Thermal Analysis & Rheology

Exploring the Sensitivity of Thermal Analysis Techniques to the Glass Transition

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ABSTRACT

Five thermal analysis techniques (DSC, modulated DSC™, TMA, DMA, and DEA) are used to characterize the glass transition temperature (Tg) for amorphous polymers. Each of these thermal techniques detects the Tg based on changes in a different material property during the glass transition. Hence, the relative sensitivities of the different techniques for detecting the Tg vary depending on the nature of the material being evaluated as well as on experimental variables such as the heating rate. This study compares the Tg information obtained from the five common thermal techniques on a typical amorphous thermoplastic. The results illustrate the types of issues that can arise.

INTRODUCTION

The glass transition is the temperature region where an amorphous material changes from a glassy phase to a rubbery phase upon heating, or vice versa if cooling. The glass transition is very important in polymer characterization as the properties of a material are highly dependent on the relationship of the polymer end-use temperature to its Tg. For example, an elastomer will be brittle if its Tg is too high, and the upper use temperature of a rigid plastic is usually limited by softening at Tg. Hence an accurate and precise measure of Tg is a prime concern to many plastics manufacturers and end use designers.

Thermal analysis, which is a generic term used to describe a family of analytical techniques that measure changes in the physical properties of a material with temperature, provides a convenient means of measuring the glass transition. Each of the thermal analysis techniques senses the glass transition based on changes in a specific material property. Table 1 summarizes the different thermal techniques, the property change(s) measured for each during the glass transition, and an indication of the relative sensitivity (relative signal change) of each for detecting the Tg.

TABLE 1
Properties Measured by TA Techniques

Technique	Property Measured	Relative Signal Change at Tg
Differential Scanning Calorimetry	Heat flow (heat capacity)	0.2
Thermomechanical Analysis	Expansion coefficient or softening	3
Dielectric Analysis	Permittivity and dielectric loss	100
Dynamic Mechanical Analysis	Mechanical strength and energy loss	200

In this study, a typical amorphous thermoplastic polymer is evaluated by all of the techniques shown in Table 1, as well as modulated DSC™, to illustrate some of the experimental trade-offs and considerations commonly encountered. A user's guide based on the results, and those for other types of polymers, is included as a summary.

EXPERIMENTAL

Materials

Two unfilled amorphous thermoplastic materials were used in this study, polycarbonate and polystyrene. Unfilled amorphous thermoplastics undergo larger property changes at the glass transition than any other polymer type or morphology. In materials where the amorphous content is reduced, such as highly crystalline or highly filled thermoplastics, or where crosslinking reduces the size of mobile polymer chains, the property changes at the glass transition will generally be reduced. The smaller signal changes decrease the sensitivities of the respective thermal techniques to the glass transition, though each technique is affected to a differing degree, as will be discussed.

The polycarbonate used was TUFFAK®A from Rohm & Haas Co. The polystyrene was Aldrich Chemicals Catalog Number 18242-7. Polycarbonate samples for DMA evaluation were prepared by cutting bars 12mm wide by 60mm long from the 3mm thick sheets received. Samples for evaluation by the other techniques were prepared by pressing 0.15mm films from the original 3mm sheets in a 155°C hot press. Polystyrene samples for DSC and TMA evaluation were prepared by pressing the polymer beads originally received into 0.2-0.5mm films in a 200°C hot press.

Instrumentation

All experiments were performed on the following thermal analysis equipment from TA Instruments: DSC 2910 with autosampler and MDSC™ upgrade, TMA 2940, DMA 983, and DEA 2970. All specimens were run under a nitrogen atmosphere. The results reported in this study were obtained from heating experiments only. Results from cooling experiments, although similar, are the topic for another study and hence are not included here.

RESULTS AND DISCUSSION

Sensitivity to Transition Representation

There are two basic representations of the glass transition which are commonly used. They are onset or step change and peak maximum. In general, the measurement based on onset or step change is subject to greater uncertainty than the measurement based on a peak maximum because the former measurement relies on the ability to accurately define baselines and tangents surrounding the transition. This is illustrated in Figures 1 and 2. Figure 1 shows the correct cursor placement for onset and peak determinations. Figure 2 shows similar determinations where cursor placement for drawing the baseline tangent has been shifted 3°C. Note that this shift results in a 1.5°C decrease in the Tg determined from the onset while no change occurs in the measured peak maximum. In general, the glass transition temperature is less subject to operator interpretation when the property measured by the specific thermal analysis technique relies on a signal peak (e.g. DMA damping, DSC heat flow derivative).

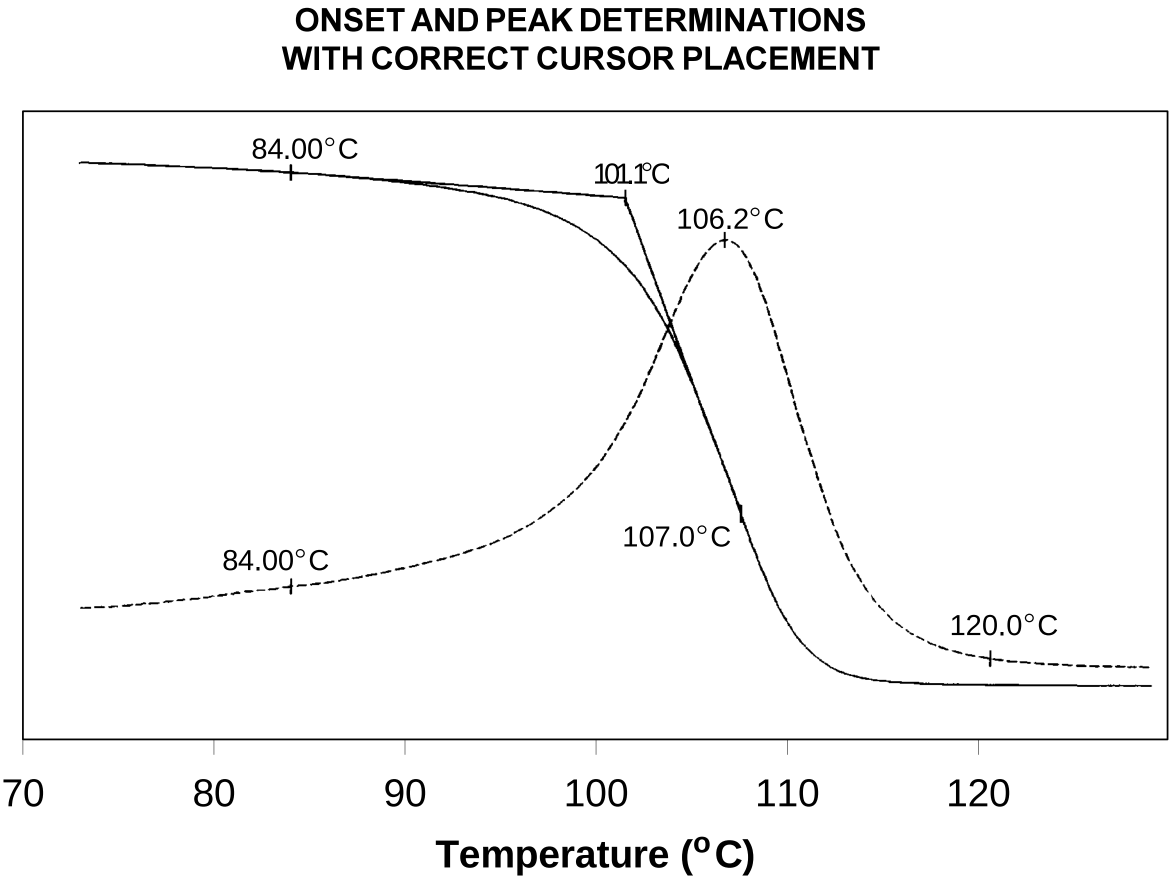


Figure 1

ONSET AND PEAK DETERMINATIONS WITH INCORRECT CURSOR PLACEMENT

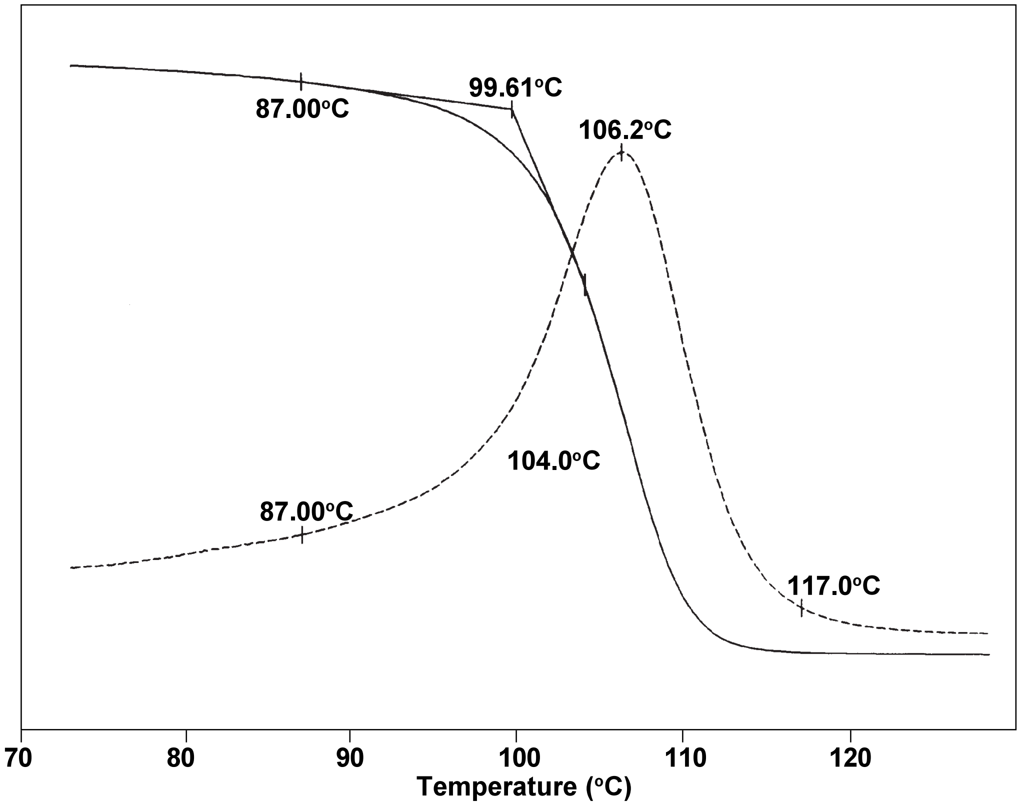


Figure 2

DSC Sensitivity

DSC, which measures heat flow to and from a specimen relative to an inert reference, is the most common thermal analysis method used to measure the glass transition. The heat capacity step change at the glass transition yields three temperature values: onset, midpoint and endset. The midpoint is usually calculated as the peak maximum in the first derivative of heat flow (see Figure 3) although it can also be calculated as the midpoint of the extrapolated heat capacities [1] before and after the glass transition.

The DSC thermal curve for polycarbonate heated at 20°C/minute is shown in Figure 3. Most DSC experiments are performed at 5 or 10°C/minute. A higher heating rate is beneficial in detecting Tg, however, because the heat flow signal associated with heat capacity change during the glass transition is enhanced with very little corresponding increase in noise, thereby increasing sensitivity.

Nevertheless, this increase in sensitivity with increased heating rate does have penalties. Both the temperature and breadth of the glass transition are affected by increased heating rates. Figure 4 shows the glass transition of polystyrene (18 mg specimen) by DSC at various heating rates. Notice that Tg shifts to higher temperatures and the transition broadens as the heating rate is increased, especially at 20 and 50°C/min. It is therefore important to report heating rate along with Tg values.

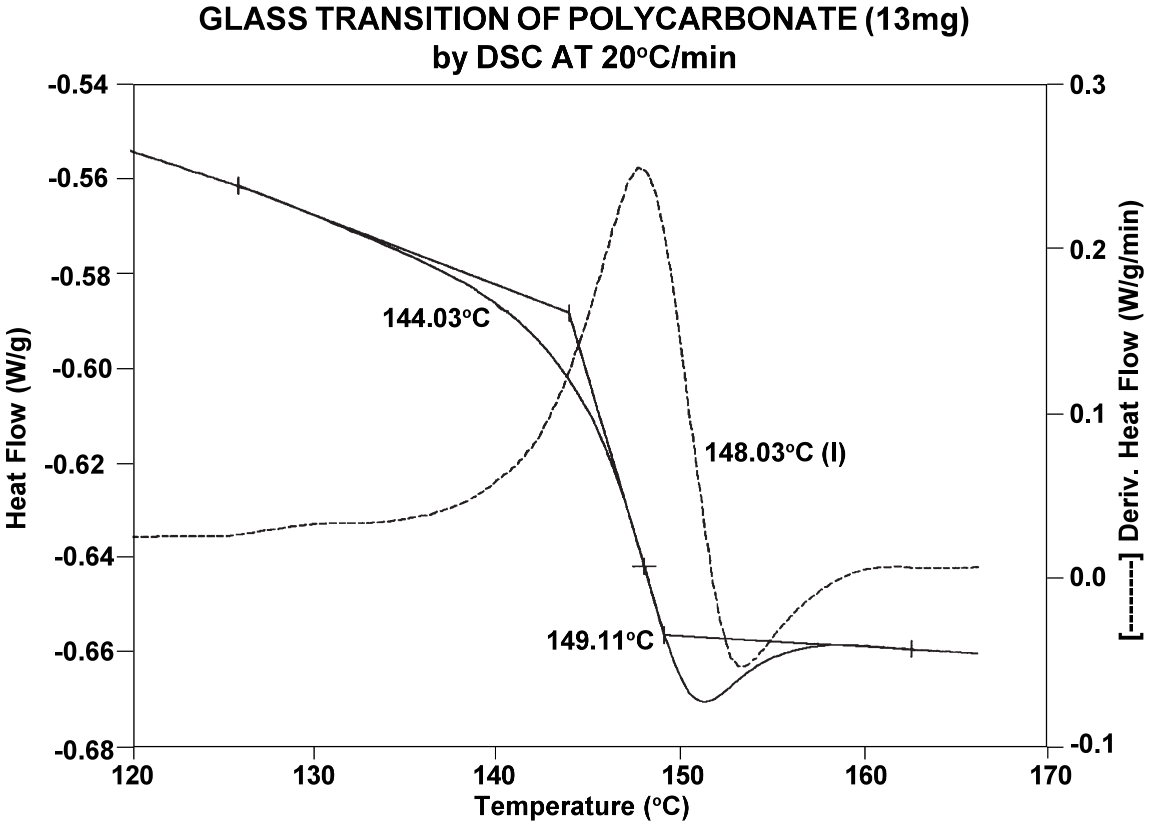


Figure 3

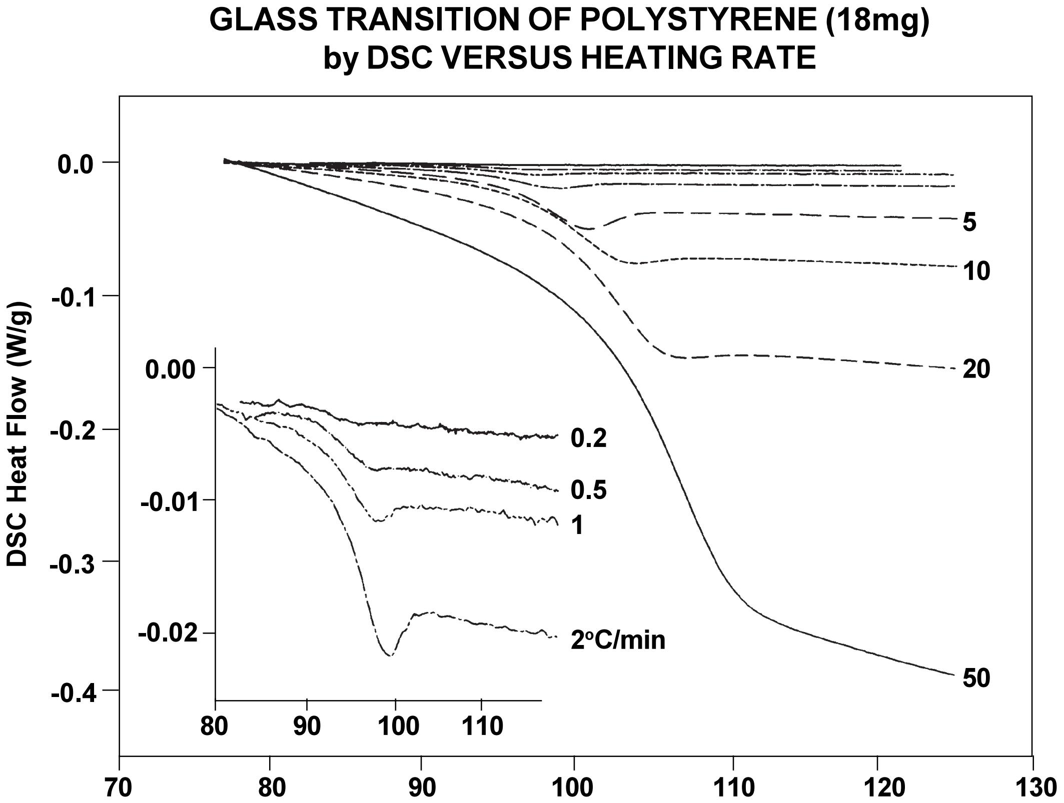


Figure 4

Three components contribute to this heating rate - related shift: instrument effects, sample thermal conductivity, and transition kinetics. The instrument effects associated with cell mass and heat transfer properties are relatively small, typically amounting to about 0.1ºC per decade change in heating rate [2,3]. Thermal conductivity effects on the other hand are more significant particularly with larger samples or with samples of low thermal conductivity. In those cases, a thermal gradient develops across the sample which broadens and shifts the Tg to higher temperature. Figure 5 illustrates that effect for polystyrene. The width of the glass transition (the difference between the onset (⊡) and the endset (◊)) is rather constant until 5°C/min where the width increases dramatically with increasing heating rate. Thus at heating rates below 5°C/min the sample thermal conductivity has little effect on the Tg measurement. Below 5°C/min, though, the Tg measurements do continue to change with heating rate. That shift (approximately 2°C per tenfold change in heating rate) can be attributed to the kinetics of the glass transition. Analysis of this data using Arrhenius kinetics yields an activation energy of 890kJ/mole. Analysis of DMA multi-frequency data by time-temperature superpositioning yields a similar activation energy, confirming the kinetic effect on Tg.

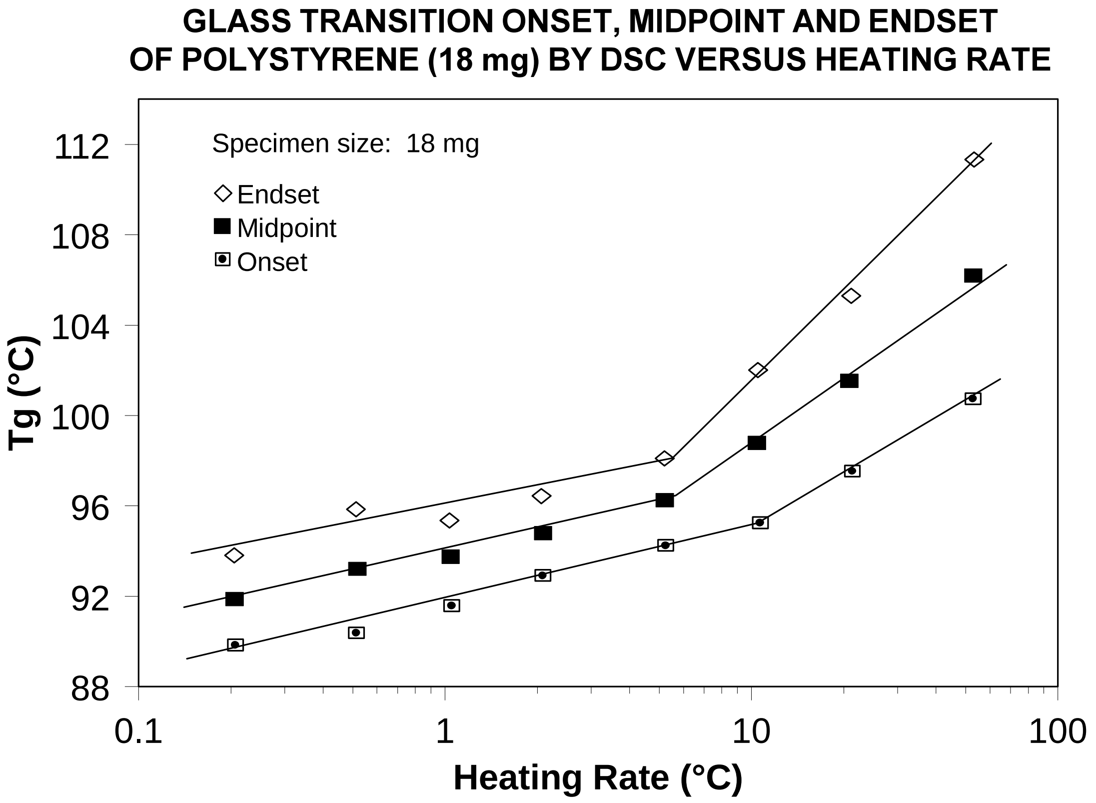


Figure 5

Volume relaxation peaks are another phenomenon observed in DSC which can affect accurate Tg measurement. These peaks occur in materials when the cooling rate encountered by the polymer during processing (thermal history) is much slower than the heating rate used during DSC evaluation (Figure 6). By imposing the proper thermal history on the material or by using modulated DSC™, the effects of volume relaxation can be reduced.

Finally, DSC measurement of Tg is significantly affected by high crystallinity in the polymers and by adding reinforcers or fillers to the polymer. Since these additional materials do not contribute to the heat capacity change measured at the glass transition, they act as “dilutants”, adding sample weight without increasing sensitivity.

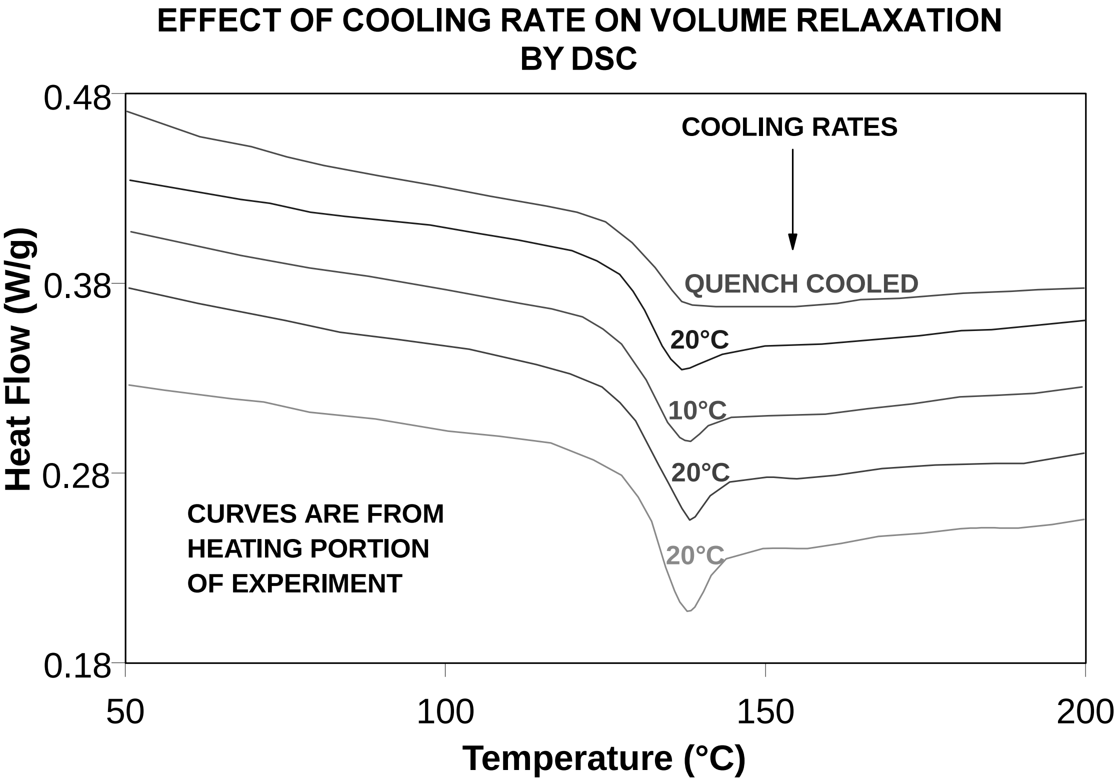


Figure 6

MDSC™ Sensitivity

Modulated DSC (MDSC) is a high performance version of conventional DSC that provides information about the reversing and nonreversing characteristics of thermal events, in addition to traditional DSC heat flow and temperature information. In MDSC a sinusoidal temperature ripple (modulation) is overlaid on the conventional linear temperature ramp to yield a modulated heating ramp. This modulated heating causes the heat flow to oscillate. Fourier transformation deconvolution converts the modulating heat flow signal into reversing and nonreversing components and directly calculates specimen heat capacity. The details of this technique are described elsewhere [4]. Briefly, reversing components of heat flow are those which are both thermodynamically reversible and kinetically feasible. The remainder of the heat flow, which includes events which are not reversible or are not kinetically rapid, is grouped into the nonreversing heat flow signal.

MDSC has value in measuring the Tg in three areas. First, it improves interpretation by separating the volume relaxation endotherm (a nonreversing phenomenon) from the reversing heat capacity change at the glass transition. Second, MDSC can separate nonreversing transitions such as cold crystallization and curing from the glass transition which is impossible by traditional DSC. Finally, sensitivity for heating rate dependent transitions such as the glass transition is increased over traditional DSC due to the high effective heating rates achieved during modulation. The following examples illustrate each of these situations.

Figure 7 is Modulated DSC scan for polycarbonate. The total heat flow (solid line) shows a Tg (inflection point) at 146.3°C. Note that this temperature is lower than that seen in Figure 3 because of the lower underlying heating rate of the MDSC experiment. The nonreversing curve (long dashes) shows a small (0.8 J/g) endothermic volume relaxation peak. The Fourier transform deconvolution separates this relaxation from the heat capacity curve (short dashes). The resulting Tg, 148.6°C, is an improved value because interference from the volume relaxation is removed.

Figure 8 shows results of an MDSC experiment on a bilayer film containing polycarbonate (PC) and amorphous polyethylene terephthalate (PET). The conventional DSC curve (solid line) shows a single broad transition between 130°C and 150°C which is difficult to interpret because it represents overlap of the polycarbonate glass transition and the PET cold crystallization exotherm. The MDSC results, on the other hand, clearly separate these two phenomena based on the fact that the polycarbonate glass transition is a reversing transition, while the PET crystallization is a nonreversing phenomenon.

GLASS TRANSITION OF POLYCARBONATE BY MDSC™ (12 MG. 5°C/min, 0.5°C AMPLITUDE AND 50 SECOND PERIOD)

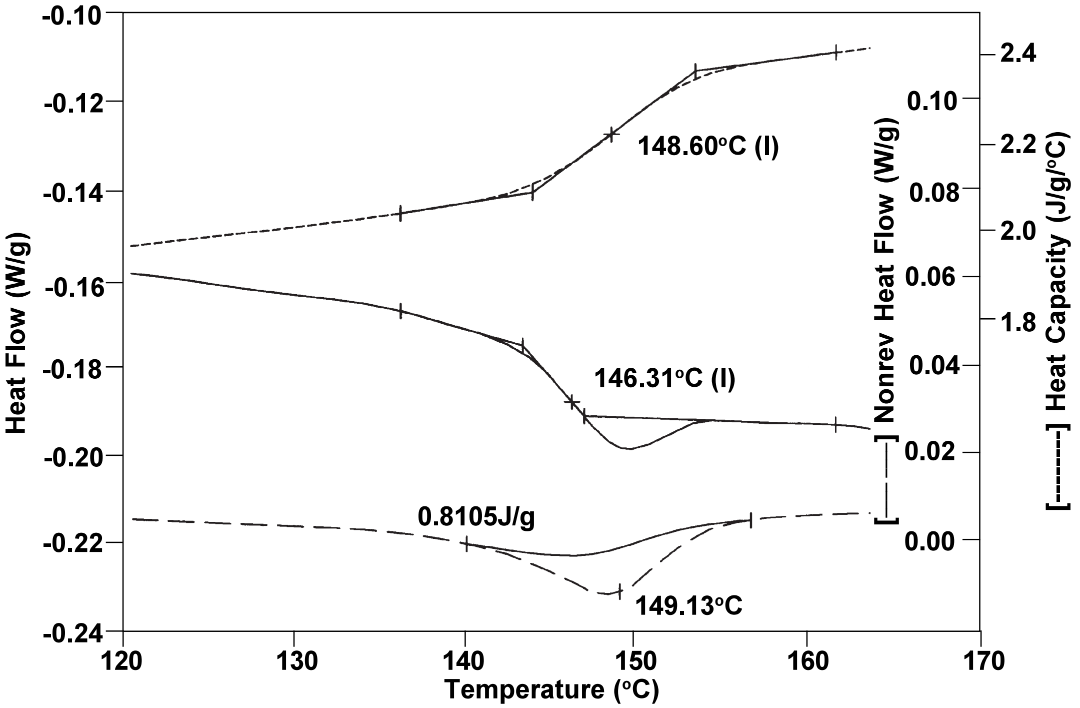


Figure 7

GLASS TRANSITION OF POLYCARBONATE BY MDSC™ IN A POLYCARBONATE/POLYETHYLENETEREPHTHALATE BILAYER FILM

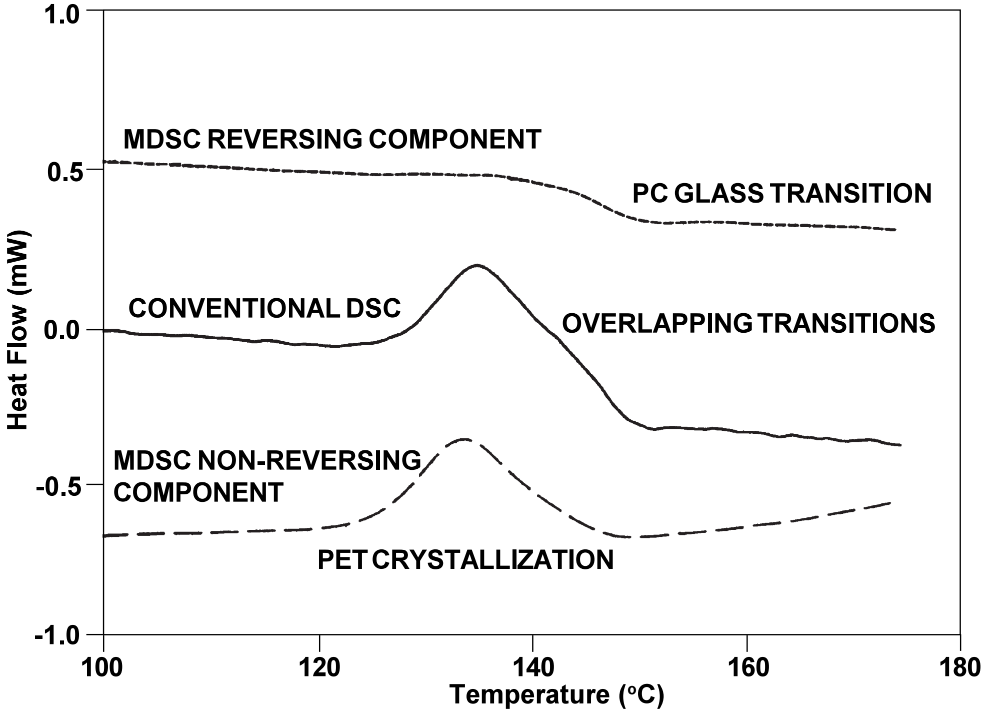


Figure 8

Figures 9 and 10 illustrate the increased glass transition sensitivity available from MDSC™. In MDSC, a low underlying heating rate (1-2°C/minute) is used, thus providing good resolution of transitions but very low sensitivity. The superimposed modulated heating profile, however, results in instantaneous heating rates which are much higher than the underlying rate, thereby increasing sensitivity to transitions such as the glass transition. The overall result is a combination of resolution and sensitivity not available from conventional DSC. Figure 9 shows a high temperature epoxy during isothermal curing at 90°C. The solid line represents the nonreversing heat flow with time and shows the exotherm associated with curing. This peak is identical to what would be observed in the conventional DSC experiment. A second signal can be measured in MDSC, however. That is the heat capacity (dashed line), which clearly shows a step decrease associated with the reduction in polymer free volume and molecular motion as the thermoset goes from a rubbery phase to a glassy phase (vitrifies). This decrease occurs after the exothermic peak maximum which implies that heat capacity changes more dramatically during crosslinking than during linear polymerization. Evaluation by DMA supports this conclusion since the storage modulus (dash-dot curve) increases at exactly the same time as heat capacity begins to decrease. The breadth of the reaction results from the diffusion control of the process during vitrification[5]. This ability to measure heat capacity and vitrification at an underlying heating rate of 0°C/minute (isothermal) is not possible in conventional DSC. Figure 10 illustrates another example where the MDSC reversing heat flow curve (broken line) indicates a Tg not observable in conventional DSC.

ISOTHERMAL CURING OF EPOXY RESIN BY MDSC™ AND DMA

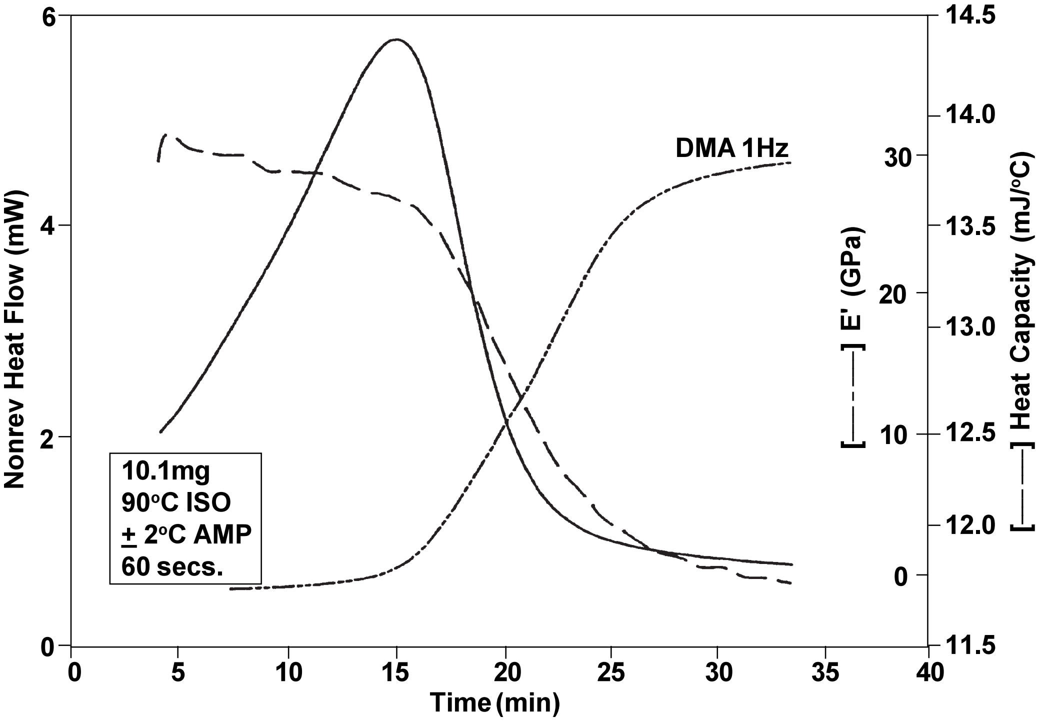


Figure 9

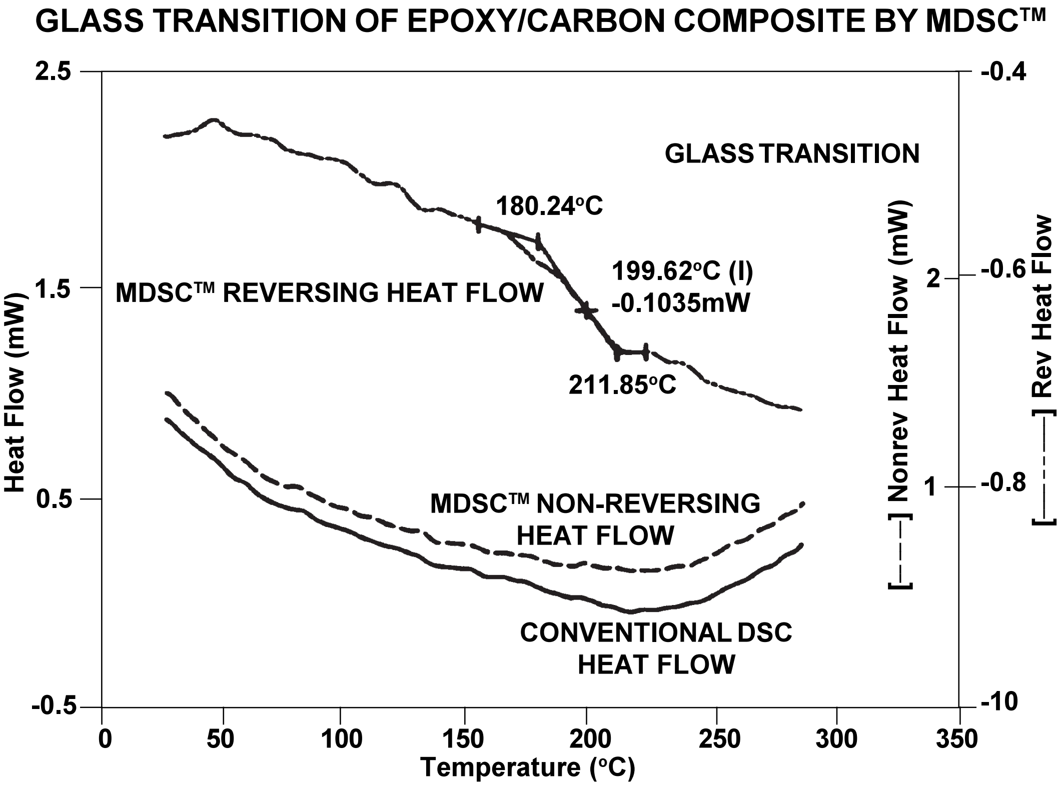


Figure 10

TMA Sensitivity

TMA is generally used to measure the glass transition based on changes in coefficient of thermal expansion which result as the free volume of the material changes at the glass transition. Figure 11 shows the Tg of polycarbonate heated at 3°C/min where the Tg is defined as the onset of change in rate of expansion (slope) at 140.2°C. For the polycarbonate specimen, as with many thermoplastics, the expansion coefficient above Tg is not as well behaved because material softening counteracts the probe motion due to thermal expansion.

Another TMA approach for determining glass transition is penetration in which a substantial force is applied to a small point on the material surface. The penetration mode detects Tg as a downward probe movement as the material becomes less rigid in the transition from glassy to rubbery behavior. This mode is used for materials which cannot support much force after Tg, or which exhibit very broad ill-defined expansion changes. Figure 12 shows the TMA penetration results for polystyrene.

Measurement of Tg by TMA is better for filled, highly crystalline, or crosslinked materials than measurement by DSC because the dimensional changes observed at Tg are usually fairly significant. On the other hand, the Tg profiles from TMA are often broad, can be affected by probe loading conditions, and may be complicated by volume relaxation effects.

GLASS TRANSITION OF POLYCARBONATE BY TMA (EXPANSION PROBE, 3°C/min AND 0.5 gram)

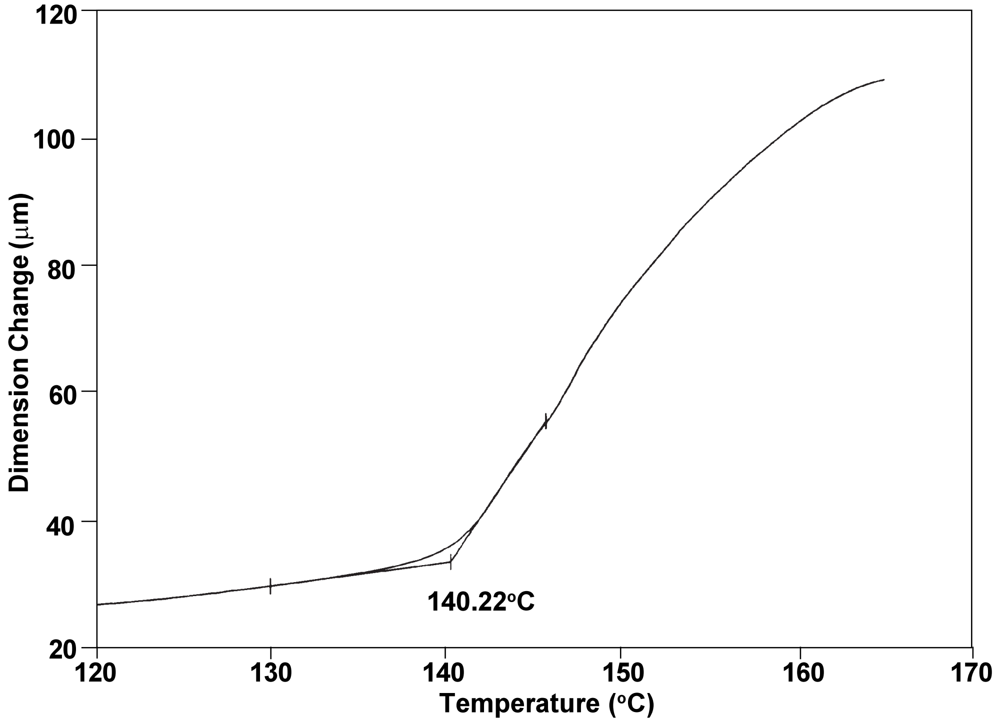


Figure 11

GLASS TRANSITION OF POLYSTYRENE BY TMA (PENETRATION PROBE, 3°C/min AND 5 grams)

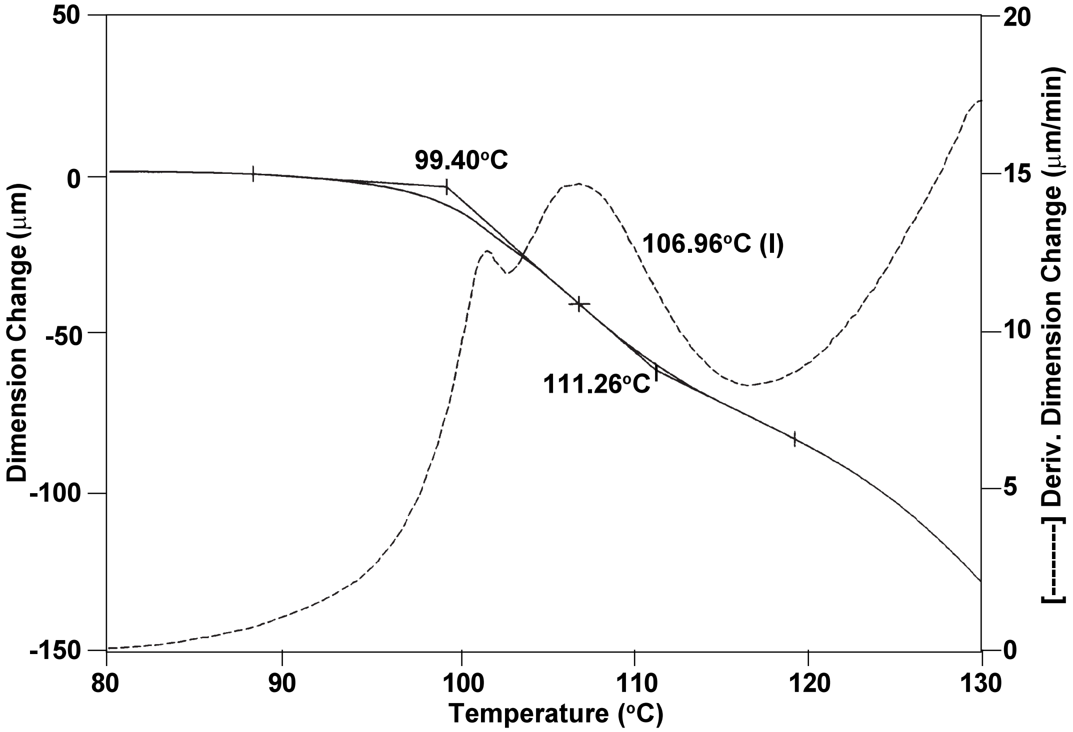


Figure 12

DMA Sensitivity

DMA measures mechanical stiffness (modulus) and energy absorption by subjecting a specimen to oscillating mechanical stress and strain within the linear viscoelastic region. At the glass transition, the increase in molecular motion within the polymer results in a dramatic step decrease (up to four decades) in the storage modulus (E') making DMA probably the most sensitive thermal technique for Tg determinations. In fact, the change in modulus signal is readily detectable even in the most highly filled, crystalline, or crosslinked material where the amorphous fraction is very small.

Energy is also absorbed as the molecular motion increases. As the specimen proceeds through the glass transition, the rate of energy absorption goes through a maximum resulting in peaks in the loss modulus (E") and Tan Delta curves. The temperatures of the three DMA events can be used to define the range of the glass transition.

For polycarbonate (3°C/min, 1 Hz), the Tg values are 141.8°C (E' onset), 147.1°C (E" peak) and 151.5°C (Tan Delta peak), see Figure 13. Each value has meaning relative to specific applications. The E' (storage modulus) onset defines the temperature at which the material's strength will begin to decrease, such that the material may no longer be able to bear a load without deforming. The peak in the loss modulus (E") represents the temperature at which the material is undergoing the maximum change in polymer mobility, which corresponds to the chemical definition of the Tg. The loss tangent (tan delta) peak describes the damping characteristics of a material and also has historical significance, since it was the first DMA property quantified and much of the DMA Tg reference data is based on the tan delta peak temperature.

The Tg measured by DMA is dependent on the oscillation frequency, because the glass transition is a second order, kinetically limited transition. That is, Tg is both time and temperature dependent. Hence, when comparing results from different DMA evaluations or when comparing DMA results to those from other thermal techniques, oscillation frequency must be appropriately chosen and kept constant. The frequency of 1 Hz is usually chosen as a compromise value which gives Tg values comparable to other thermal methods while allowing collection of data at a sufficient rate to permit reasonable experimental times. DMA experiments using multiple frequencies provide additional information useful for defining kinetic parameters for the glass transition, which permit prediction of material properties over broader frequency ranges [6] such as those the material could encounter in actual end-use.

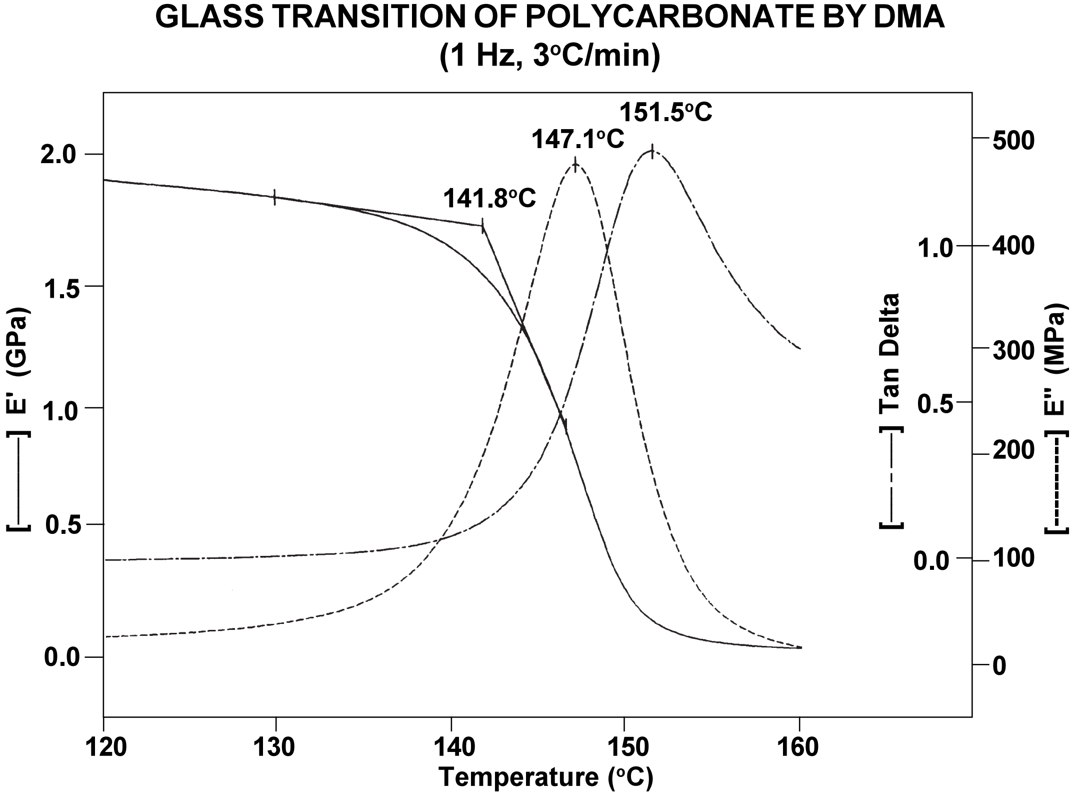


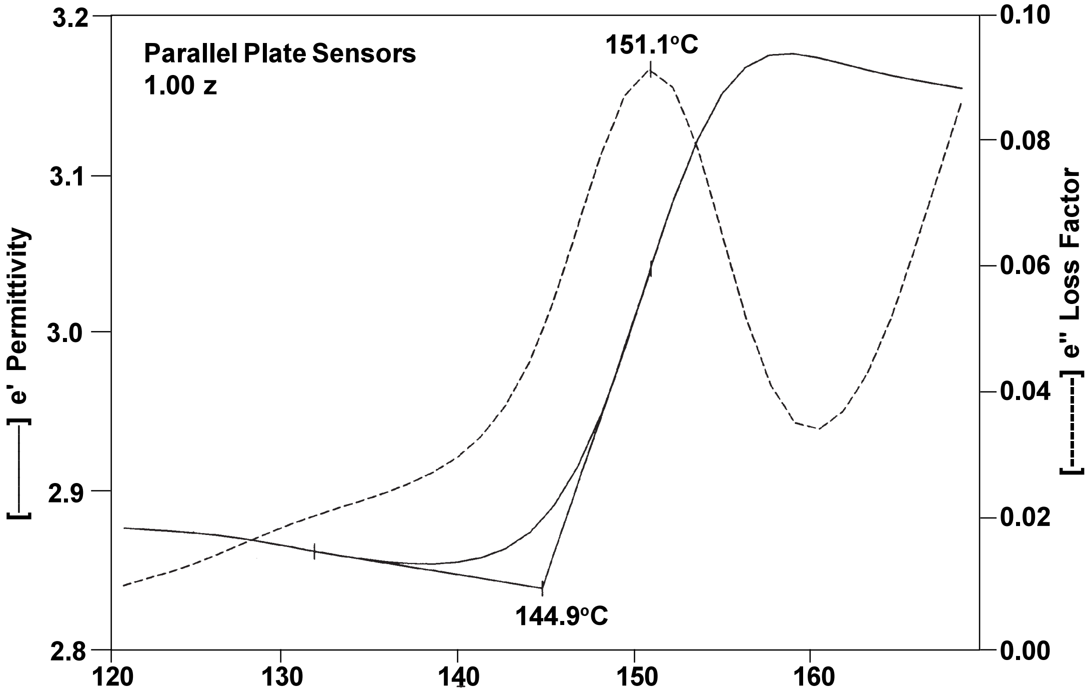
Figure 13

DEA Sensitivity

DEA measures the ability of dipoles and trace ions present in a material to align with an oscillating electric field. The increase in molecular motion associated with the glass transition allows the dipoles or ions in an amorphous polymer to more freely align with the electric field and dissipate energy. The sensitivity of the DEA to the Tg is dependent on the strength of permanent dipoles and the amount and mobility of ions in the polymer. The glass transition of polycarbonate (3°C/min, 1Hz) is measured as the onset of the increase in the permittivity signal (e') at 144.9°C, and as the peak (151.1°C) in the loss factor (e"), (see Figure 14).

The Tg measured by DEA is frequency dependent as with the DMA. Dielectric properties can easily be measured over a very wide frequency range (more than 8 orders of magnitude), since high electrical frequency is much more readily achieved than its mechanical counterpart. The wide frequency range allows measurement of subtle transitions as well as multiple-mechanism transitions that are sensitive to the frequency of measurement.

Dielectric analyzers can measure Tg on a wide variety of samples including films, liquids and powders. Furthermore, dielectric loss is a sensitive probe that allows measurement of properties of filled materials. DEA on the other hand, is limited to materials that have a reasonable level of dipole groups or trace ions present (polyolefins for example are not easily evaluated by DEA), and DEA does not work for materials which are electrically conductive.



GLASS TRANSITION OF POLYCARBONATE FILM BY DEA (1 Hz, 3°C/min)

Figure 14

SUMMARY

In this study, DMA is the most sensitive technique for measuring the Tg, followed by DSC which is about one half as sensitive as DMA. TMA and DEA are less sensitive techniques for the polycarbonate studied since these methods exhibit larger signal to noise ratios. The order of these sensitivities is different than expected based solely upon the relative signal strengths in Table 1. The fact that DSC is more sensitive than expected can be attributed to the superior baseline performance (noise reduction) of modern DSC instrumentation combined with the use of a high heating rate. DEA, on the other hand, is less sensitive than expected because of the absence of strong molecular dipoles in polycarbonate. Despite sensitivity differences, however, the Tg temperatures observed for polycarbonate by the five thermal analysis techniques showed good agreement (Table 2).

TABLE 2
Glass Transition of Polycarbonate by TA Techniques

Method	Thermal Conditions	Onset (°C)	Midpoint (°C)	Endset (°C)
DSC	20°C/min.	144.0	148.0	149.1
MDSC™	5°C/min, 0.5°C amp, 50 sec period	144.0	148.6	153.5
TMA	30°C/min, 0.5 g load	140.2	N/A	N/A
DMA	3°C/min. 1 Hz	141.8	147.1	151.5
DEA	3°C/min. 1 Hz	144.9	151.1	N/A

Although there is insufficient space in this brief overview to study a broad spectrum of polymeric materials, a large amount of work has already been done in our applications laboratory on evaluating glass transitions. Table 3 is a summary based on that work. This table indicates the relative utility of the different thermal techniques for evaluating Tg in different materials and should be a useful starting point when selecting techniques for evaluating new materials.

TABLE 3
Preferred Thermal Methods

Polymer Type	DSC	MDSC™	TMA	DMA	DEA
Amorphous	best	best	best	best	better
Semi-crystalline	better	best	best	best	better
Highly crystalline	good	good	best	best	better
Plasticized	better	best	better	best	better
Thermosetting resin	best	best	better	better	best
Cured thermoset	good	better	better	best	better
Elastomer	better	best	better	best	better
Glass Filled	good	good	better	best	better
Carbon Filled	good	good	better	best	good
Volume Relaxation Present	(a)	best	(a)	better	better

a) Volume relaxation may interfere with Tg precision.

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