

Comparison of Thermal Techniques for Glass Transition Assignment. II. Commercial Polymers

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ABSTRACT: The differential scanning calorimetry glass transition (DSC T_g), measured by ASTM test method E-1356, and the dynamic mechanical analysis glass transition (DMA T_g), measured using a new definition of the DMA T_g , generally agree within $\pm 4^\circ\text{C}$ for a wide variety of commercially available polymers. The DMA T_g is defined as the average of E'' and $\tan \delta$ peak temperatures measured at a 1 rad/s oscillation frequency. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 191–195, 1997

INTRODUCTION

It is a pleasure to contribute to this celebratory symposium in honor of Prof. John Gillham. Earlier in his career, Prof. Gillham worked at these labs, formerly called American Cyanamid, and developed the torsional braid technique that he brought to Princeton University. Historically, then, we are heirs to his lifelong interest in dynamic mechanical properties of polymers and, particularly, thermosets. As a continuation of that tradition, we offer this article in his honor.

Until recently, there were few quantitative comparisons in the literature for glass transitions (T_g) measured by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The authors reviewed the literature in an earlier article.¹ At about the same time, a comprehensive monograph of articles presented at a symposium on the assignment of the glass transition² appeared. The editor of that monograph argued that, whatever the fundamental glass transition, T_{g^*} , of a material, laboratory experiments can measure only an operationally defined T_g where the two are related by T_g

$= T_{g^*} + \text{SYSTEM}$.³ Given that understanding, we propose to show conditions where the SYSTEM components are comparable both for DSC and DMA T_g measurements.

Previously,¹ we showed that, based on the analogy illustrated in Figure 1, the average of the DMA E'' and $\tan \delta$ peak temperatures measured at 1 rad/s corresponds to the DSC heat capacity shift midpoint measured by the ASTM E-1356 DSC test method⁴ within $\pm 2^\circ\text{C}$ on average. We emphasized that this relationship is strictly empirical. It does not address the issue of whether the DSC heat capacity shift midpoint is the best thermodynamic definition of the glass transition. However, because DSC is widely used to characterize polymer T_g , a corresponding DMA definition has practical utility. We adopted as operational definitions the midpoint of the heat capacity shift (ASTM E-1356) for the DSC T_g and the average of E'' and $\tan \delta$ peak temperatures measured at a 1 rad/s oscillation frequency for the DMA T_g . Previously, however, polymer films of only two chemical types were tested. The present investigation extends that work to study a number of commercially available polymers.

EXPERIMENTAL

Materials

Commercially available polymers used in this study are identified in Table I. The polyimide,

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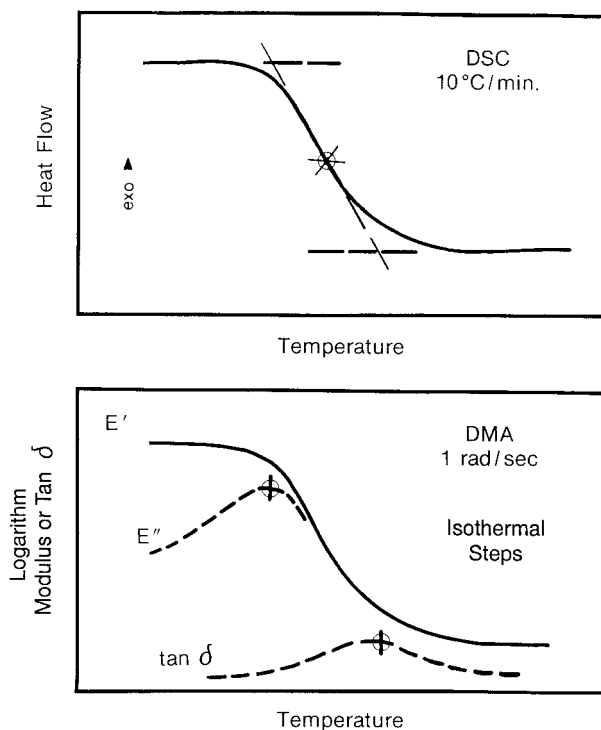


Figure 1 DSC/DMA analogy.

poly(ethylene terephthalate), and nylon 6 materials were thin films (0.01–0.05 mm thick); the others were thicker plaques (0.5–3.0 mm thick). Materials were tested as received, except the PET

soda bottle which was annealed at 120–130°C to flatten specimens and nylon 6 which was dried for > 3 days at room temperature in a nitrogen-purged glove box to remove absorbed water.

Methods

Calibration and measurement details were discussed previously.¹ In general, the DSC method includes Mettler TA-4300 instrument calibration at a 10°C/min heating rate, sample testing according to the ASTM E-1356 test method, and heat capacity shift midpoint determination for the second heating cycle, i.e., after first annealing the sample above T_g .

Rheometrics RSA II DMA measurements, at 1 rad/s (0.16 Hz) oscillation frequency, were performed in a series of isothermal steps 3°C apart. Measurements were made either in tension (films) or dual cantilever beam bending, depending upon sample stiffness. Strain was adjusted to be in the linear viscoelastic range for each sample. In some instances, repeat analyses were performed on the same specimen.

RESULTS

Figures 2 and 3 show typical DSC and DMA curves and illustrate the assignment of the T_g for

Table I Polymer Sample Identification

<u>Polyurethanes</u>
AIRTHANE® PET-91A—Air Products and Chemicals, Inc. [Poly(ether urethane)]
AIRTHANE® PST-90A—Air Products and Chemicals, Inc. [Poly(ester urethane)]
<u>Poly (methyl methacrylate) (PMMA)</u>
ACRYLITE® FF—Cyrro Industries
<u>Polyimide</u>
UPILEX® 12.5R—Ube Industries, Ltd.
<u>Acrylonitrile–butadiene–styrene (ABS)</u>
CRYOLAC® Auto Grade ABS—General Electric
<u>POLY (ethylene terephthalate) (PET)</u>
MYLAR®—I.E. DuPont De Nemours, Inc. Soda bottle (annealed 120–130°C)
<u>Nylon 6</u>
VAC-PAK® HS 6262 CO-EX—Dixico, Inc.

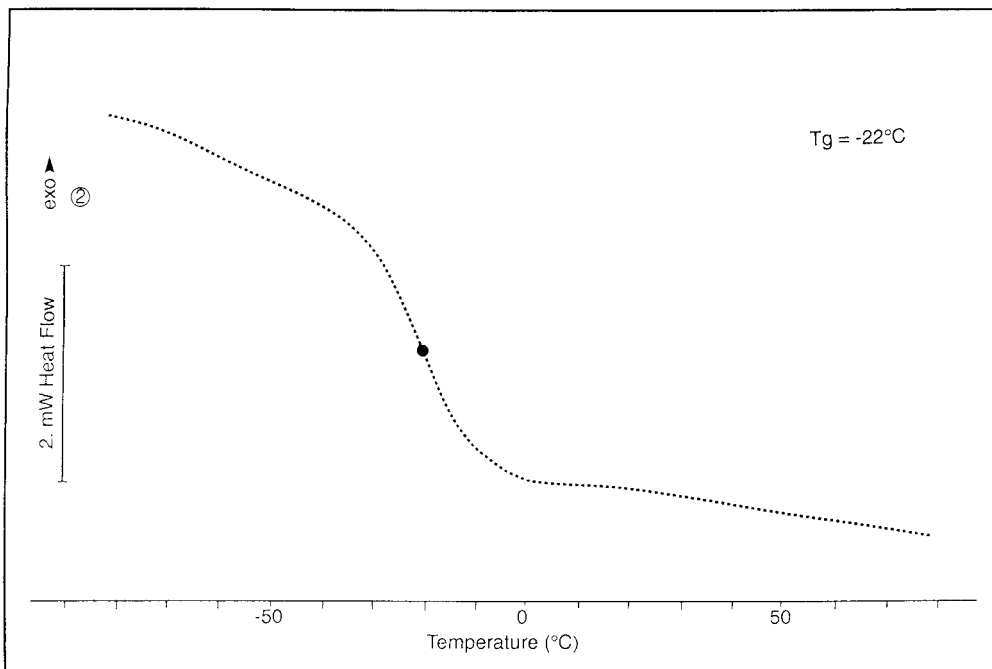


Figure 2 DSC thermal curve: AIRTHANE® PST-90A.

AIRTHANE® PST-90A. Table II summarizes all test results. Each data line in Table II represents a separate specimen and multiple data on a single line are repeat analyses using a single specimen.

In some instances, the DSC technique of annealing just above the T_g , specified in ASTM E-

1356, was compared with quenching from the melt, an alternative technique frequently used in thermal analysis. Table III illustrates how T_g results are different for both PET samples. For annealed specimens, DSC T_g was 101°C , and for melt/quenched specimens, $77\text{--}82^\circ\text{C}$.

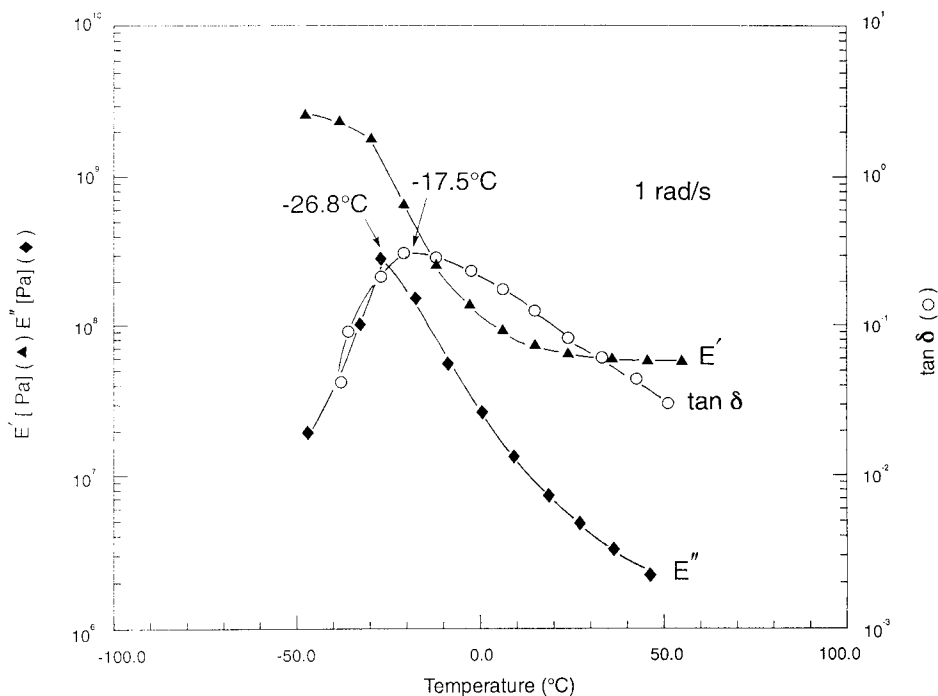


Figure 3 DMA thermal curve: AIRTHANE® PST-90A.

Table II DSC and DMA Data Summary

Sample	DSC T_g (°C)	DMA T_g (°C)	ΔT_g (°C)
<u>Polyurethane</u>			
AIRTHANE® PET-91A	-67, -67	-64	-3
AIRTHANE® PST-90A	-22 -22	-22 -23	0 1
<u>PMMA</u>			
ACRYLITE® FF	107 105	107 106, 109	0 -3
<u>Polyimide</u>			
UPILEX® 12.5R	275 273	277 276, 278	-2 -4
<u>ABS</u>			
CYCOLAC® ABS	(-83), 100 (-85), 101	(-88), 101 (-89), 103	(5), -1 (4), -2
<u>PET</u>			
MYLAR®	100, 100 103	104 98, 103, 101	-4 +2
Soda bottle	96 103	104 104, 111, 110	-8 -5
<u>Nylon 6</u>			
VAC-PAK® HS 6262 CO-EX	62 55 63 56	68, 56 64, 63, 64	0 -9

Separate data line for each specimen tested. Multiple data on a single line are repeat analyses on a single specimen. Parentheses indicate a second, low-temperature, T_g .

DISCUSSION

For semicrystalline polymers in general, and PET in particular, it is well known that T_g increases with degree of crystallization.⁵ Processing, e.g., biaxial orientation in blow-molded PET soda bottles, also affects the T_g .^{5,6} Because annealing above T_g maximizes crystallinity and quenching from the melt minimizes it, measured DSC T_g 's are different. For semicrystalline polymers, the DMA T_g is comparable with the DSC T_g for samples annealed as specified by ASTM E-1356, but not for melt-quenched samples.

Water content is known to affect the nylon 6 DSC T_g .⁷ In Table II, the difference between the DSC T_g and the DMA T_g for nylon 6 specimens ranges from 0 to 9°C. We believe that this difference is due to residual water, even though efforts were made to dry the samples. However, when all results are averaged, the DSC T_g and the DMA T_g agree within $\pm 4^\circ\text{C}$.

Previously, the authors reported agreement be-

tween the DSC T_g and the DMA T_g , on average, to within $\pm 2^\circ\text{C}$. Rather than reporting the average difference, the absolute difference is reported in

Table III Annealing vs. Melt/Quenched DSC Testing of PET

Sample	Conditions	DSC T_g (°C)
MYLAR	Annealed	100, 100 103
	Melt/Quenched	82 82
Soda bottle	Annealed	96 103
	Melt/quenched	77 76, 79

Separate data line for each specimen tested. Multiple data on a single line are repeat analyses on a single specimen.

the present investigation. The absolute difference between the DSC T_g and the DMA T_g is $\pm 4^\circ\text{C}$, except for nylon 6, where water is a problem.

CONCLUSIONS

The DSC T_g is defined as the heat capacity shift midpoint (ASTM E-1356 DSC test method), and the DMA T_g , as the average of the E'' and $\tan \delta$ peak temperatures measured at 1 rad/s. Using these definitions, the DSC T_g and the DMA T_g generally agree within $\pm 4^\circ\text{C}$ for a variety of chemically different, commercially available polymers. Exceptions are melt-quenched semicrystalline polymers and polymers with absorbed water.

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