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Development of Dynamic Mechanical Analyzer (DMA) Calibration and Testing Procedures

2013 Technical Review

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Development of Dynamic Mechanical Analyzer (DMA) Calibration and Testing Procedures

- Motivation and Key Issues
  - Determining the glass transition temperature (Tg) by DMA is critical for characterizing polymeric materials
    - Material service temperature determination
    - Quality control tool to validate curing process
  - Lack of well defined calibration and testing procedures
    - ASTM D7028 and SACMA SRM 18R refer to the equipment manufacturer's recommendations in many cases.
      - Thermocouple location
      - Temperature calibration standards
    - Leads to poor lab-to-lab and equipment-to-equipment reproducibility
      - Round robin testing of ASTM D7028 (report number D30-1004 dated December 15th, 2007) provides a poor reproducibility standard deviation of 13.36° F.
      - Significant reproducibility issues with several material qualification programs for FAA aircraft certification.
  - Accurate and reproducible Tg determination is critical to safety wherever polymer matrix composites are utilized.

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Development of Dynamic Mechanical Analyzer (DMA) Calibration and Testing Procedures

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  - George Parker, Boeing
  - John Moylan, Delsen

Development of Dynamic Mechanical Analyzer (DMA) Calibration and Testing Procedures

- Objective
  - Reduce the lab-to-lab and equipment-to-equipment variability of Tg measurements by developing universal guidelines for temperature calibration and testing procedures for DMA equipment to enhance pre-existing testing standards.
  - Improve industry applications and safety
    - Material service temperature definition
    - Quality control

Development of Dynamic Mechanical Analyzer (DMA) Calibration and Testing Procedures

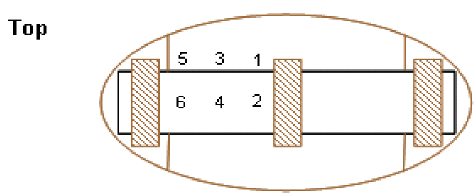
- Approach
  - Research areas that potentially influence Tg determination and reproducibility.
    - Thermocouple location
    - Specimen dimensions
    - Temperature calibration
      - Calibration materials
      - Application of calibration materials
  - Develop universal guidelines for temperature calibration and testing procedures for DMA equipment.
  - Evaluate developed guidelines for lab-to-lab and equipment-to-equipment reproducibility through round robin testing.
  - Further evaluate developed guidelines by comparing to DSC and TMA test results.

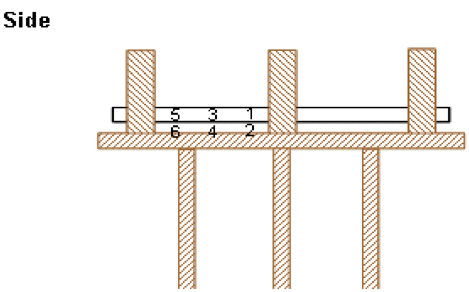
Thermocouple Location

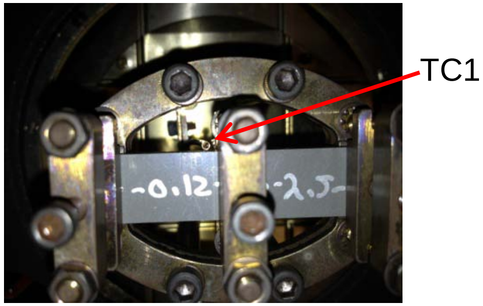
- Thermocouple (TC) Location Evaluation
  - ASTM D7028 section 11.9 remarks, "*Follow the manufacturer's manual or recommendations to position the thermocouple. Typically the thermocouple should be as close to the sample as possible*."
  - Manufacturers recommend that the thermocouple proximity should be close to the sample, as well, but do not provide any specifics.
  - The fixture acts has a heat sink, affecting heat transfer to the sample.
    - Evaluate TC location, respective of location to fixture
    - Evaluate TC location, respective of location to sample

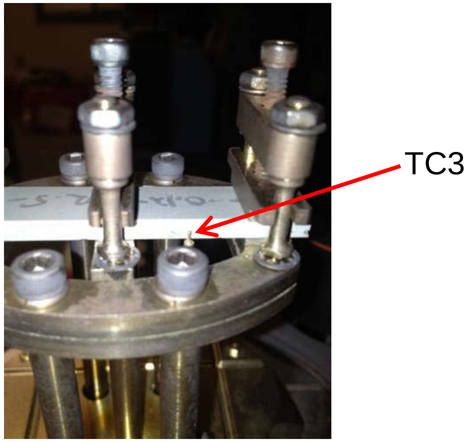
Thermocouple Location – Test Configurations

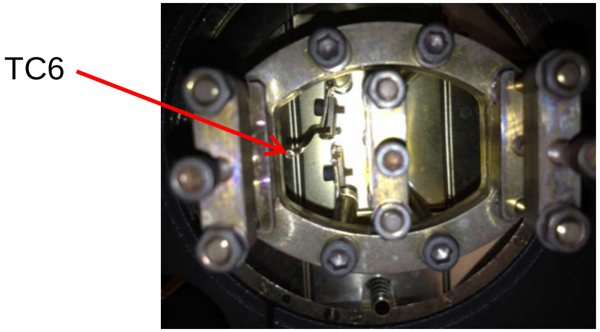
TC Location	Test Method	Specimens per Material (Number of Materials)		Material ID
		50mm 3-pt Bend Fixture	35mm Dual Cantilever Fixture	
1	ASTM D7028 & Figure 1	1 x (4)	1 x (4)	180F-Tg-EPXY 350F-Tg-EPXY 500F-Tg-BMI 600F-Tg-PI
2		1 x (4)	1 x (4)	180F-Tg-EPXY 350F-Tg-EPXY 500F-Tg-BMI 600F-Tg-PI
3		1 x (4)	1 x (4)	180F-Tg-EPXY 350F-Tg-EPXY 500F-Tg-BMI 600F-Tg-PI
4		1 x (4)	1 x (4)	180F-Tg-EPXY 350F-Tg-EPXY 500F-Tg-BMI 600F-Tg-PI
5		1 x (4)	1 x (4)	180F-Tg-EPXY 350F-Tg-EPXY 500F-Tg-BMI 600F-Tg-PI
6		1 x (4)	1 x (4)	180F-Tg-EPXY 350F-Tg-EPXY 500F-Tg-BMI 600F-Tg-PI











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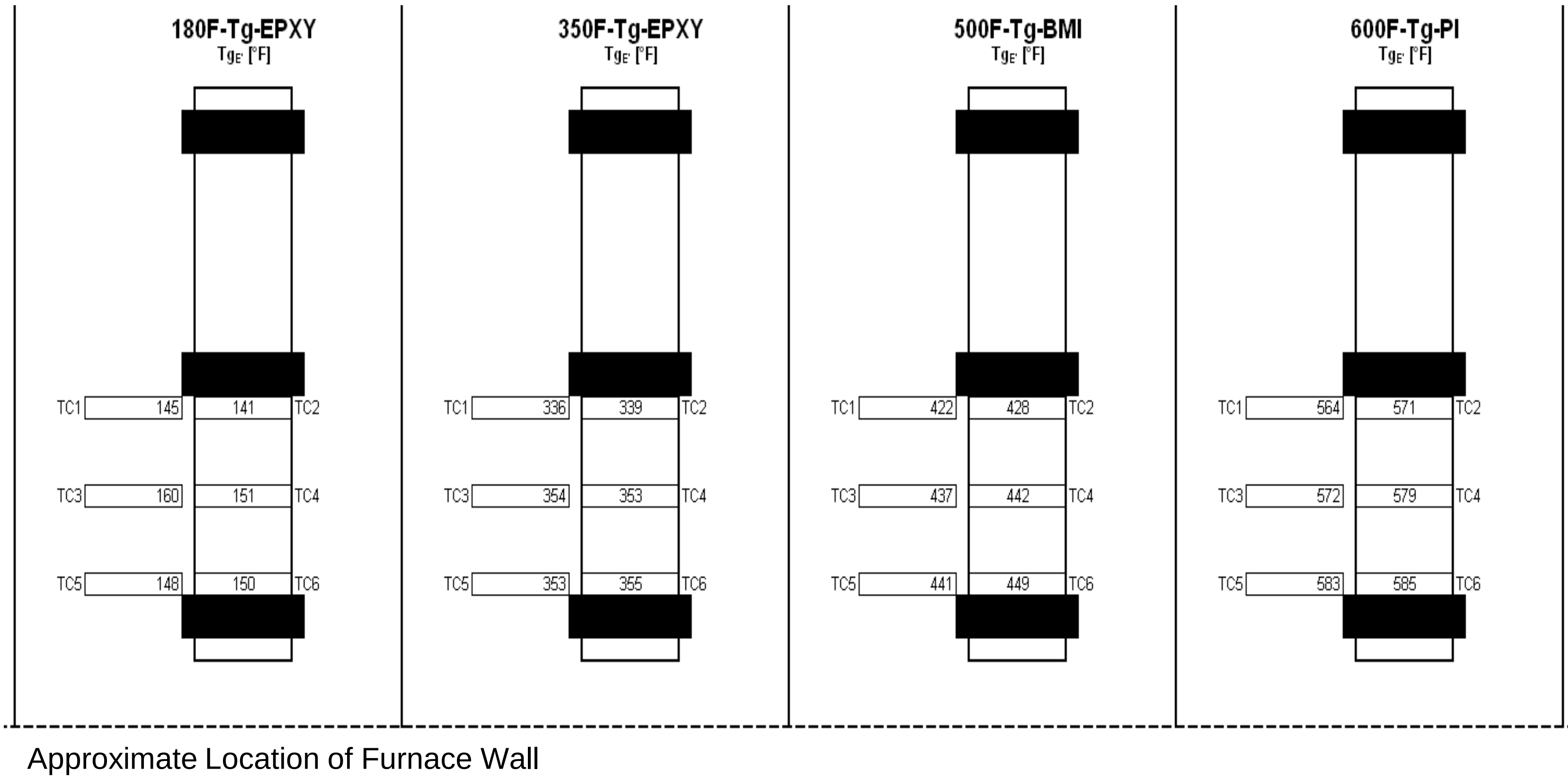
Thermocouple Location – Test Results

35mm Dual Cantilever Fixture



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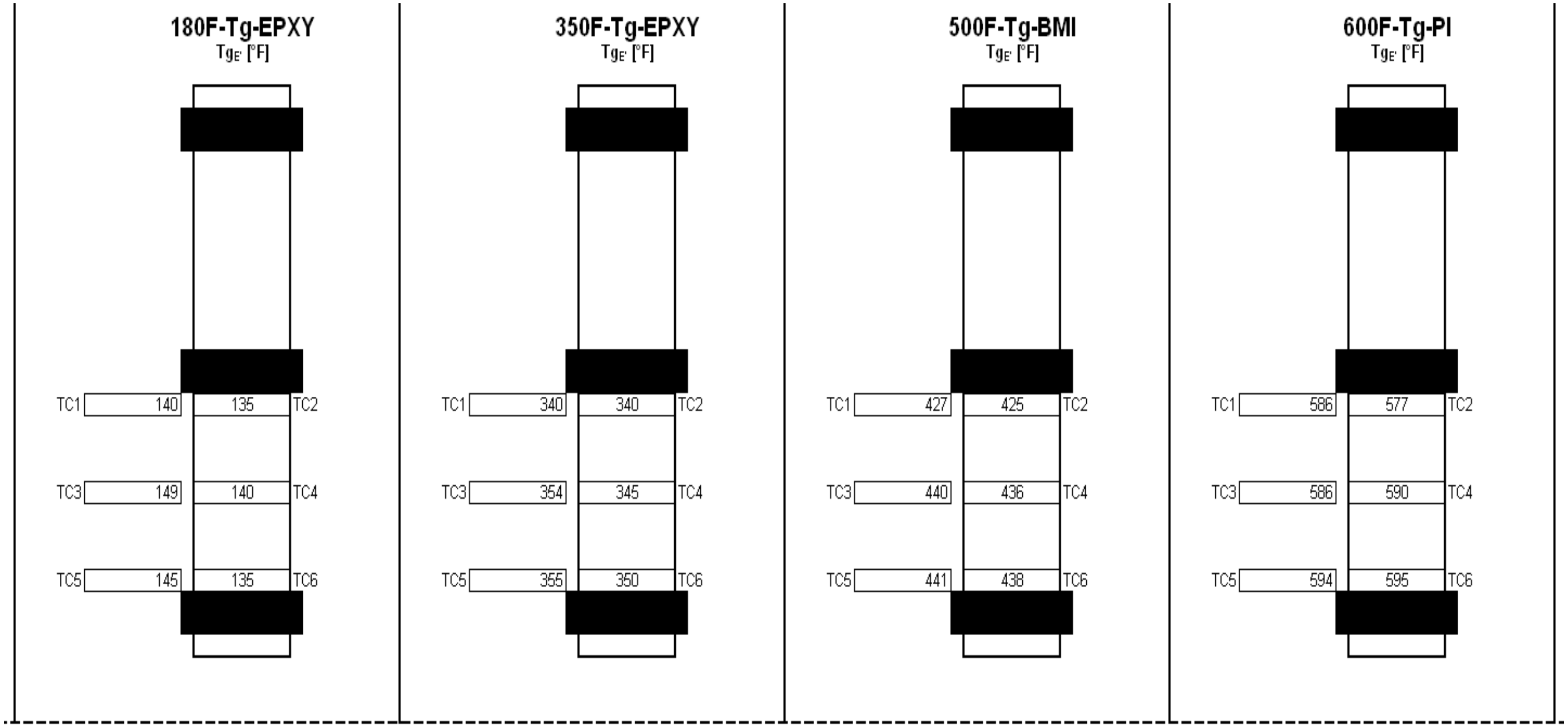
Thermocouple Location – Test Results

50mm 3-Point Bend Fixture



Approximate Location of Furnace Wall

Thermocouple Location – Conclusion

- Thermocouple (TC) Location Evaluation
  - Significant differences between TC locations
  - The fixture acts has a heat sink, affecting heat transfer to the sample. This is evident by low Tg values observed at TC1 and TC2.
  - The proximity of the test specimen to the furnace becomes more critical at higher temperatures
- Recommend TC3 Location
  - LocationsTC2, TC4, and TC6 can result in a damaged TC if a highly deformable material is tested.
  - Location TC3 is least affected by the fixture heat sink and furnace proximity.
  - Tg values obtained at TC3 were in the top half of all TC locations

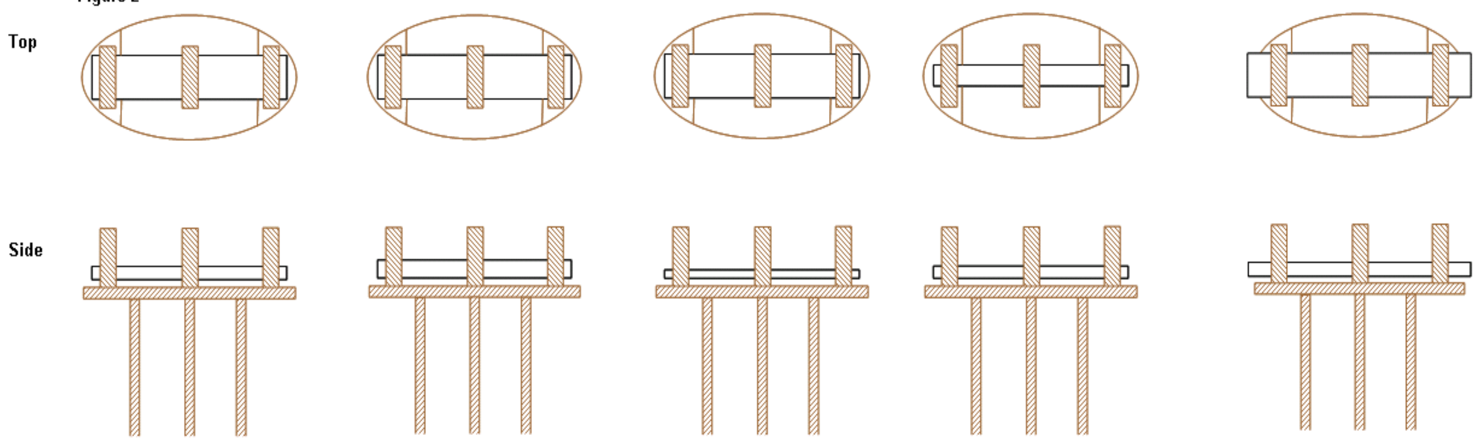
Specimen Dimensions

- Specimen Dimensions Evaluation
  - Determine if specimen dimensions affect Tg
    - Evaluate changes in thickness
    - Evaluate changes in width
    - Evaluate changes in length
  - Possible effects include
    - Thermal lag
    - Specimen stiffness

Specimen Dimensions – Test Configurations

Property	Test Method	Support Dimensions			Specimens per Material (Number of Materials)		Material ID
		Thickness (in.)	Width (in.)	Length (in.)	50mm 3-pt Bend Fixture	35mm Dual Cantilever Fixture	
Glass Transition Temperature (Tg), Dry, by DMA	ASTM D7028 & Figure 2	0.08	0.5	2.5	1 x (1)	1 x (1)	350F-Tg-EPXY
		0.12	0.5	2.5	1 x (1)	1 x (1)	350F-Tg-EPXY
		0.04	0.5	2.5	1 x (1)	1 x (1)	350F-Tg-EPXY
		0.08	0.25	2.5	1 x (1)	1 x (1)	350F-Tg-EPXY
		0.08	0.5	2.25	1 x (1)	1 x (1)	350F-Tg-EPXY

Figure 2



Thickness X Width X Length

0.08" X 0.5" X 2.5"
a. Baseline Specimen

0.12" X 0.5" X 2.5"
b. Variable Thickness Specimen

0.04" X 0.5" X 2.5"
c. Variable Thickness Specimen

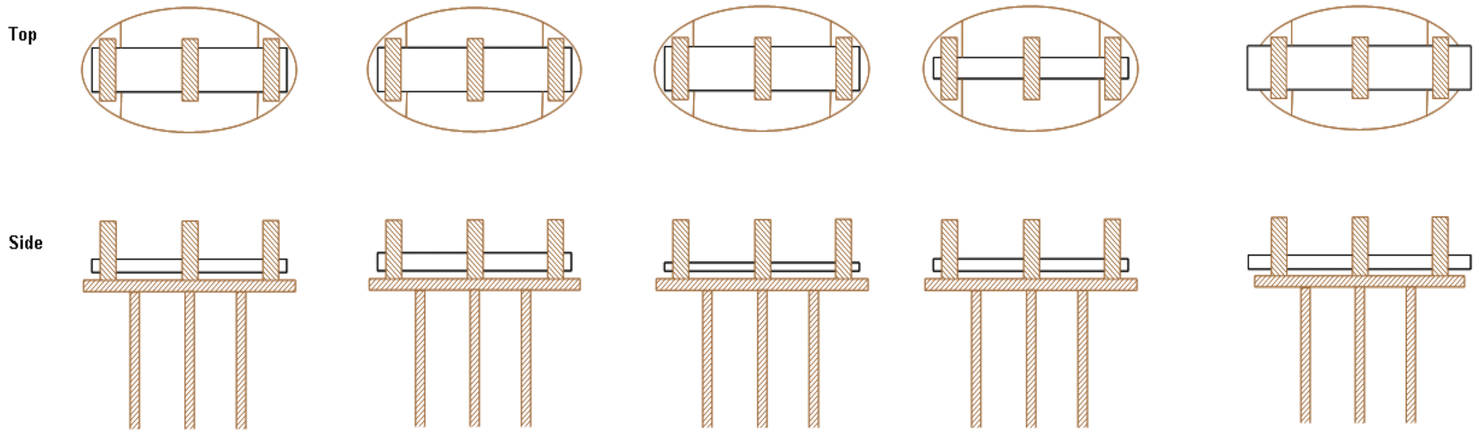
0.04" X 0.5" X 2.5"
d. Variable Width Specimen

0.08" X 0.5" X 3.0"
e. Variable Length Specimen

Specimen Dimensions – Test Results

Property	Test Method	Support Dimensions			Tg_E [°F]		Material ID
		Thickness (in.)	Width (in.)	Length (in.)	50mm 3-pt Bend Fixture	35mm Dual Cantilever Fixture	
Glass Transition Temperature (Tg), Dry, by DMA	ASTM D7028 & Figure 2	0.08	0.5	2.5	371	374	350F-Tg-EPXY
		0.12	0.5	2.5	365	375	350F-Tg-EPXY
		0.04	0.5	2.5	385	384	350F-Tg-EPXY
		0.08	0.25	2.5	381	385	350F-Tg-EPXY
		0.08	0.5	2.25	372	373	350F-Tg-EPXY

Figure 2



Thickness X Width X Length

0.08" X 0.5" X 2.5"
a. Baseline Specimen

0.12" X 0.5" X 2.5"
b. Variable Thickness Specimen

0.04" X 0.5" X 2.5"
c. Variable Thickness Specimen

0.04" X 0.5" X 2.5"
d. Variable Width Specimen

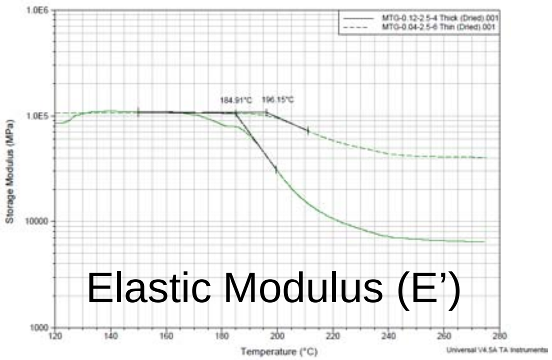
0.08" X 0.5" X 3.0"
e. Variable Length Specimen

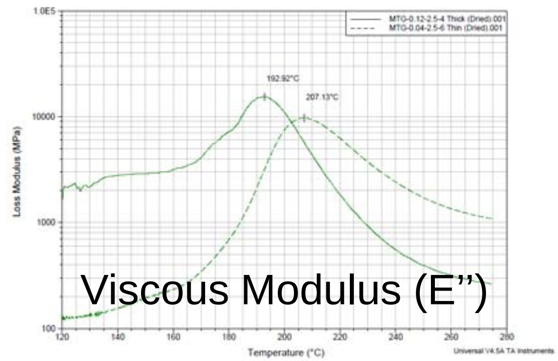
Specimen Dimensions – Conclusion

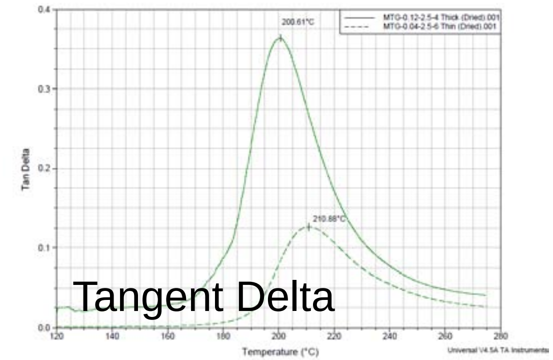
Thickness dependent material behavior

0.12” (Thick) ———
0.04” (Thin) - - - - - - -

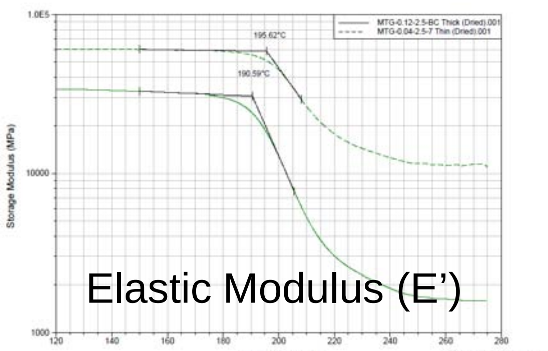
50mm 3-Pt Bend Fixture

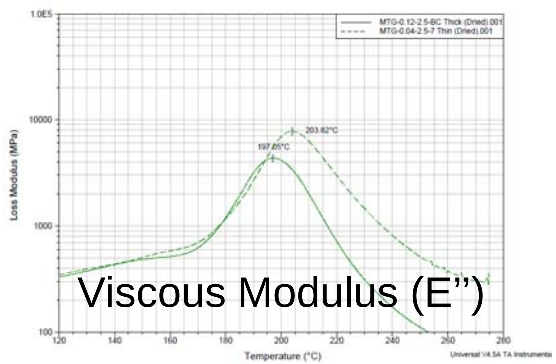


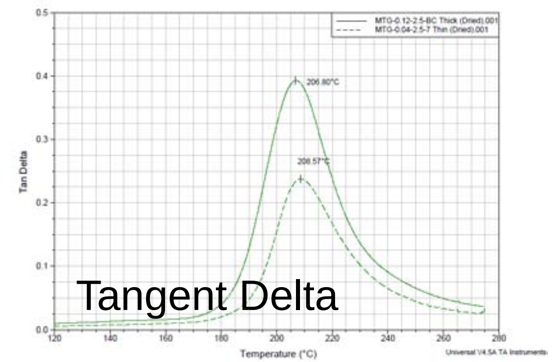




35mm Dual Cantilever Fixture







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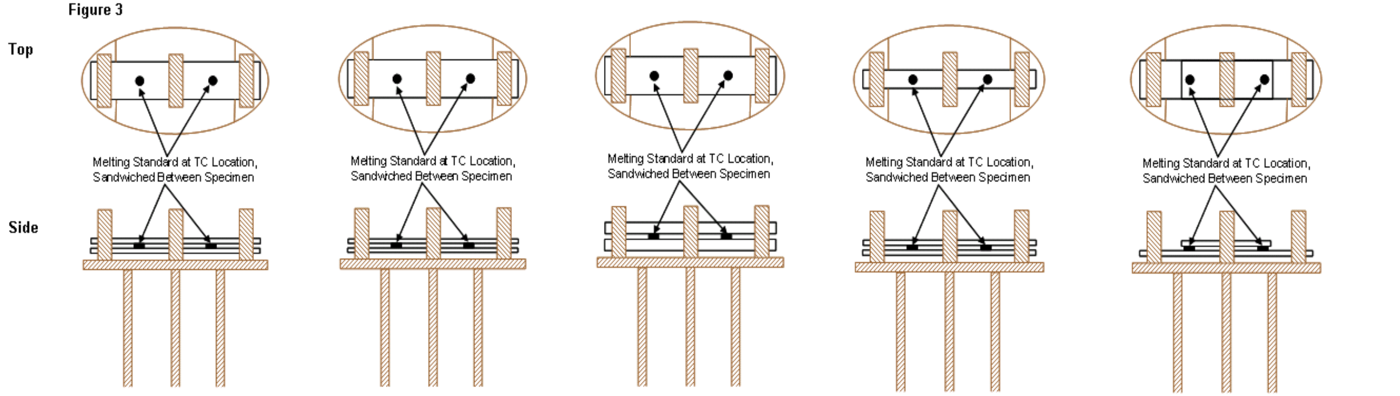
Temperature Calibration

- Temperature Calibration Evaluation
  - ASTM D7028, section 9.1 states, "*The DMA equipment shall be calibrated in accordance with Test Method E 1867 for temperature signals and in accordance with the equipment manufacturer's recommendation for the storage modulus*."
  - ASTM E1867 lists NIST traceable temperature calibration standards
    - Indium, Tm = 156.6 ° C
    - Tin, Tm = 231.9 ° C
    - Lead, Tm = 327.5 ° C
    - Zinc, Tm = 419.5 ° C
  - ASTM E 1867 does not address the need for a rigid span support to hold the calibration standard.
    - Evaluate calibration support beam dimensions/configuration
    - Evaluate calibration support beam materials

Temperature Calibration – Support Dimensions & Configurations

Property	Test Method	Support Dimensions			Specimens per Material (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 & Figure 3	0.04	0.5	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F-Tg-BMI
		0.02	0.5	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F-Tg-BMI
		0.06	0.5	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F-Tg-BMI
		0.04	0.25	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F-Tg-BMI
		0.04	0.5	Bottom, 2.5 Top, 1.5	1 x (1)	1 x (1)	500F-Tg-BMI
Tin Melting Temperature		0.04	0.5	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F-Tg-BMI
		0.02	0.5	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F-Tg-BMI
		0.06	0.5	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F-Tg-BMI
		0.04	0.25	Bottom, 2.5 Top, 2.5	1 x (1)	1 x (1)	500F-Tg-BMI
		0.04	0.5	Bottom, 2.5 Top, 1.5	1 x (1)	1 x (1)	500F-Tg-BMI

Figure 3



Bottom Thickness,Top Thickness X Bottom Width,Top Width X Bottom Length,Top Length

0.04",0.04" X 0.5",0.5" X 2.5",2.5" **a. Baseline Specimen**

0.02",0.02" X 0.5",0.5" X 2.5",2.5" **b. Variable Thickness Specimen**

0.06",0.06" X 0.5",0.5" X 2.5",2.5" **c. Variable Thickness Specimen**

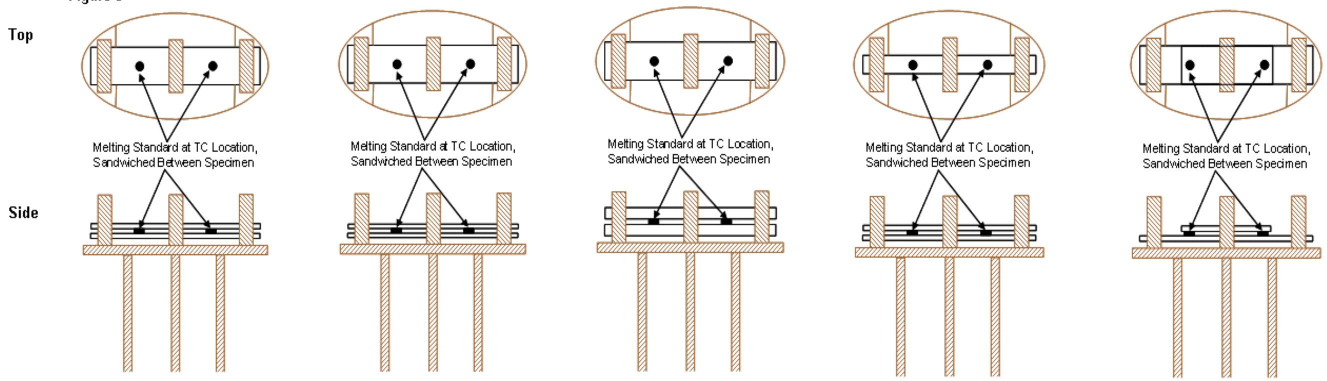
0.04",0.04" X 0.25",0.25" X 2.5",2.5" **d. Variable Width Specimen**

0.04",0.04" X 0.5",0.5" X 2.5",1.5" **e. Variable Length Specimen**

Temperature Calibration – Support Dimensions & Configurations, Test Results

Property	Test Method	Support Dimensions			T_m [°F]		Material ID
		Thickness (in.)	Width (in.)	Length (in.)	50mm 3-pt Bend Fixture	35mm Dual Cantilever Fixture	
Indium Melting Temperature (313.88°F)	ASTM E1867 & Figure 3	0.04	0.5	Bottom, 2.5 Top, 2.5	323	335	500F-Tg-BMI
		0.02	0.5	Bottom, 2.5 Top, 2.5	321	333	500F-Tg-BMI
		0.06	0.5	Bottom, 2.5 Top, 2.5	323	334	500F-Tg-BMI
		0.04	0.25	Bottom, 2.5 Top, 2.5	326	344	500F-Tg-BMI
		0.04	0.5	Bottom, 2.5 Top, 1.5	321	334	500F-Tg-BMI
Tin Melting Temperature (449.38°F)	ASTM E1867 & Figure 3	0.04	0.5	Bottom, 2.5 Top, 2.5	458	471	500F-Tg-BMI
		0.02	0.5	Bottom, 2.5 Top, 2.5	455	467	500F-Tg-BMI
		0.06	0.5	Bottom, 2.5 Top, 2.5	458	467	500F-Tg-BMI
		0.04	0.25	Bottom, 2.5 Top, 2.5	458	472	500F-Tg-BMI
		0.04	0.5	Bottom, 2.5 Top, 1.5	456	470	500F-Tg-BMI

Figure 3



Bottom Thickness,Top Thickness X Bottom Width,Top Width X Bottom Length,Top Length

0.04",0.04" X 0.5",0.5" X 2.5",2.5"
a. Baseline Specimen

0.02",0.02" X 0.5",0.5" X 2.5",2.5"
b. Variable Thickness Specimen

0.06",0.06" X 0.5",0.5" X 2.5",2.5"
c. Variable Thickness Specimen

0.04",0.04" X 0.25",0.25" X 2.5",2.5"
d. Variable Width Specimen

0.04",0.04" X 0.5",0.5" X 2.5",1.5"
e. Variable Length Specimen

Temperature Calibration – Support Material

Polymer Matrix Material for Comparison to Evaluation of Support Materials

Property	Test Method	Specimens per Material (Number of Materials): 50mm 3-pt Bend Fixture	Specimens per Material (Number of Materials): 35mm Dual Cantilever Fixture	Material ID
Indium Melting Temperature	ASTM E1867	3 x (3)	3 x (3)	350F-Tg-EPXY 500F-Tg-BMI 600F-Tg-PI
Tin Melting Temperature	ASTM E1867	3 x (2)	3 x (2)	500F-Tg-BMI 600F-Tg-PI
Specific Heat Capacity, Thermal Conductivity, and Thermal Diffusivity	ASTM E1461	1 x (4)		180F-Tg-EPXY 350F-Tg-EPXY 500F-Tg-BMI 600F-Tg-PI

Support Material Evaluation

Property	Test Method	Specimens per Material (Number of Materials): 50mm 3-pt Bend Fixture	Specimens per Material (Number of Materials): 35mm Dual Cantilever Fixture	Material ID
Indium Melting Temperature	ASTM E1867	3 x (4)	3 x (4)	Macor Alumina Silicate Silica Glass Steel
Tin Melting Temperature	ASTM E1867	3 x (4)	3 x (4)	Macor Alumina Silicate Silica Glass Steel
Specific Heat Capacity, Thermal Conductivity, and Thermal Diffusivity	ASTM E1461	1 x (4)		Macor Alumina Silicate Silica Glass Steel

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Temperature Calibration – Support Material, Test Results

Indium Tm = 313.88°F, Tin Tm = 449.38°F

50mm 3-pt Bend Fixture		
Material ID	**Indium Tmavg [°F]**	**Tin Tmavg [°F]**
350F-Tg-EPXY	319.77	-
500F-Tg-BMI	320.06	454.42
600F-Tg-PI	317.72	453.16
Polymer Matrix Avg	**319.18**	**453.79**
Alumina Silicate	322.84	455.74
Macor	316.74	453.01
Silica Glass	317.61	453.72
Steel	330.83	461.62

35mm Dual Cantilever Fixture		
Material ID	**Indium Tmavg [°F]**	**Tin Tmavg [°F]**
350F-Tg-EPXY	330.27	-
500F-Tg-BMI	330.41	463.80
600F-Tg-PI	327.84	462.52
Polymer Matrix Avg	**329.51**	**463.16**
Alumina Silicate	330.34	463.79
Macor	328.50	460.49
Silica Glass	328.16	460.80
Steel	336.60	467.14

Temperature Calibration – Support Material, Test Results

Material	Thermal Diffusivity [mm^2/s] α at T = 77°F	α at T = 300°F	α at T = 450°F
180F-TG-EPOXY	0.255		
350F-TG-EPOXY	0.407	0.331	
500F-TG-BMI	0.404	0.341	0.310
600F-TG-PI	0.418	0.348	0.319

Material	Description	Thermal Diffusivity [mm^2/s] α at T = 77°F	α at T = 300°F	α at T = 450°F
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

Temperature Calibration – Conclusion

- Calibration Support Beam Geometry
  - No significant differences seen with variable dimensions
  - Recommend using a similar size calibration support beam as the intended test specimen
- Calibration Support Beam Material
  - Macor, Lavastone and soda lime glass were all found to be good materials.
    - Comparable melting temperatures to melting temperatures found using polymer matrix composite calibration support beams
    - Similar thermal diffusivities to polymer matrix composites
  - Recommend using Macor
    - Relatively easy to obtain
    - Easily machineable
    - Consistent formulation

Development of Dynamic Mechanical Analyzer (DMA) Calibration and Testing Procedures

- Development of Calibration and Testing Procedures
  - Utilized data from the DMA evaluations
    - TC location
    - Specimen dimensions
    - Span support dimensions/configuration
    - Span support material
  - Distributed new calibration and testing procedures and materials to labs for round robin testing for evaluation of procedures.
    - Low-to-high Tg materials are being evaluated
    - Specimens are being tested after dry and wet environmental conditioning

Inter-Laboratory Testing – Test Matrix

Property	Test Method	Specimens per Material (Number of Materials)												Material ID
		Laboratory, 50mm 3-pt Bend Fixture						Laboratory, 35mm Dual Cantilever Fixture						
		Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	
DMA Temperature Calibration	ASTM E1867	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	Indium Zinc
DMA Temperature Verification		1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	1 x (2)	Indium Zinc
Glass Transition Temperature (Tg), Dry, by DMA	ASTM D7028	3 x (5)	3 x (5)	3 x (5)	3 x (5)	3 x (5)	3 x (5)	3 x (5)	3 x (5)	3 x (5)	3 x (5)	3 x (5)	3 x (5)	180F-Tg-EPXY 350F-Tg-EPXY 500F-Tg-BMI 600F-Tg-PI Polycarbonate
Glass Transition Temperature (Tg), Wet, by DMA		3 x (4)	3 x (4)	3 x (4)	3 x (4)	3 x (4)	3 x (4)	3 x (4)	3 x (4)	3 x (4)	3 x (4)	3 x (4)	3 x (4)	180F-Tg-EPXY 350F-Tg-EPXY 500F-Tg-BMI 600F-Tg-PI

Inter-Laboratory Testing – Test Results

- Round Robin Test Results
  - Tests have been completed from three of the six labs
    - The standard deviation of the dry tested samples is much improved from the ASTM D 7028 round robin.
    - The standard deviation of the wet tested samples is worse than that obtained from the ASTM D 7028 round robin.
    - Two of the labs required relatively thin (0.06”) samples and the third and remaining labs are using a relatively thick (0.12”) sample.
    - There is reason to believe that the thin samples lost more moisture than the thick samples before the Tg was reached.
  - All round robin results will be reported in the FAA report.

	Standard Deviation of the Glass Transition Temperature [°F]					
	Dry $Tg_{E'}$	Dry $Tg_{E''}$	Dry $Tg_{\tan\delta}$	Wet $Tg_{E'}$	Wet $Tg_{E''}$	Wet $Tg_{\tan\delta}$
ASTM D 7028 Round Robin (2007)	18.628	18.753	16.259	13.254	12.544	13.281
Current Round Robin w/ Calibration Procedures	6.640	6.568	5.325	15.476	17.129	21.750

Development of Dynamic Mechanical Analyzer (DMA) Calibration and Testing Procedures

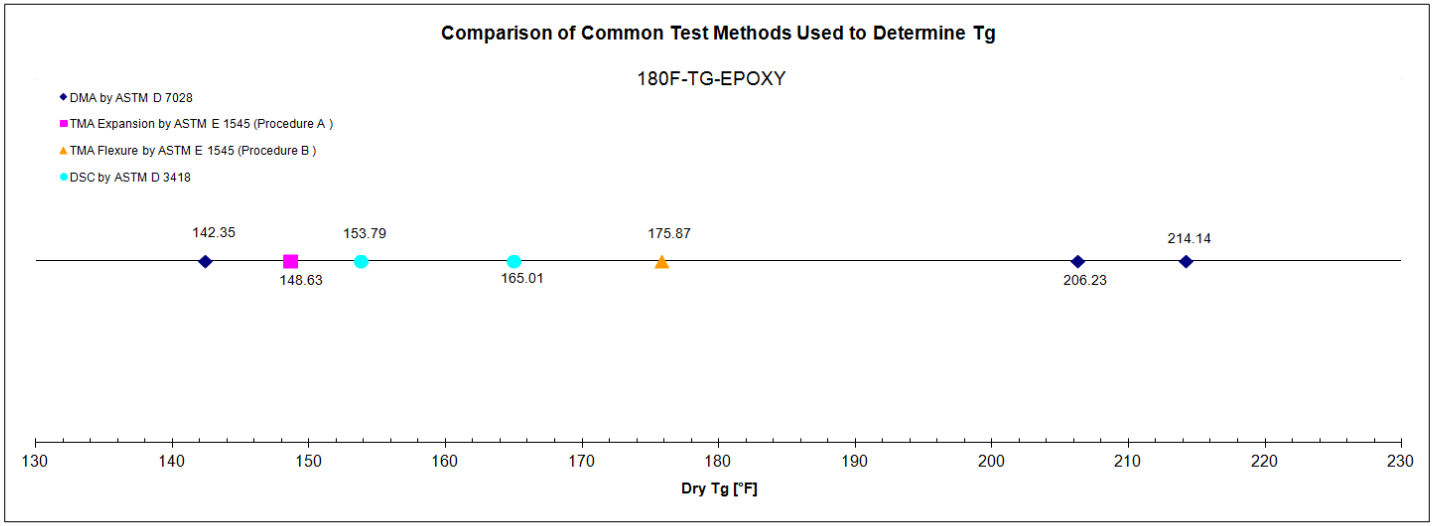
- Viability of New Calibration and Testing Procedures
  - Data from round robin testing will be analyzed to determine adequacy of the new procedures.
  - Additional thermal analysis techniques were used on a small scale to further characterize the capabilities of these procedures.
    - Differential Scanning Calorimetry (DSC) by ASTM D3418
    - Thermo-Mechanical Analysis (TMA) by expansion method ASTM E1545 (procedure A)
    - Thermo-Mechanical Analysis (TMA) by flexure method ASTM E1545 (modified procedure B)

Comparison to DSC & TMA Techniques

Property	Test Method	Specimens per Material (Number of Materials)	Material ID
Glass Transition Temperature (Tg), Dry, by DSC	ASTM D3418	3 x (5)	180F-Tg-EPXY 350F-Tg-EPXY 500F-Tg-BMI 600F-Tg-PI Polycarbonate
Glass Transition Temperature (Tg), Dry, by TMA Expansion	ASTM E1545, Procedure A	3 x (5)	180F-Tg-EPXY 350F-Tg-EPXY 500F-Tg-BMI 600F-Tg-PI Polycarbonate
Glass Transition Temperature (Tg), Dry, by TMA Flex	ASTM E1545, Modified Procedure B	3 x (5)	180F-Tg-EPXY 350F-Tg-EPXY 500F-Tg-BMI 600F-Tg-PI Polycarbonate

Comparison to DSC & TMA Techniques – Test Results

Material	Specimen Number	Glass Transition Temperature [°F]						
		DMA by ASTM D 7028 (NIAR Calibration Procedures)			TMA Expansion by ASTM E 1545 (Procedure A)	TMA Flexure by ASTM E 1545 (Procedure B)	DSC by ASTM D 3418	
		Dry $Tg_{E'}$	Dry $Tg_{E''}$	Dry $Tg_{tan\delta}$	Dry Tg_{Exp}	Dry Tg_{Flex}	Dry Tg_{eig}	Dry Tg_{mg}
180F-TG-EPOXY	Mean	142	206	214	149	176	154	165
350F-TG-EPOXY	Mean	363	375	388	364	361	363	375
500F-TG-BMI	Mean	519	548	559	520	503	506	527
600F-TG-PI	Mean	614	641	657	609	609	601	618
Polycarbonate	Mean	297	298	313	301	297	291	301



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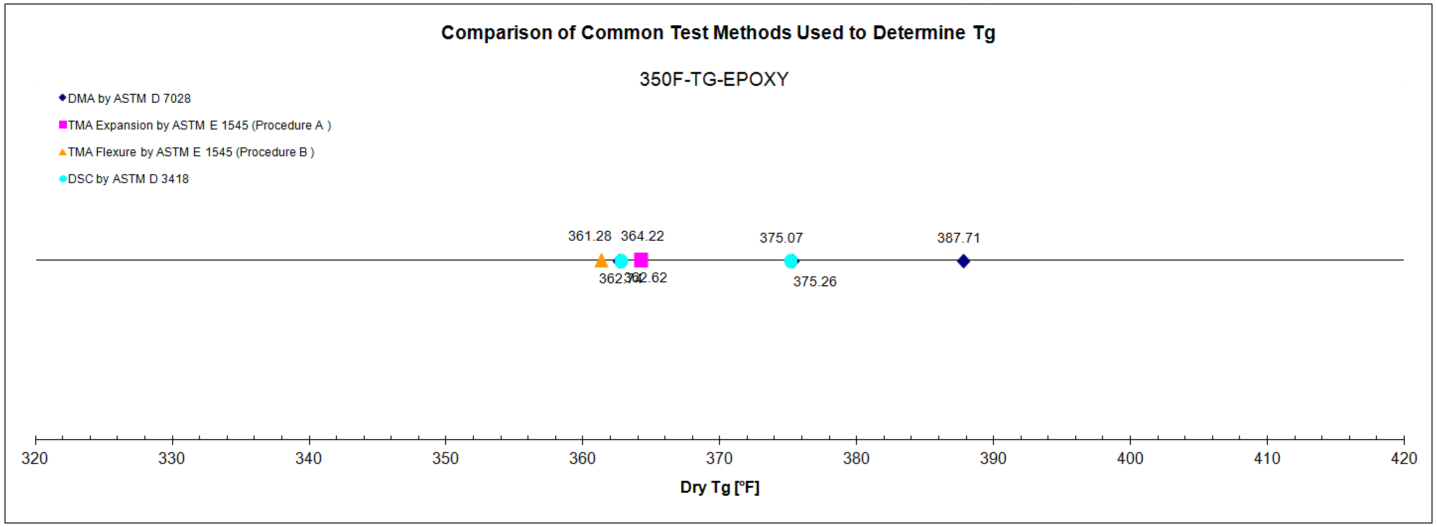
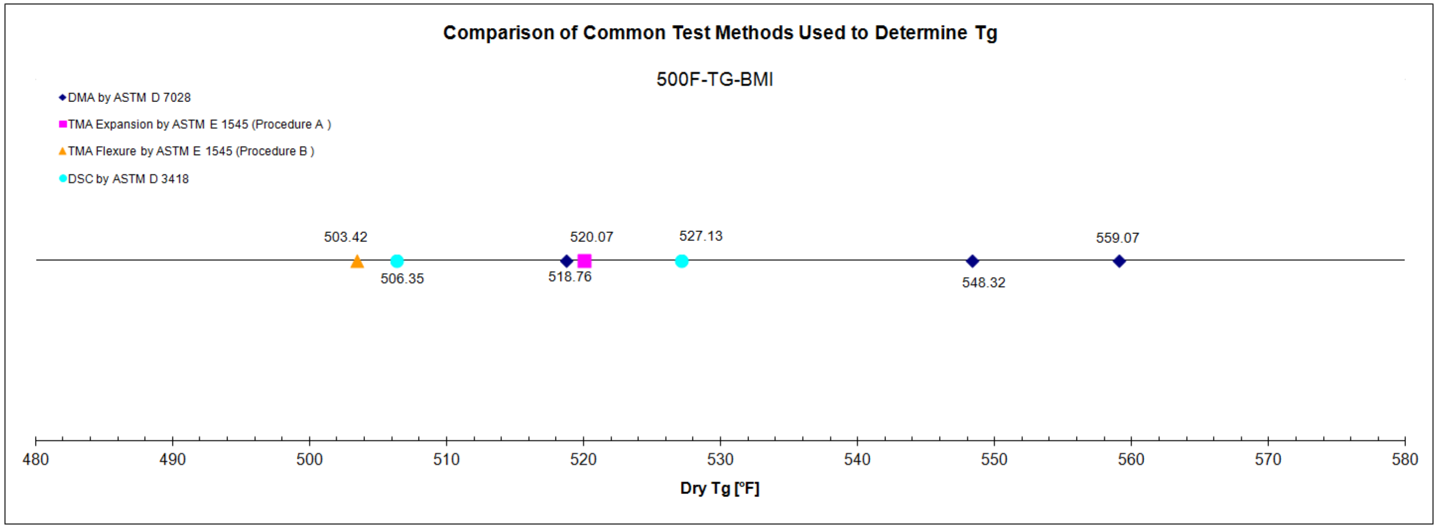
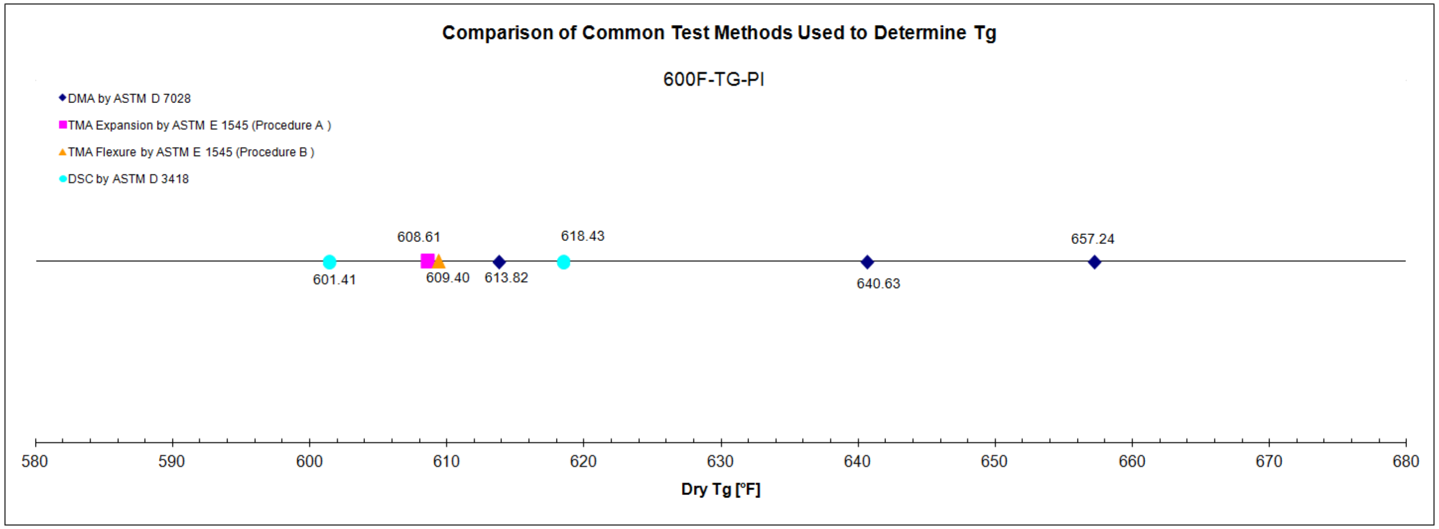
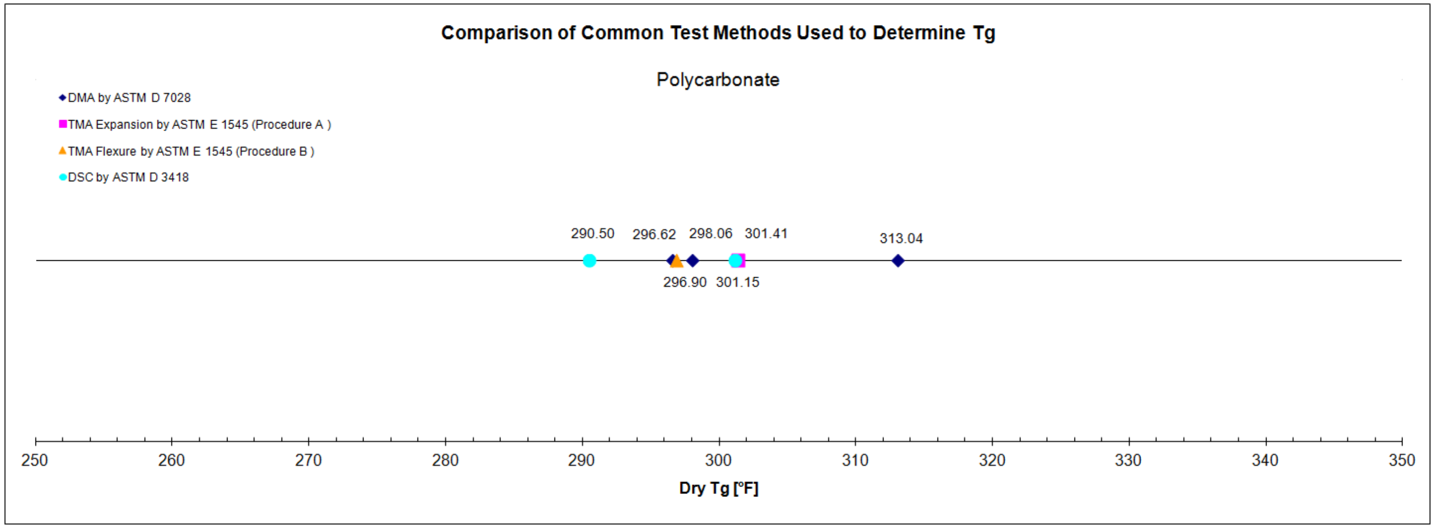
Comparison to DSC & TMA Techniques – Test Results





Comparison to DSC & TMA Techniques – Test Results

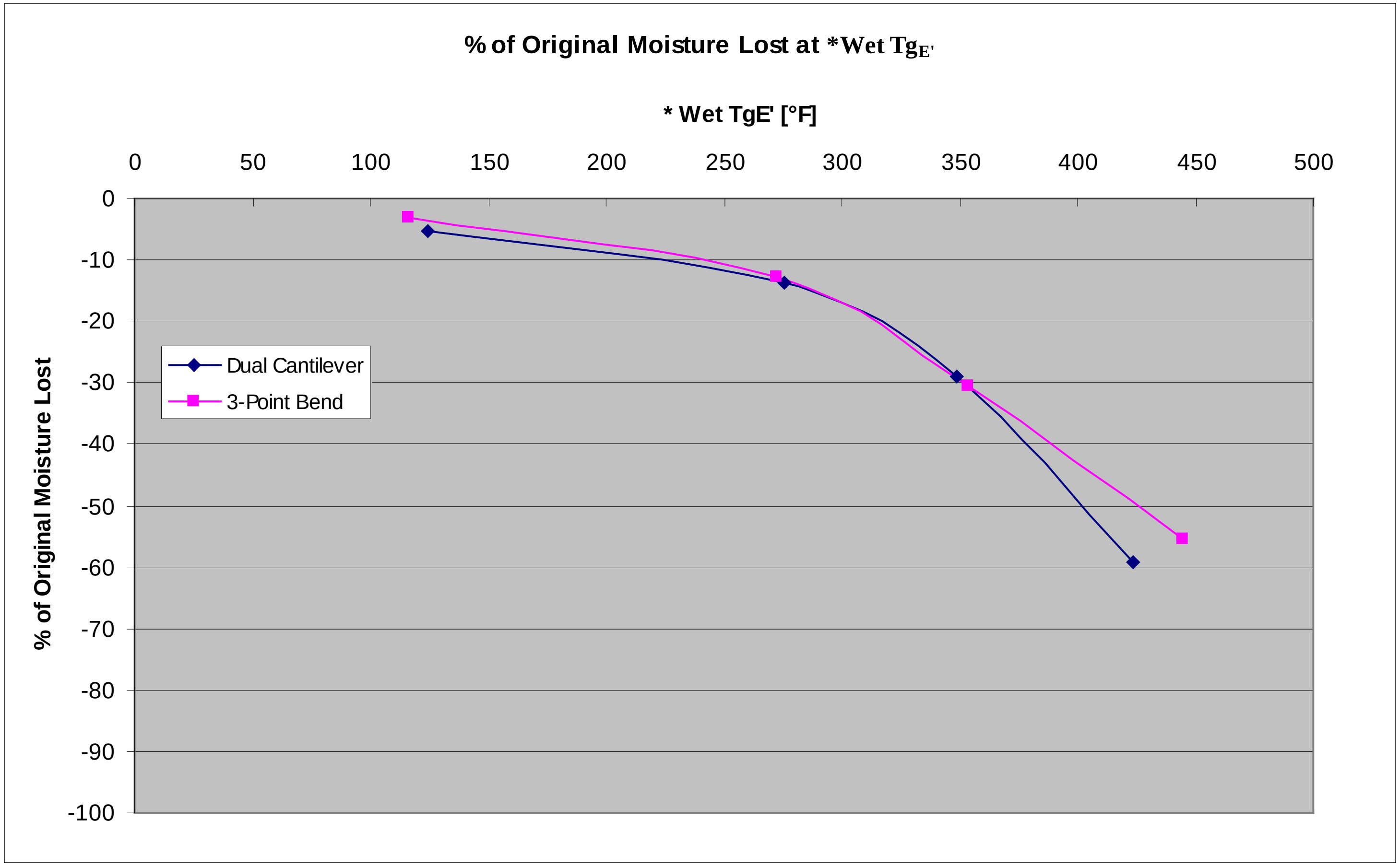




Looking Forward

- Benefit to Aviation
  - Improvement in industry applications and safety
    - Material service temperature definition
    - Quality control
- Future needs
  - Further evaluate differences observed due to dimensional variation of specimens
    - Look at equations used to determine the elastic and viscous modulus
    - Look at potential thermal lag issues
  - Study methods to improve wet Tg reliability

Looking Forward – Moisture Loss During Heat Up



End of Presentation.

Thank you.

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