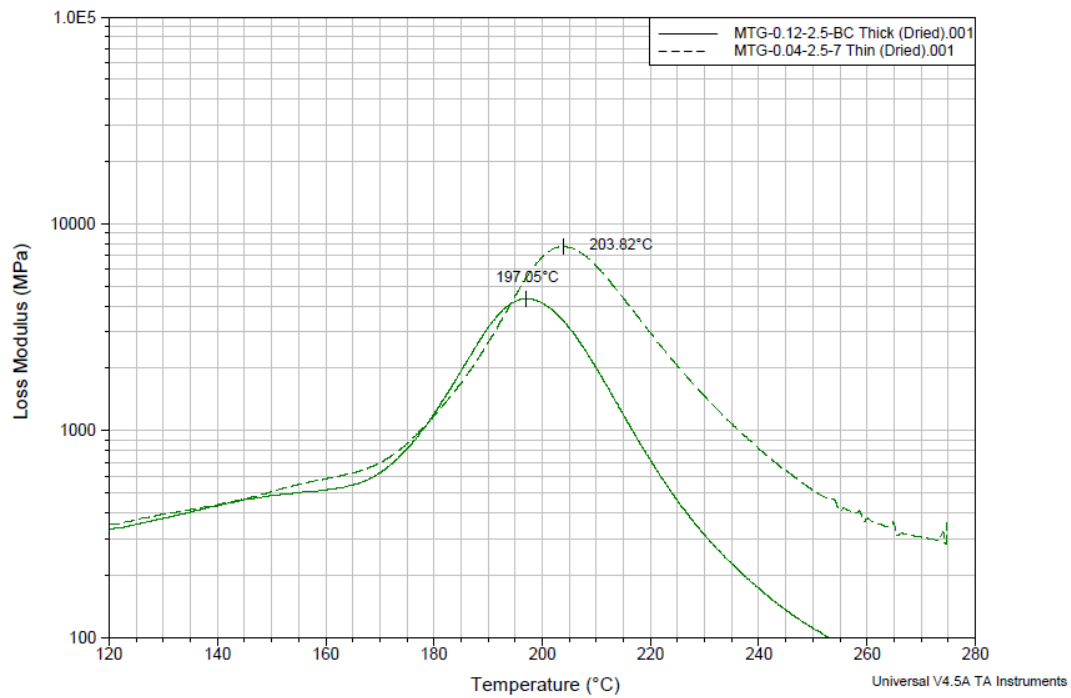


**Figure 18. Plot of  $Tg_{\tan\delta}$  for 0.04" and 0.12" thick specimens for 50mm 3-point bend fixture tests**

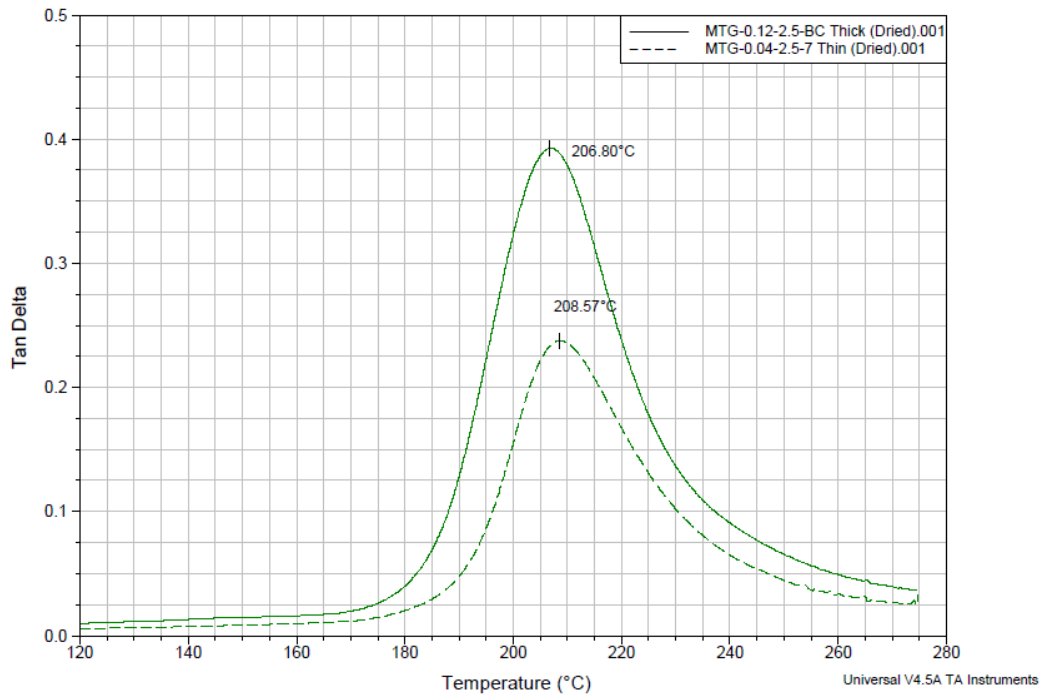
The DMA plots of the 0.04" and 0.12" thick specimens from the dual cantilever test for  $Tg_{E'}$ ,  $Tg_{E''}$ , and  $Tg_{\tan\delta}$  are shown in figures 18–20, respectively. The 0.04" thick specimen is represented by a dashed line and the 0.12" thick specimen is represented by a solid line.



**Figure 19. Plot of  $T_{gE'}$  for 0.04'' and 0.12'' thick specimens for 35mm dual cantilever fixture tests**



**Figure 20. Plot of  $T_{gE''}$  for 0.04'' and 0.12'' thick specimens tests for 35mm dual cantilever fixture**



**Figure 21. Plot of  $Tg_{\tan\delta}$  for 0.04" and 0.12" thick specimens for 35mm dual cantilever fixture tests**

The viscoelastic behavior of the thin and thick samples is noticeably different (see figures 17–20). The change in the  $E'$  curve over the glass transition is much shallower for the thin samples for both fixtures. Because  $E'$  is the elastic modulus, it should behave according to elastic beam theory.

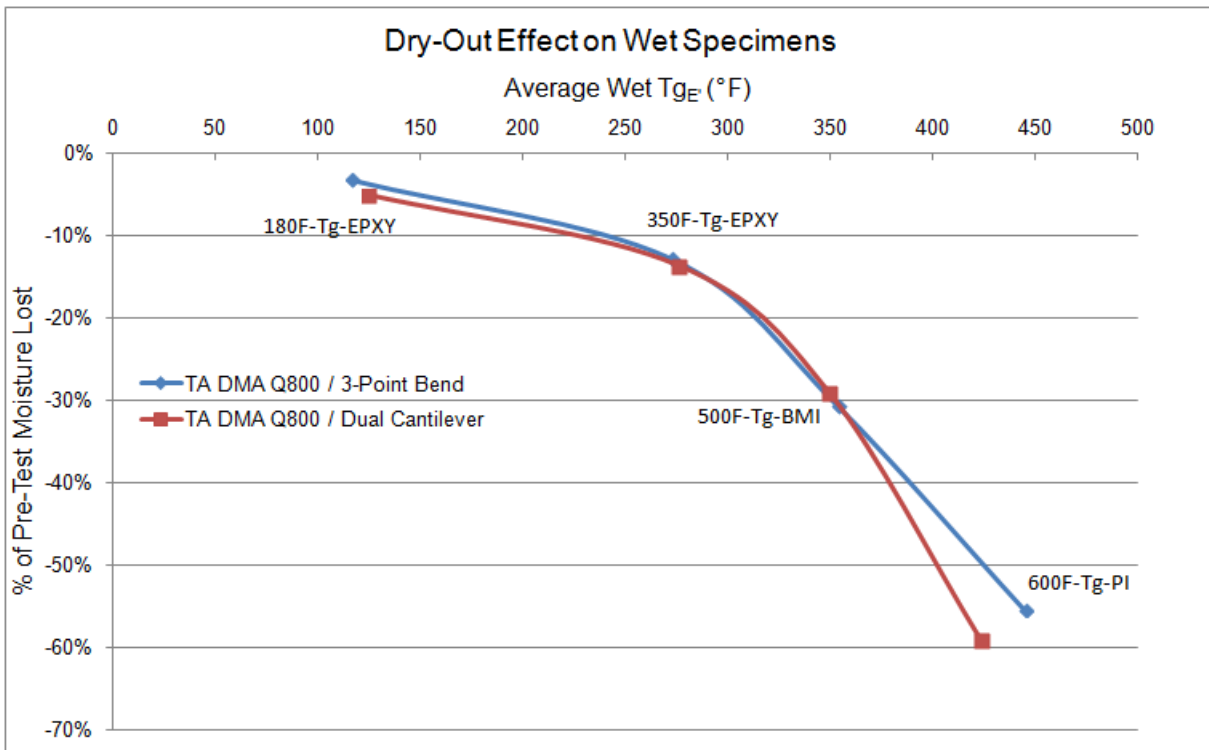
The Q800 relies on the Timoshenko beam theory and force/displacement information to calculate elastic properties. This viscoelastic model is suited for homogeneous isotropic materials, not orthotropic (composite) materials. Shear deformation is accounted for with Poisson's ratio, in which the Q800 defaults to a ratio of 0.44, unless the operator defines a value. This is higher than most fiber reinforced polymer matrix composites. A viscoelastic model for orthotropic materials would improve the ability of the DMA instrument to accurately determine the viscoelastic properties of fiber-reinforced polymer matrix materials.

#### 4.3 DRY-OUT EFFECT ON WET $Tg$

The specimen dimensions are known to affect the moisture content of wet specimens. The ASTM D30 committee considered the dry-out effect of wet specimens when establishing ASTM D7028-07 by increasing the recommended heating rate from 1°C/min in ASTM E1640-04 [14] to 5°C/min in ASTM D7028-07 [2]. A heating rate of 5°C/min was considered a compromise between the thermal lag and dry-out effect

The dry-out effect was apparent in the interlaboratory study. A side study was conducted on additional wet specimens to better understand this effect and its temperature relationship. In this

side study, additional wet specimens were tested identically to the interlaboratory tests, but instead, these tests were stopped at the average wet  $T_{gE'}$ . The specimens were immediately removed from the furnace and weighed. The change between the pre-test weight and the weight taken after the test (at the average wet  $T_{gE'}$ ) was considered to be the amount of moisture lost before the  $T_{gE'}$  was reached. The amount of moisture loss was then compared to the amount of moisture absorbed during the conditioning process (pre-test moisture content). This was done for each material for the 3-point bend and dual cantilever fixtures for the 0.12" thick specimens and graphed as a function of the average wet  $T_{gE'}$  in figure 21.



**Figure 22. Plot of moisture loss due to the pre- $T_g$  temperature exposure during the DMA test**

The dry-out effect is more prevalent for the wet specimens of high  $T_g$  materials. This is explained by Fick's second law of diffusion. The diffusion coefficient is directly related to temperature, therefore, as temperature increases the moisture diffusion coefficient also increases. Because wet specimens of high- $T_g$  materials are exposed to higher temperatures and longer exposure times during the DMA test, a larger amount of moisture is lost before the  $T_g$  is reached.

Additionally, the dry-out effect is more severe for thin samples. Fick's second law of diffusion explains this from the theoretical side and the interlaboratory study indicates this experimentally. There were no remaining thin, wet specimens after the interlaboratory study; therefore the dry-out effect was not evaluated for the thin, wet specimens.

## 5. CONCLUSIONS AND RECOMMENDATIONS

Dynamic mechanical analysis (DMA) is the preferred thermal analysis technique for determining the glass transition temperature ( $T_g$ ) of polymer matrix composites because it is more sensitive to  $T_g$  measurements than other thermal analysis techniques. An interlaboratory study was developed and conducted by the American Society for Testing and Materials for its D7028-07 test standard ( $T_g$  by DMA) in 2007. The results of the study indicated that reproducibility was poor between DMA instruments and laboratories.

Poor reproducibility of  $T_g$  measurements creates uncertainty in cases in which  $T_g$  measurements are used. Service temperature and process control determinations may be difficult to establish if reproducibility of  $T_g$  measurements remains poor.

The goal of this research was to improve laboratory-to-laboratory and instrument-to-instrument reproducibility for DMA  $T_g$ .

To accomplish this, multiple variables that influence  $T_g$  measurements were evaluated. The variables evaluated included: thermocouple (TC) location, specimen dimensions, and calibration support beam dimensions and materials. These evaluations were made using a TA Instruments DMA Q800. The results may not be equivalent for all DMA instrument models. TC guidelines and temperature calibration procedures were also developed and evaluated as part of the interlaboratory study.

The results show that the location of the TC used to measure the temperature of the specimen drastically affects the measured temperature. The current recommendation that the TC be located within 1mm–2mm of the test specimen is inadequate by itself. The results revealed that the specimen temperature at different locations varied as much as 18°F and 27°F for the 3-point bend and dual cantilever fixtures, respectively. Positioning the specimen TC to the side of the specimen (within 1mm–2mm) and mid-way between the fixture points is recommended. This position minimizes the influence from the fixture (heat sink effect) and the proximity of the furnace sidewall (heat generated through the furnace sidewall). Test users may benefit from a similar evaluation on their particular DMA instrument.

Specimen dimensions were not thoroughly evaluated in this research; however, some insight was obtained despite the limited scope of the evaluation. Specimen thickness was shown to have a noticeable effect on the  $T_g$  measurement. There was a 14°F difference between a thin (0.04") and thick (0.12") specimen tested on the 3-point bend fixture. A similar finding was observed when specimens with the same dimensions were tested on the dual cantilever fixture. This result was a 10°F difference. Specimen thickness also appeared to be the source of problems in the interlaboratory study. Two instruments required thinner specimens because of instrument limitations. The effect on the dry  $T_g$  was established in the specimen dimensions evaluation; however, the dry-out effect on the wet specimens was not thoroughly evaluated. The wet  $T_g$  values reported from the instruments requiring thinner specimens were slightly over 100°F higher in the most extreme case (600F- $T_g$ -PI). There was not a significant difference for the other materials, but the 500F- $T_g$ -BMI case was inconclusive because most of the data from the thin specimens did not allow for  $T_g$  values to be determined.

Dimensional variation of the calibration support beam had little effect on the melting temperature of the calibration melting standards. This indicated that the thermal lag effect was negligible at tests run at a heating rate of 5°C/min. The best practice would be to use a calibration support beam that is similar in size to the intended test specimen.

Materials with similar diffusivities to the intended test material can be used as a calibration support beam if they can maintain their rigidity beyond the melting temperature of the calibration melting standards. Machinability and availability are other aspects when considering the material to be used as the calibration support beam.

The recommended TC guidelines and temperature calibration procedures developed in this study improved laboratory-to-laboratory and instrument-to-instrument reproducibility, maintained repeatability, and showed consistency with other thermal analysis techniques. With implementation of the developed TC guidelines and temperature calibration procedures, the reproducibility standard deviation of the  $T_{gE'}$  was reduced from approximately 15°F to just below 8°F. The repeatability standard deviation was nearly unchanged (about 3°F compared to just over 2°F). Compared to other thermal analysis techniques, the  $T_{gE'}$  determined from the interlaboratory study resulted in conservative values.  $T_{gE'}$  values were less than the average of all  $T_g$  measurements taken for each material, but were only the lowest  $T_g$  measurement for the 180F- $T_g$ -EPXY material.

A viscoelastic model for orthotropic materials would improve the ability of the DMA instrument to accurately determine the viscoelastic properties of fiber-reinforced polymer matrix materials.

Additional research on the use of thin versus thick specimens, different heating rates and exposure times could help address data reproducibility.

A normalization process using moisture loss (initial and final weight) of the sample over the duration of the test (until  $T_g$ ) could help address data reproducibility.

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14. ASTM International, "Standard Test Method for Assignment of the Glass Transition Temperature by Dynamic Mechanical Analysis (ASTM E1640-04)," 2004, West Conshohocken, Pennsylvania.

## APPENDIX A—TA INSTRUMENTS DYNAMIC MECHANICAL ANALYZER Q800

### A.1 TA INSTRUMENTS Q800 DYNAMIC MECHANICAL ANALYZER DESCRIPTION

The TA Instruments Q800 Dynamic Mechanical Analyzer (DMA) is a thermal analytical instrument used to test the mechanical properties of many different materials [A-1–A-3]. Furthermore, the Q800 is the 3rd generation of DMA instruments from TA Instruments and integrates state-of-the-art technologies in hardware and software. The instrument enables the test operator to make measurements of the test specimen by mounting the specimen to one of several fixtures. The fixtures for the Q800 were developed using finite element analysis to minimize mass and compliance. The Q800 combines a controller and associated software to establish the thermal analysis system.

The Q800 DMA instrument utilizes CHROMEL<sup>®</sup>/ALUMEL<sup>®</sup> for the specimen and reference thermocouples (TC). The position of these TCs can be positioned to accommodate the various fixture configurations.

TA Instruments developed the Q800 to operate over a temperature range of -145°C–600°C with the ability to heat the furnace up to a rate of 20°C/min. The Q800 enables the operator to determine changes in specimen properties from a choice of seven different experimental variables. These variables include temperature, time, frequency, stress, force, displacement, and strain. The Q800 has the ability to test samples in various forms. The instrument uses interchangeable fixtures, enabling the operator to determine properties such as modulus, damping, creep, stress relaxation, glass transitions, and softening points.

Figures A-1–A-7 provide additional information about the Q800. The instrument shown in figures A-1 and A-4–A-7 was used in this study.



**Figure A-1. TA instruments DMA Q800 furnace / test section [A-2]**



Figure A-2. TA instruments DMA Q800 test section [A-3]

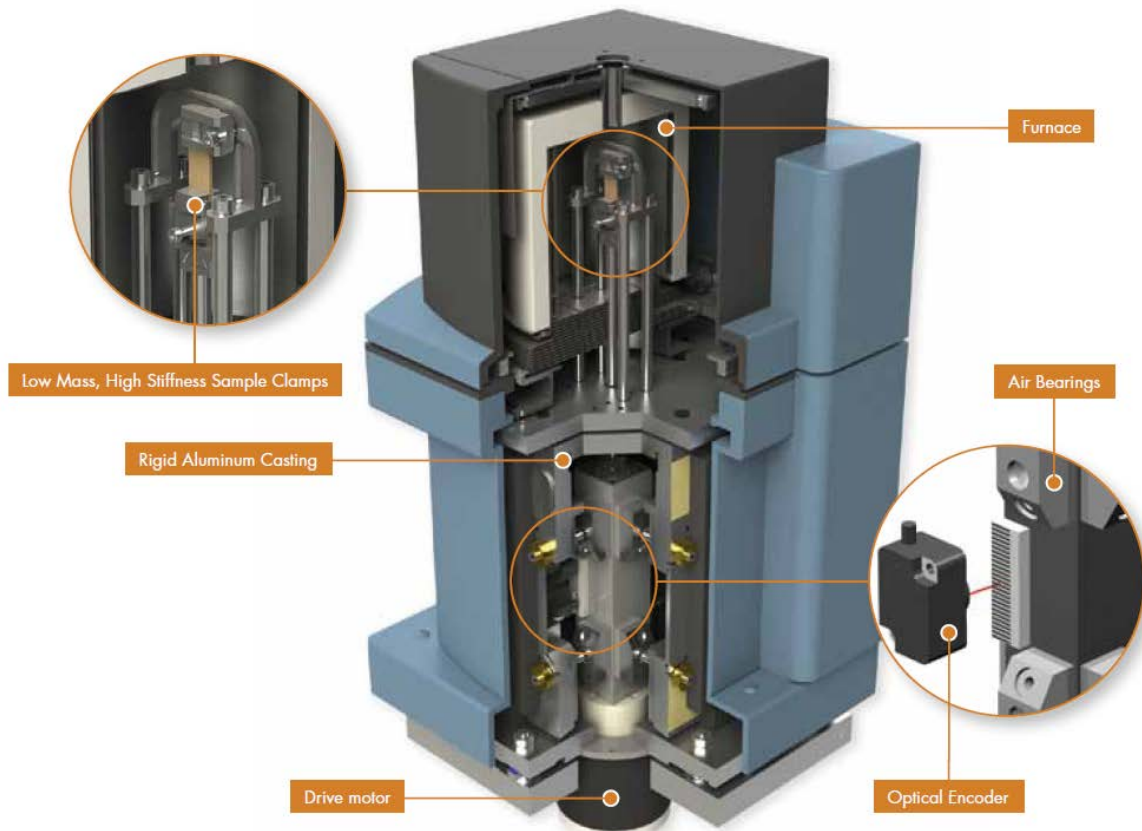
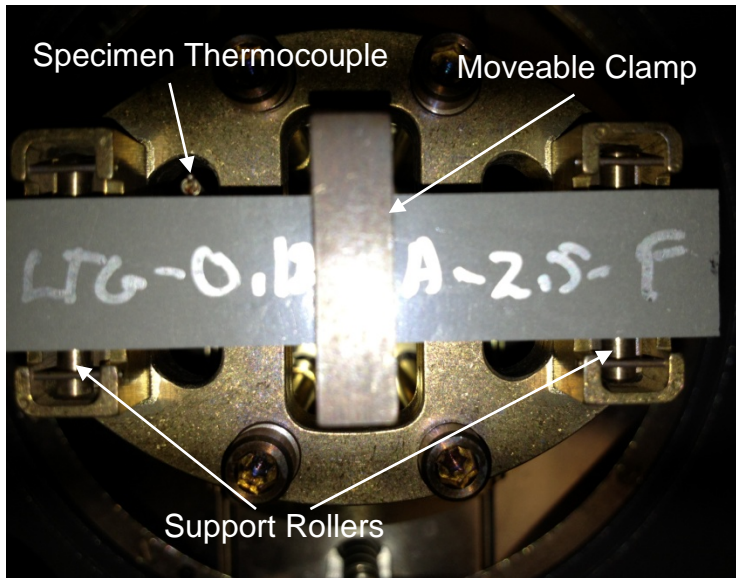
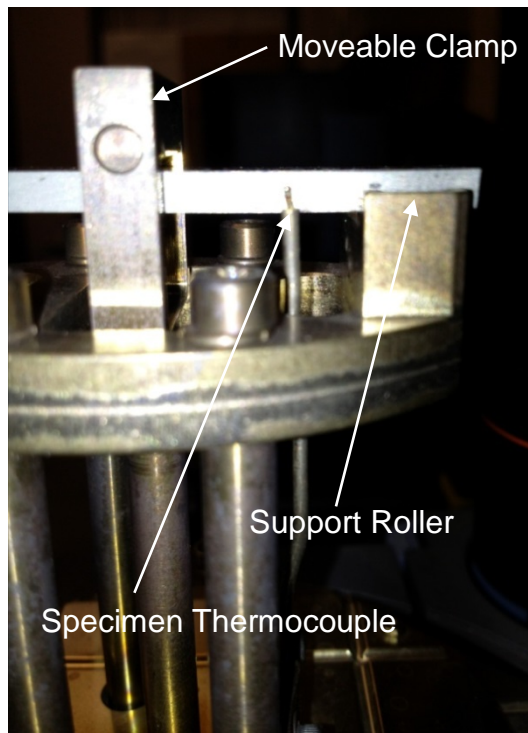


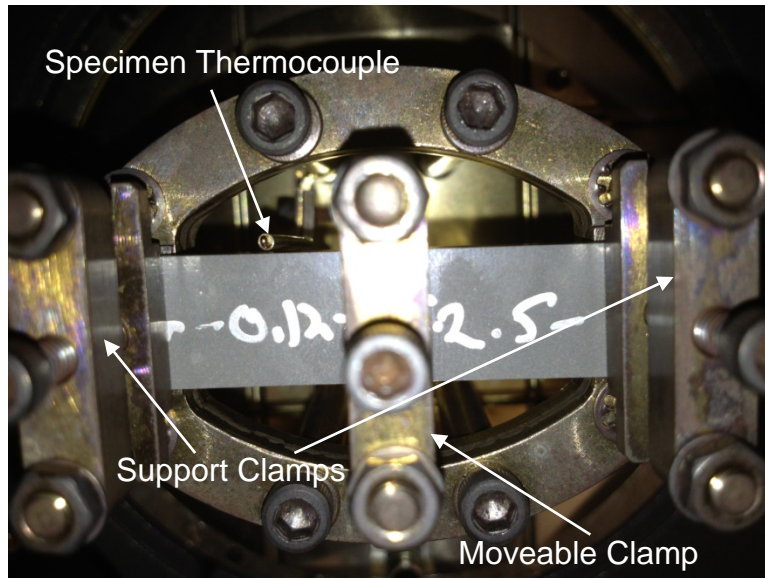
Figure A-3. TA Instruments DMA Q800 schematic [A-3]



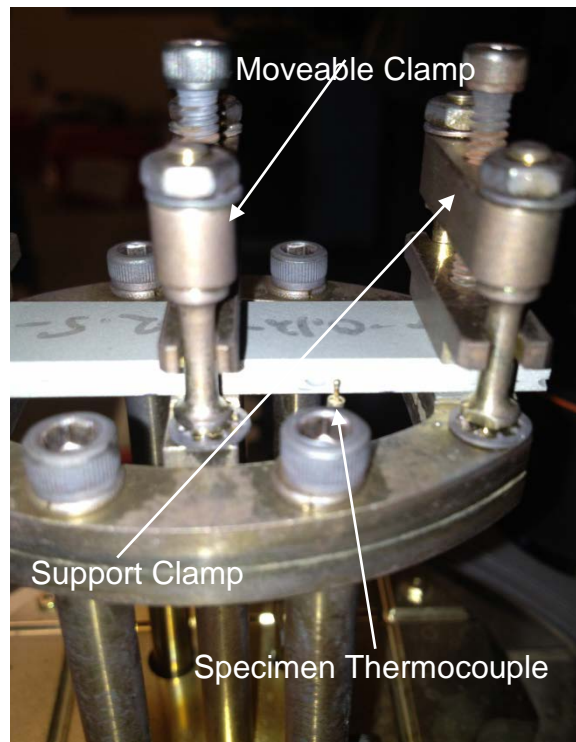
**Figure A-4. TA Instruments DMA Q800 test setup (3-point bend fixture, TC location 3) top view [A-2]**



**Figure A-5. TA instruments DMA Q800 test setup (3-point bend fixture, TC location 3) side view [A-2]**



**Figure A-6. TA instruments DMA Q800 test setup top view (dual cantilever fixture, TC location 3) [A-2]**



**Figure A-7. TA instruments DMA Q800 test setup side view (dual cantilever fixture, TC location 3) [A-2]**

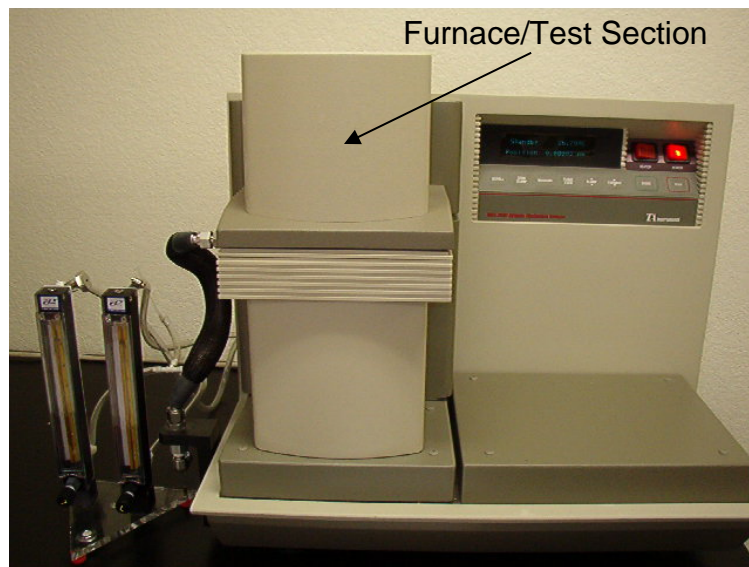
## A.2 REFERENCES

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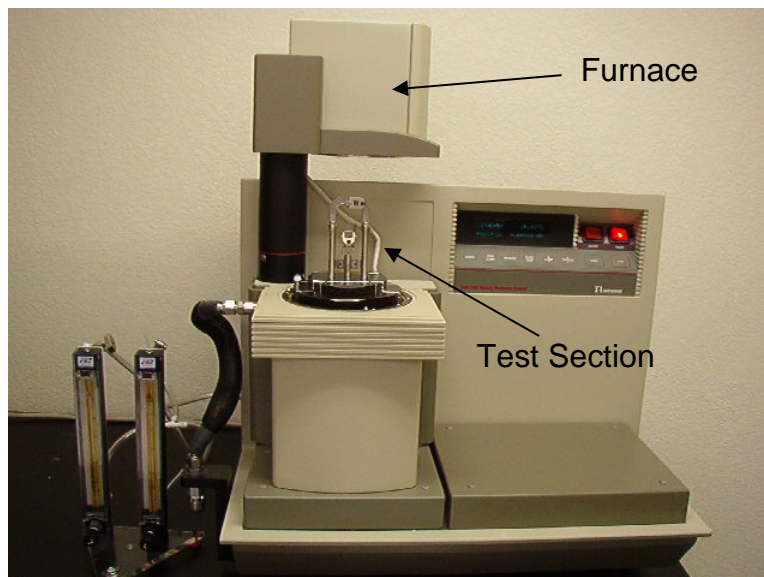
APPENDIX B—TA INSTRUMENTS DYNAMIC MECHANICAL ANALYZER 2980  
(INSTRUMENT PICTURES)

B.1 TA INSTRUMENTS 2980 DYNAMIC MECHANICAL ANALYZER DESCRIPTION

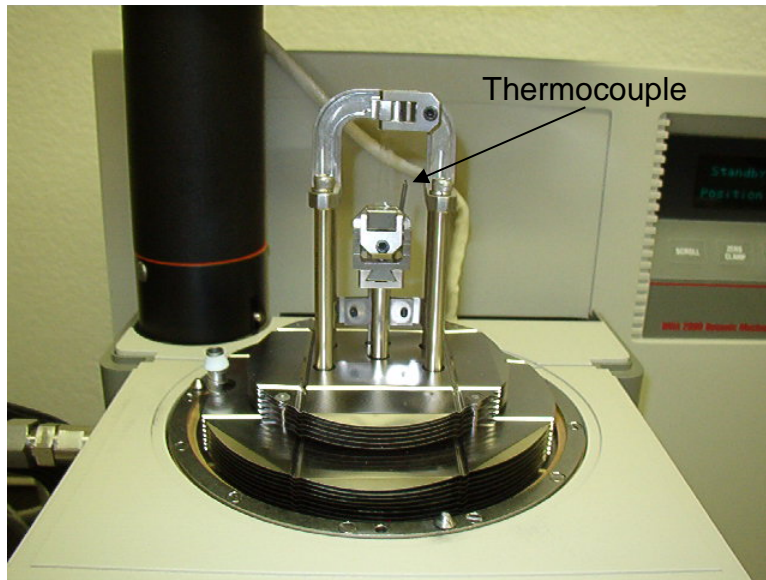
The TA Instruments 2980 Dynamic Mechanical Analyzer (DMA) is a thermal analytical instrument used to test the mechanical properties of many different materials. The analyzer is shown in figures B-1–B-4 [B-1–B-2]. The instrument shown in these figures is not the actual instrument used in this study. These figures are provided to familiarize the reader with various components of the instrument.



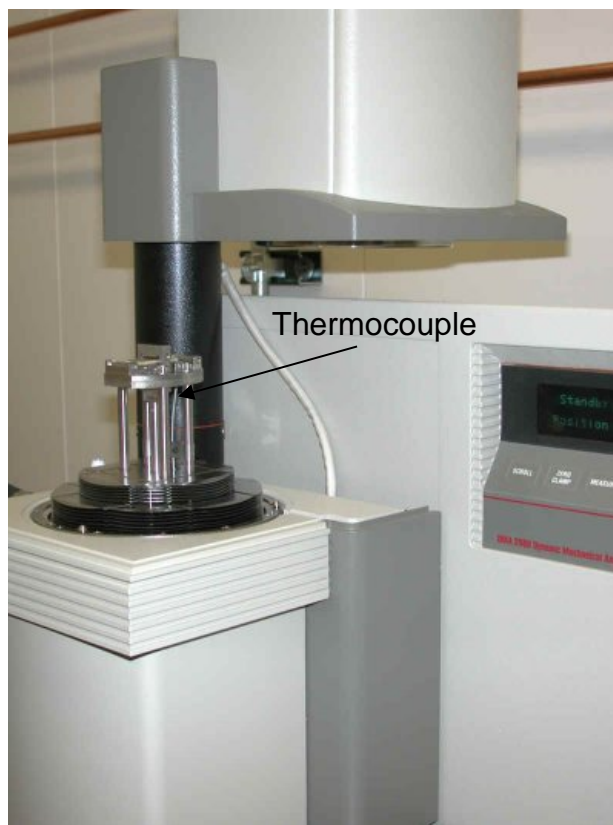
**Figure B-1. TA instruments DMA 2980 overview [B-1]**



**Figure B-2. TA instruments DMA 2980 test section [B-1]**



**Figure B-3. TA instruments DMA 2980 (tension clamp) [B-1]**



**Figure B-4. TA instruments DMA 2980 (3-point bend clamp) [B-2]**



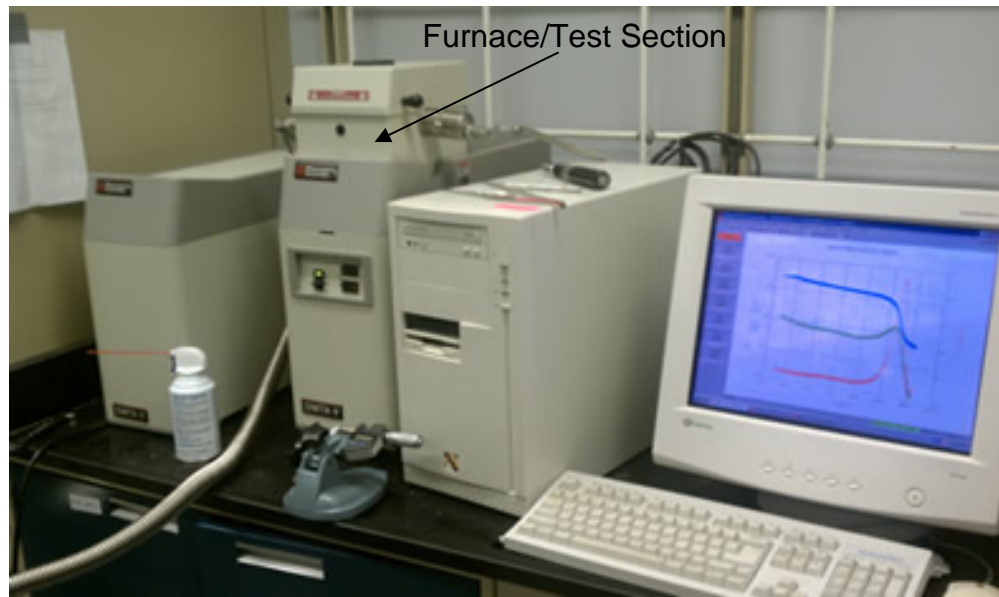
## B.2 REFERENCES

- B-1 LabX, available at [http://www.labx.com/v2/adsearch/morepics.cfm?pic\\_ref=498660&adnumb=498660%20\(2980%20pictures\)](http://www.labx.com/v2/adsearch/morepics.cfm?pic_ref=498660&adnumb=498660%20(2980%20pictures)) (accessed November 18, 2013).
- B-2 University of Wisconsin – Madison, Polymer Engineering Center, available at [http://pec.engr.wisc.edu/research/research\\_017.html](http://pec.engr.wisc.edu/research/research_017.html) (accessed November 18, 2013).

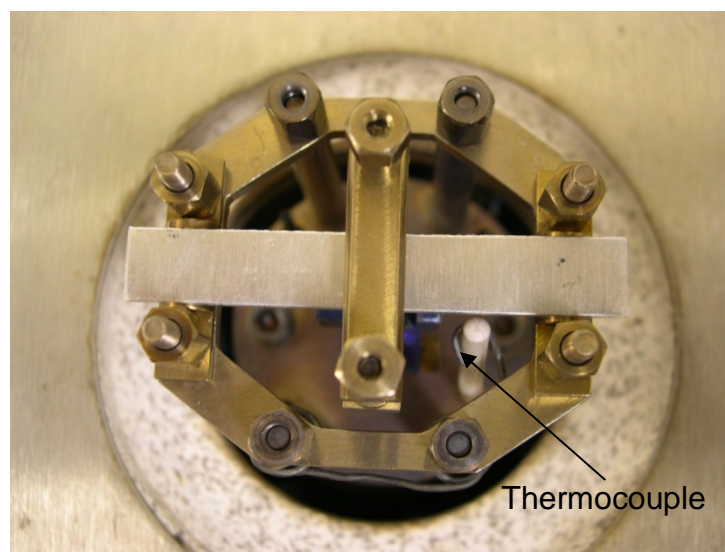
## APPENDIX C—RHEOMETRIC SCIENTIFIC MK V DMTA (INSTRUMENT PICTURES)

### C.1 RHEOMETRIC SCIENTIFIC MK V DMTA DESCRIPTION

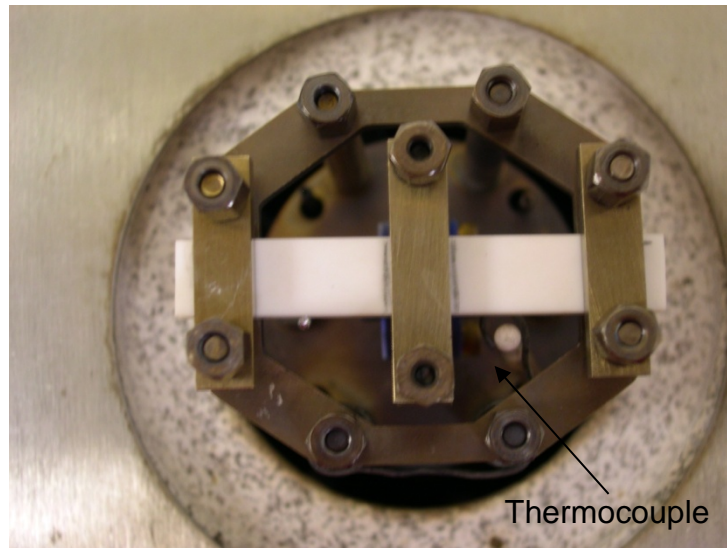
The Rheometric Scientific Mk V Dynamic Mechanical Thermal Analyzer (DMTA) is a thermal analytical instrument used to test the mechanical properties of many different materials. The analyzer is shown in figures C-1–C-3 [C-1–C-2]. The instrument shown in figure C-1 is not the actual instrument used in this study. The instrument shown in figures C-2–C-3 was used in this study. These figures are provided to familiarize the reader with various components of the instrument.



**Figure C-1. Rheometric scientific DMTA [C-1]**



**Figure C-2. Rheometric scientific DMTA Mk V (3-point bend clamp) [C-2]**



**Figure C-3. Rheometric scientific DMTA Mk V (dual cantilever clamp) [C-2]**

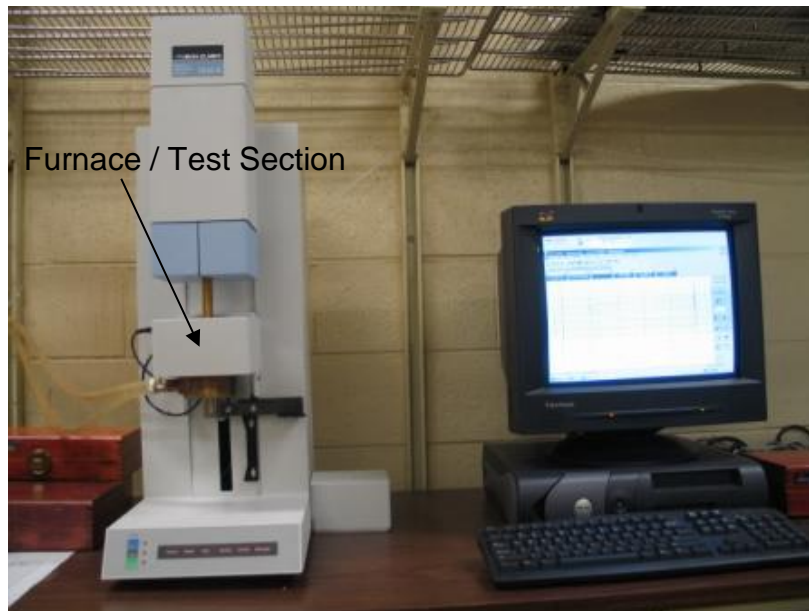
#### C.1 REFERENCES

- C-1 University of Southern Mississippi, Nazarenko Research Group, available at <http://www.usm.edu/nrg/lab.html> (accessed November 19, 2013).
- C-2 Wu, J., Hexcel, Chemical and Thermal Characterization Laboratory, 2013.

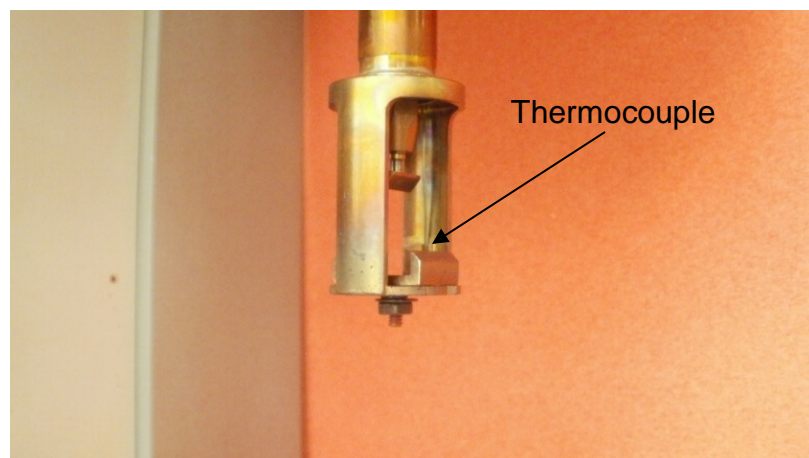
APPENDIX D—PERKIN ELMER DYNAMIC MECHANICAL ANALYZER 7E  
(INSTRUMENT PICTURES)

D.1 PERKIN ELMER DYNAMIC MECHANICAL ANALYZER 7E DESCRIPTION

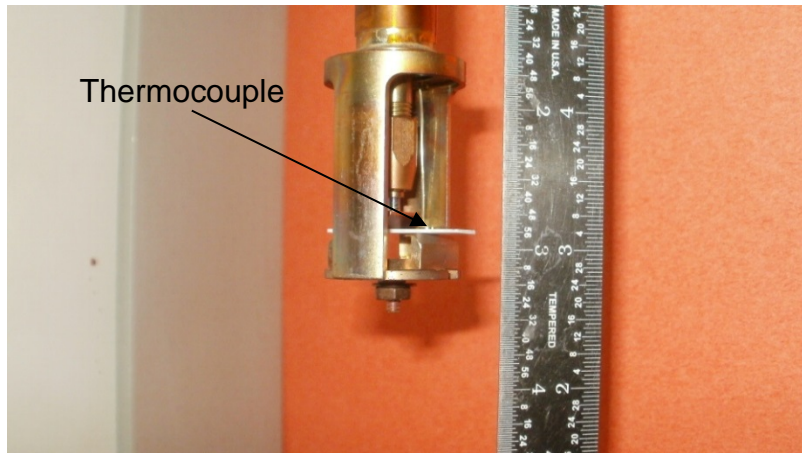
The Perkin Elmer 7e Dynamic Mechanical Analyzer (DMA) is a thermal analytical instrument used to test the mechanical properties of many different materials. The analyzer is shown in figures D-1–D-4 [D-1–D-2]. The instrument shown in figure D-1 is not the actual instrument used in this study. The instrument shown in figures D-2–D-4 was used in this study. These figures are provided to familiarize the reader with various components of the instrument.



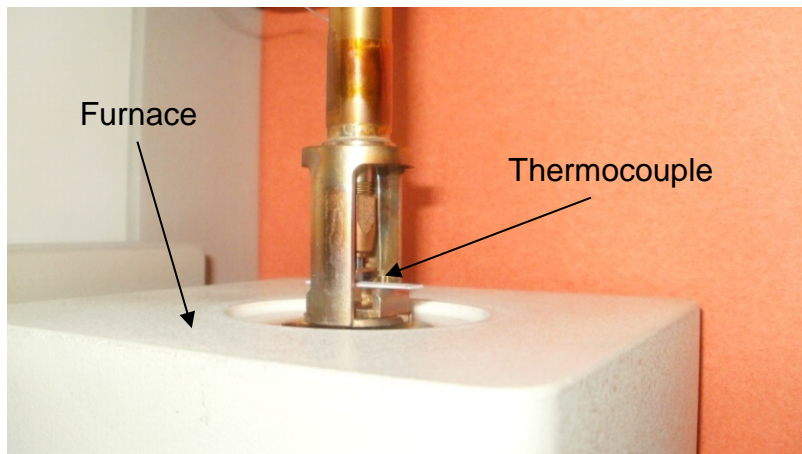
**Figure D-1. Perkin Elmer DMA 7e [D-1]**



**Figure D-2. Perkin Elmer DMA 7e (3-point bend clamp) [D-2]**



**Figure D-3. Perkin Elmer DMA 7e (3-point bend clamp) thermocouple[D-2]**



**Figure D-4. Perkin Elmer DMA 7e (3-point bend clamp) furnace and thermocouple [D-2]**

## D.2 REFERENCES

D-1 Michigan State University, Biocomposites Testing Laboratory, available at <https://www.msu.edu/~matuana/Laboratory.htm> (accessed November 19, 2013).

D-2 Sparks, D., Intec, 2013.

# APPENDIX E—PROPOSED GUIDE FOR THERMOCOUPLE POSITIONING AND TEMPERATURE CALIBRATION OF DYNAMIC MECHANICAL ANALYSIS

The information provided in this appendix is the work of the authors of this report. It is formatted similarly to an ASTM standard for ease of implementation.

## 1. Scope

1.1. This standard method describes the temperature calibration procedures of dynamic mechanical analyzers (DMA) from -150 to 500°C for the purpose of glass transition temperature determination of high modulus polymer matrix composites and gives guidance for instrument thermocouple positioning.

1.2. The instrument should be calibrated according to the instrument manufacturer's recommendations with exception to details described in this test method.

1.3. SI units are the standard, but English units may be reported along with SI units.

## 2. Referenced Documents

### 2.1. ASTM Standards:

D 7028 – Standard Test Method for Glass Transition Temperature (DMA  $T_g$ ) of Polymer Matrix Composites by Dynamic Mechanical Analysis (DMA)

E 473 – Terminology Relating to Thermal Analysis and Rheology

E 1142 – Terminology Relating to Thermophysical Properties

E 1867 – Standard Test Method for Temperature Calibration of Dynamic Mechanical Analyzers

2.2. DMA Instrument Manufacturer's User's Manual

## 3. Terminology

### 3.1. Definitions:

3.1.1. Many technical terms used in this test method are referenced in ASTM E 473 and E 1142.

3.1.2. Calibration Support Beam – A rigid beam which spans the fixture to support the temperature calibration standard

3.1.3. TC – Thermocouple

3.1.4. CS – Calibration Sample

## 4. Summary of Test Method

4.1. The DMA instrument thermocouple location is addressed and recommendations have been established as part of this test method.

4.2. Melting point reference standards are utilized to determine actual melting temperatures for well-known melting reference materials in order to develop a

temperature correction equation for adjusting measured temperatures. This test method relies on a calibration support beam to span the fixture and allow the melting point reference standard to maintain a resistive force. A static force is applied to the melting reference material, and the displacement of the material is recorded and plotted against the temperature. The observed melting point is determined by measuring the onset of a large change in the displacement as a result of the melting of the reference standard. The observed melting points of multiple melting reference materials are used for temperature calibration. The calibration support beam material, location of the reference standard within the calibration support beam, location of the thermocouple, and many other factors have been known to affect the DMA results. This standard provides the procedures and guidance to minimize these testing interferences to ensure reproducible test results.

## 5. Significance and Use

5.1. Different temperature calibration techniques have been found to significantly affect temperature measurements. Since the DMA instrument is used to measure viscoelastic properties over a temperature range, accurate temperature measurements are critical.

## 6. Interferences

6.1. The heating rate for DMA tests has been known to influence temperature transitions. In order to minimize this interference, the same heating rate should be used for both temperature calibration and testing.

6.2. A difference in purge gas type or a change in purge rates may alter results. In order to minimize this interference, the same purge gas and purge rate should be used for both temperature calibration and testing.

6.3. The thermocouple location of the DMA instrument relative to the test sample, test fixture, and furnace is critical for accurate temperature measurements. In order to minimize this interference, the thermocouple location should not be altered; the same location should be used for both temperature calibration and testing. In addition, guidance on the most suitable location is provided by this standard. Temperature differences of more than 10°C have been

observed at different locations along the length of a sample. Heat distribution within the furnace and heat transfer to the sample varies between models and manufacturers of DMA instruments.

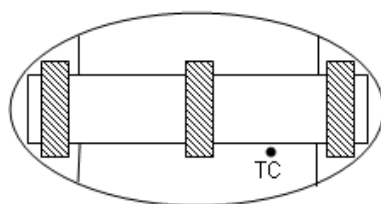
6.4. This method lists several materials that are recommended for use as the calibration support beam. The support beam is required for the temperature calibration process; it acts as a support for the reference standard to rest on. Since it is in direct contact with the reference standard, its thermal properties have profound influence on the melting point of the reference standard. These materials should have similar thermal properties (thermal diffusivity) to that of the actual test samples (i.e. high modulus polymer matrix composites), yet maintain their rigidity to much higher temperatures. Other materials may be used, but should have a similar thermal diffusivity to the actual test samples. The dimensions of the calibration support beam have not been known to noticeably affect the results obtained from the temperature calibration, but its dimensions should be similar to the test sample of interest.

6.5. The heating rate, purge gas type and rate, thermocouple location, and fixture used for testing should be established before temperature calibration. Once these parameters have been established, the instrument should be temperature calibrated and these test parameters should not be changed throughout testing. Any changes to these parameters will require the temperature calibration to be repeated.

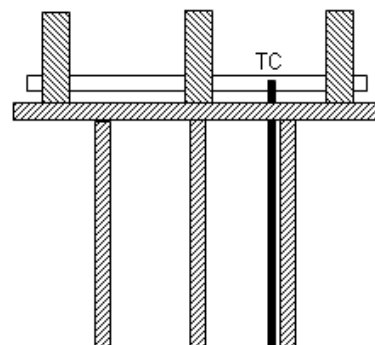
6.6. This method only applies to the temperature calibration for bending geometries of deformation.

## 7. Apparatus

7.1. A Dynamic Mechanical Analyzer capable of meeting the requirements outlined in ASTM D 7028.



Top



Side

FIGURE 1 Recommended Thermocouple Location

## 8. Calibration Materials

8.1. Two Point Calibration – Select two calibration standards from ASTM E 1867 that are near the temperature range of interest. The standards should be of high purity and NIST traceable. Report the selected standards.

8.2. Calibration Support Beam – Select a material from TABLE 1. Report the selected material and dimensions of the calibration support beam.

TABLE 1 Calibration Support Beam Materials - Thermal Diffusivity

Material	Description	Thermal Diffusivity [mm <sup>2</sup> /s]		
		$\alpha$ at T = 25°C	$\alpha$ at T = 149°C	$\alpha$ at T = 232°C
Macor	Glass-Ceramic	0.844	0.727	0.684
Lavastone	Alumina-Silicate	2.00	1.39	1.17
Soda Lime Glass	Silicate Glass	0.505	0.477	0.461

Note 1: Other materials may be used, but they should have a similar thermal diffusivity to the actual test samples over the temperature range of interest. Thermal diffusivity properties for several common types of materials are presented in TABLE 2.

TABLE 2 Common Polymer Matrix Composites - Thermal Diffusivity

Material	Description	Thermal Diffusivity [mm <sup>2</sup> /s]		
		$\alpha$ at T = 25°C	$\alpha$ at T = 149°C	$\alpha$ at T = 232°C
Epoxy Adhesive	Unreinforced Composite	0.255		
Carbon/Epoxy	Reinforced Composite	0.407	0.331	
Carbon/Bismaleimide	Reinforced Composite	0.404	0.341	0.310
Carbon/Polyimide	Reinforced Composite	0.418	0.348	0.319

## 9. Thermocouple Positioning

9.1. Mount a sample in the bending fixture with the same dimensions as the test sample of interest to spatially represent the test setup as shown in FIGURE 1.

9.2. Position the thermocouple 1mm to 2mm away from the edge of the mounted sample and halfway between mounting points. It is not recommended that the thermocouple be placed under the specimen because it may become damaged if the sample excessively displaces during the test.

Note 2: Some DMA instruments do not allow thermocouple movement. In this case, record the thermocouple location relative to the sample, fixture, and furnace wall.

**10. Procedure**

10.1. This test method utilizes a two point calibration, which assumes that the relationship between the observed onset melting temperature ( $T_o$ ) and actual specimen temperature ( $T_i$ ) is linear. This relationship is expressed by the equation

$$T_i = (T_o \times S) + I$$

where  $S$  and  $I$  are the slope and intercept of a straight line, respectively.

10.2. If the DMA instrument has a temperature table that corrects for temperature calibration, be certain it is cleared. This will revert the instrument temperature settings to the default settings originally established by the instrument manufacturer.

10.3. Prepare two 2 - 5 mg samples of the calibration standard with a uniform thickness between 0.15 mm and 0.25 mm.

Note 3: The sample may need to be pressed to obtain the desired thickness.

10.4. Position one calibration sample between a lower and upper calibration support beam. The sample

should be centered widthwise and aligned with the thermocouple when mounted. Position the second calibration sample an equal distance from the center of the calibration support beam as the first calibration sample as shown in FIGURE 2.

Note 4: Marking the calibration support beam with these locations may facilitate the positioning of the calibration samples.

10.5. Mount the calibration support beam and calibration samples. Center the calibration support beam and verify that the calibration samples are in the correct location. The mounted configuration should look similar to FIGURE 2.

Note 5: If using the dual or single cantilever fixture, hand tightening the fixture screws is generally sufficient to obtain quality data. Excessive torque may break the calibration support beam.

10.6. Apply a static force that does not deform the calibration sample below the melting point, but that will deform the calibration sample at the melting point sufficiently to produce instantaneous deformation. A static force of 1N is recommended.

10.7. Perform the calibration runs at the heating rate of interest. ASTM D 7028 recommends 5°C/min. Other heating rates may be used but must be reported.

Note 6: The temperature calibration should always be performed at the heating rate at which the intended specimens will be tested.

10.8. Measure and record the temperature and displacement from at least 30°C below to 20°C above the melting point of the calibration standard. The calibration sample should be equilibrated 50°C below its melting point.

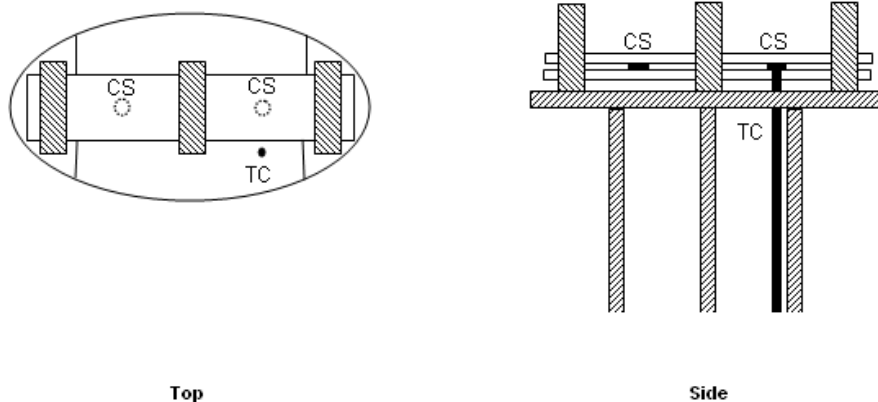


FIGURE 2 Temperature Calibration Setup



## 11. Calculation

11.1. Find the melting point ( $T_o$ ) of the calibration sample from the displacement curve (see FIGURE 3).

11.1.1. Construct a tangent to the displacement curve over a temperature region below the apparent transition temperature.

11.1.2. Construct a tangent to the displacement curve where there is an apparent instantaneous change in displacement.

11.1.3. Determine the temperature at which point these tangent lines intersect. Report this as the observed transition temperature ( $T_o$ ).

11.2. Correct the measured temperature:

11.2.1. Once the transition temperature ( $T_o$ ) is determined for two different calibration standards, the temperature correction equation can be determined. The slope and intercept can be determined by the following equations:

$$S = [T_{c1} - T_{c2}] / [T_{o1} - T_{o2}]$$

$$I = [(T_{o1} \times T_{c2} - (T_{c1} \times T_{o2})) / [T_{o1} - T_{o2}]$$

where

$S$  = slope

$I$  = intercept

$T_{c1}$  = correct melting point for calibration standard 1

$T_{c2}$  = correct melting point for calibration standard 2

$T_{o1}$  = observed melting point for calibration standard 1

$T_{o2}$  = observed melting point for calibration standard 2

11.2.2. By finding  $S$  and  $I$ , the actual specimen temperature can be determined from the experimentally observed temperature.

11.2.3. If the DMA instrument has a temperature table which corrects for temperature calibration, input the observed and correct melting temperatures into the correction table. The instrument will then automatically adjust the experimentally observed temperature and report the actual temperature.

11.2.4. See the appendix for examples of invalid tests. Tests that are invalid will need to be repeated.

## 12. Verification

12.1. After the temperature calibration has been performed and the correction equations have been applied, temperature verification should be conducted by repeating runs with each calibration standard. The verification melting points should be  $\pm 1^\circ\text{C}$  of the correct melting points ( $T_{c1}$  and  $T_{c2}$ ). Otherwise, the calibration procedures should be repeated.

12.2. Temperature verification should be routinely performed to ensure temperature accuracy of the DMA instrument.

## 13. Report

13.1. Report the following information:

13.1.1. Manufacturer and model of the DMA instrument,

13.1.2. Calibration standards and their purity,

13.1.3. Calibration support beam material and dimensions,

13.1.4. Purge gas type, purity, and flow rate,

13.1.5. Heating rate,

13.1.6. Values of  $T_{c1}$  and  $T_{c2}$ ,

13.1.7. Values of  $T_{o1}$  and  $T_{o2}$  determined from calibration and verification.

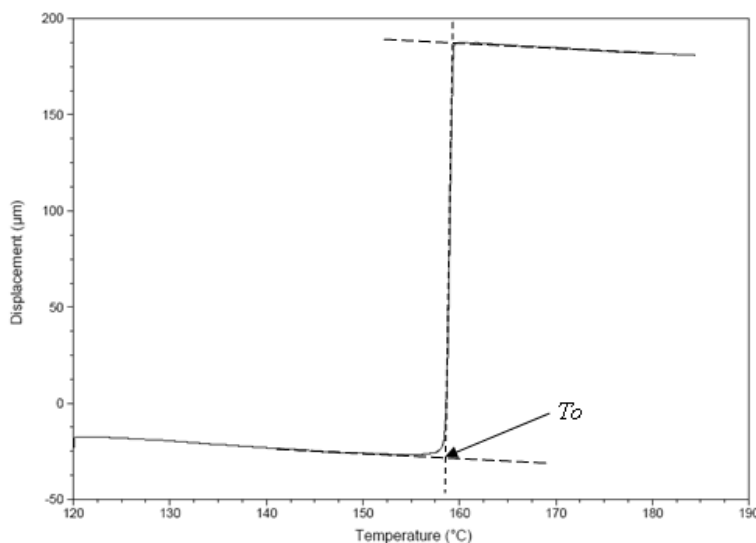


FIGURE 3 Transition Temperature

## Appendix

### Examples of Calibration Test Plots

#### A.1. Invalid Melting/Transition Curves

A.1.1. This test method assumes the displacement of the calibration standard to be instantaneous during melting. If the displacement curve departs from the baseline by more than 2 °C, the test is considered invalid and must be repeated. See FIGURE A1 and A2.

#### B.1. Valid Melting/Transition Curves

B.1.1. Examples of valid melting/transition curves are presented in FIGURE B1 and B2.

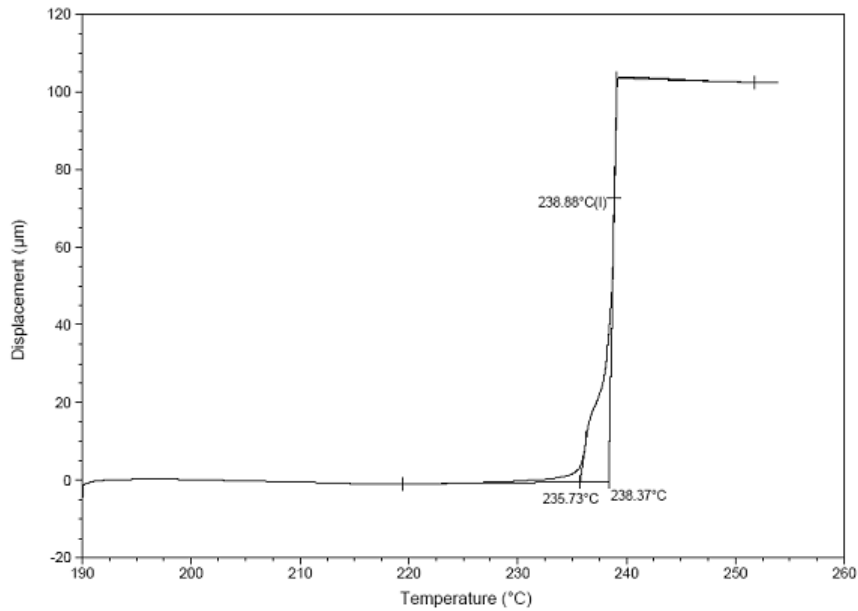


FIGURE A1 Invalid Calibration Result, (238.37 °C - 235.73 °C) > 2 °C

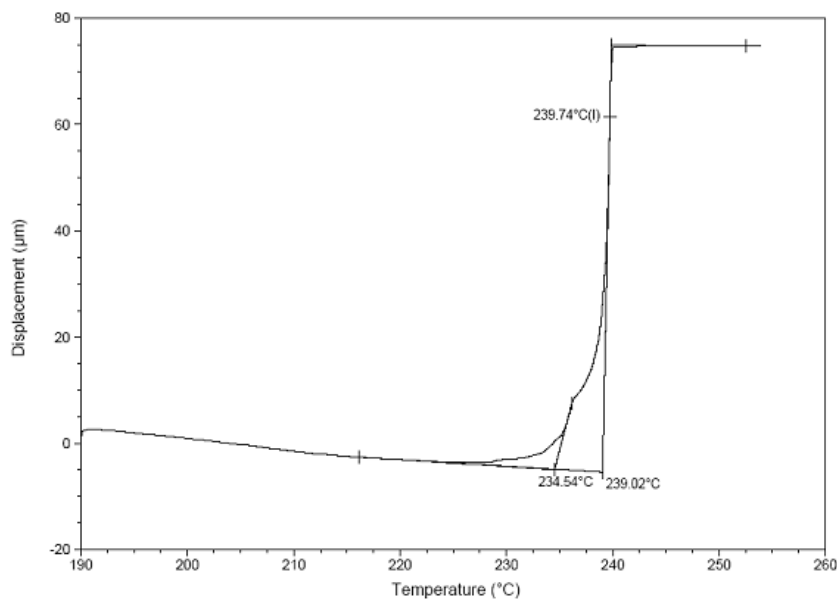
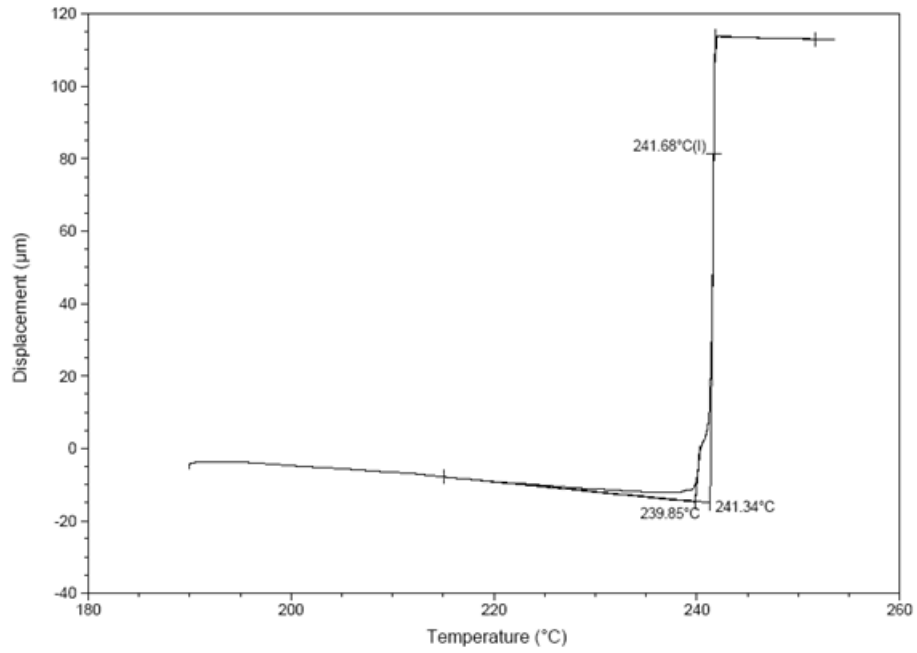
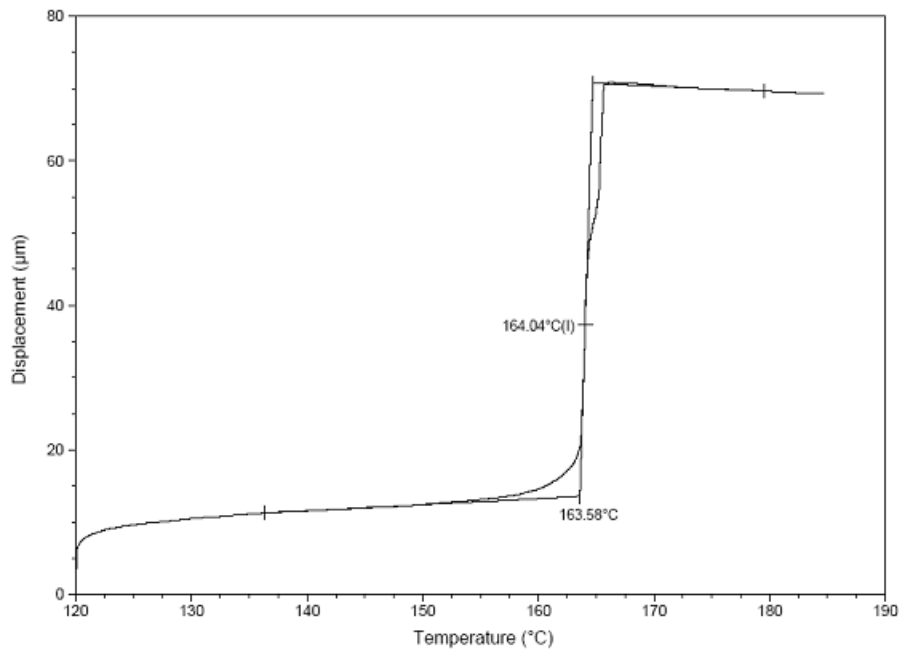


FIGURE A2 Invalid Calibration Result, (239.02 °C - 234.54 °C) > 2 °C



**FIGURE B1 Valid Calibration Result, (241.34 °C - 239.85 °C) < 2 °C**



**FIGURE B2 Valid Calibration Result, Secondary Transition Is After Inflection Point**