

Differential Scanning Calorimetry and Differential Thermal Analysis

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The importance of thermal analysis methods in thermal and material science has proved awesome. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have had a great impact on material science by enabling the measurement of a great number of physical and chemical properties. These techniques have allowed elucidation of endothermic and exothermic processes at temperatures ranging from very low (-120°C) to high (DSC 600°C and DTA 1800°C).⁽¹⁻⁶⁾ Some of the physical properties measured by these thermal analytical methods include melting transitions, crystallization temperatures, enthalpy of fusion and crystallization, specific heat capacity, liquid crystal transitions, vaporization, sublimation, solid–solid transitions, thermal conductivity and the glass transition temperature.⁽⁷⁻¹⁴⁾ Chemical properties monitored by DSC and DTA are dehydration, decomposition, oxidative reactions, solid state reactions, chemisorption, combustion, polymerization, curing and catalyzed reactions.⁽¹⁵⁻¹⁹⁾

In DTA, the temperature difference between the substance and a reference material is measured as a function of temperature, while the substance and reference material are subjected to a controlled temperature program.⁽²⁰⁾

In DSC, the difference in energy input into a substance and a reference material is measured as a function of temperature, while the substance and reference material are subjected to a controlled temperature program.⁽²¹⁾ Two modes, power compensation DSC and heat flux DSC, can be distinguished, depending on which method of measurement is used.^(22,23)

The following is a review of DSC and DTA and their role in thermal science. The root of thermal analysis is the determination of heat and temperature. Heat is a macroscopic quantity and has its origin in molecular motion.⁽²⁴⁾ DTA measures the temperature difference between a sensitive reactive material and an inert reference as a function of time and temperature. DTA measurements provide information about transition temperatures as well as kinetic time-based phenomena and thermodynamic properties. DSC is a step above DTA in that it measures quantitative heats of reaction and transitions. Both thermal methods can differentiate first order thermodynamic changes like fusion, and second order thermodynamic changes like a glass transition temperature, T_g . This chapter will focus mainly on fundamentals, instrumentation and applications of DSC.

1 INTRODUCTION

1.1 Differential Scanning Calorimetry: Heat Flux and Power Compensated Methods

The function of DTA and DSC instruments and the values they measure will be reviewed. An important innovation of DSC, modulated temperature differential scanning calorimetry (MTDSC), will also be examined in detail.

Some of the first commercial analytical instruments that measure heat flow into or out of a sample as the sample is undergoing a transition have been referred to by a variety of names. They include quantitative differential thermal analysis (QDTA),⁽²⁵⁾ dynamic differential calorimetry (DDC), dynamic enthalpic analysis (DEA), and DSC. The latter, DSC, is widely accepted as the term used to describe modern instruments that are scanning calorimeters. DSC is defined here based on what it measures: heat flow. The International Confederation of Thermal Analysis⁽²⁶⁾ has adopted this position in describing DSC. The generic definition of DSC is the accepted definition and is based on equivalency of results obtained, general usage in the literature, comparisons of temperature profiles, and comparison to classical calorimetry.

DSC uses a temperature transducer as its primary sensor. In nearly all commercial differential scanning calorimeters, the heat flow output is based on the difference in temperature between sample and reference as recorded by the temperature sensor. The sensors in differential temperature devices are thermocouples or thermopiles. Thermocouples are also used in DTA and therein lies the confusion of calling the DSC, a DTA. However, there are some fundamental differences between these two techniques.

In conventional DTA, the temperature sensor is placed in the sample, while in the DSC, the temperature sensors

are located external to the sample. Boersma⁽²⁷⁾ states that this experimental condition, external sensors, must be met in order to make calorimetric measurements. Semiquantitative calorimetric measurements have been accomplished when the DTA conditions operate in both modes, first when the sensor is in contact with the sample, and then when the sensor is removed from the sample. The TA Instruments (TAI) high temperature DTA is capable of either mode.⁽²⁵⁾ Without sample couple liners present, the instrument performs as a classical nonquantitative DTA. With liners, however, accuracy and precision of calorimetric measurements of 5% can be observed. DSC typically provides calorimetric accuracy and precision to better than 1%. It is desirable to have constant calorimetric sensitivity, but it is not a necessary condition for a DSC instrument. Differential scanning calorimeters with constant calorimetric sensitivity where the calibration constant is not a function of temperature have an output directly in heat flow units of milliwatts.

Differential scanning calorimeters operate by one of two methods, differential temperature and temperature servo measurements. An example of the differential temperature instrument is the TAI DSC 910 system. Figure 1 is a cross-sectional view of this DSC cell. The cell uses a constantan disk as its primary means of heat

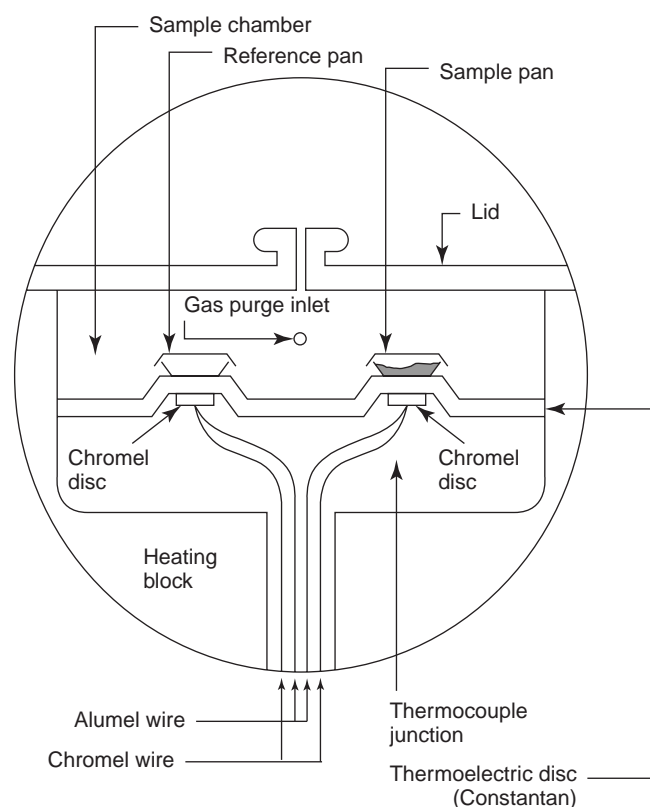


Figure 1 Cross-sectional view of a DSC cell.

transfer to the sample and reference positions, as one element of the temperature measuring thermoelectric junctions. The experimental sample and reference are placed in containers or pans that rest on raised platforms on the constantan disk. Heat is transferred through the disk and into the sample and reference via the containers. The differential heat flow to the samples and reference is monitored by chromel–constantan area thermocouples formed by the junction of the constantan disk and a chromel disk that covers the underside of each platform. The differential temperature, T , from the sample and reference thermocouples, is fed to a variable high-gain amplifier where the signal is amplified, electronically scaled to read directly in heat flow units and finally displayed on the y -axis. Chromel and alumel wires are connected to the underside of the chromel disk and the resultant chromel–alumel thermocouple is used to monitor the sample temperature directly.

When a sample is programmed at a constant heating rate through its melt, the heat capacity of the sample increases in theory to infinity and the sample temperature becomes invariant. Therefore, a temperature is developed between the sample and the reference temperature which is constantly rising. This temperature signal is proportional to the heat flowing into the sample endothermically as part of the transition. When the amplified and scaled signal presented to the computer in milliwatts is integrated over time, a value for the heat in millijoules associated with the transition is obtained.⁽²⁴⁾

The second type of instrument, the temperature servo system, is shown in Figures 2 and 3.⁽²⁵⁾ In this design, the sample and reference pans are placed in close contact with platinum resistance thermocouples (PRTs) which are used to measure their temperature at any given moment. In addition, the unit has two individual heaters that control the heat flow to these samples.

When the sample is temperature programmed through its melt, the sample temperature becomes essentially invariant, and the difference temperature signal, ΔT , developed between it and the reference is amplified, scaled and displayed as the output from the device, see Figure 3.^(25,28) The process continues when the differential

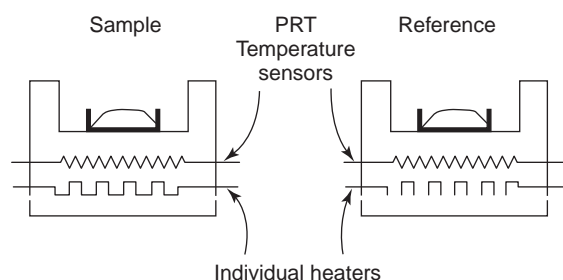


Figure 2 Schematic diagram of power compensated DSC cell.

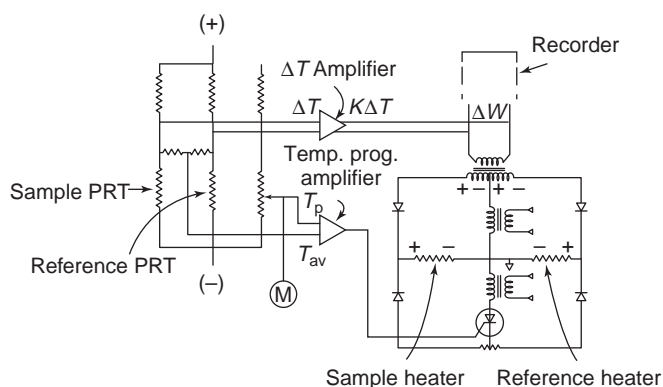


Figure 3 Schematic diagram of temperature servo system.

power is supplied back to the sample heater attempting to reduce the temperature difference between the sample and reference. The operating principle of a servo system requires the restoring signal, in this case a voltage signal to the differential heater, to be proportional to the offset, the temperature difference. If the temperature difference is zero, no differential power could be supplied by the servo system. An actual zero temperature difference can exist only if the servo amplifier gain is infinite; and it is not.

Calorimetry is the scientific field dealing with the measurement of the heat or energy content of various chemical and physical reactions. In a typical classical adiabatic calorimetric experiment, a chemical reaction may be carried out in a sealed container insulated from heat losses to the outside world. From the known heat capacity (C_p) of both the insulated container and its contents and the small measured change in temperature (ΔT) of that system, the heat content of the chemical reaction, H , can be calculated, Equation (1):

$$H = \Delta T \times C_p \quad (1)$$

The experiment is usually designed so that the change in system temperature remains small, usually several Kelvin. Under these conditions C_p is constant. From these experiments we derive the definition of the calorie which is the unit of measurement for heat content or energy, or the amount of heat necessary to raise the temperature of 1 g of water at 15 °C, by 1 °C.

In DSC, the temperature profile of a sample seldom exceeds a few tenths of a degree. Therefore DSC instruments operate well under classical calorimetry conditions, from which thermodynamic data are almost exclusively obtained.⁽²⁴⁾

Differential scanning calorimeters based on heat flux or power compensated measures the same quantity, the heat flow into (endothermic) or out of (exothermic) a sample.

1.2 Review of Modulated Temperature Differential Scanning Calorimetry

An innovation in DSC that has become a widely accepted technique is MTDSC.^(29–38) It provides the same qualitative and quantitative information about physical and chemical changes as conventional DSC. MTDSC, however, provides unique thermochemical data that are not accessible with DSC. MTDSC overcomes the limitations of conventional DSC. The effects of baseline slope and curvature are reduced, thereby increasing the sensitivity of the system. Overlapping events such as molecular relaxation and glass transitions can be separated. Heat capacity can be more easily measured using this technique which requires a minimum number of experiments.

MTDSC uses the same conventional heat flux DSC cell system. Uniquely, it uses a different heating profile for the sample and reference as supplied by the furnace. Specifically, a sinusoidal modulation or oscillation is superimposed on the conventional linear heating ramp. Experimental procedures can vary from method to method for DSC, DTA, MTDSC and pressure differential scanning calorimetry (PDSC).

2 EXPERIMENTAL PROCEDURES

2.1 Optimization of Differential Scanning Calorimetry Thermal Properties

The optimization of DSC is critical in acquiring accurate and precise data. Inspect the DSC cell and assure its good condition. For example, clean the thermal sensors by heating to 500 °C in air to burn off any decomposed materials. Use a brush to wipe off any debris that will interfere with the transfer of heat flow from the sample to the thermal sensor. Always use a purge gas. Typical inert gases are nitrogen and helium. Helium is used to enhance heat transfer. A nominal flow rate is set at 50 mL min⁻¹ for most instruments. Oxidative gases are oxygen or air at 21% oxygen and 79% nitrogen.

2.2 Calibration, Standards and Standard Methods

The instrument must be calibrated for temperature and heat flow on a regular basis. American Society for Testing and Materials, ASTM E697⁽³⁹⁾ can be used to calibrate the DSC temperature (x -axis). ASTM E968⁽⁴⁰⁾ is used to calibrate the heat flow (y -axis). The ASTM E1860⁽⁴¹⁾ protocol is used to establish elapsed time, which is especially important when considering International Standardization Organization (ISO) 9000 certification.

An excellent resource of known temperatures and heat of fusion for many standards is given in Table 1,⁽⁴²⁾ where

Table 1 Enthalpy of melting for standards^a

Material	Melt temperature (°C)	Heat of fusion		Refs.
		(J g ⁻¹)	(+/-)	
Cyclopentane	-151.16 (crystal)	68.69		52
Cyclopentane	-135.06 (crystal)	4.88		52
<i>n</i> -Pentane	-132.66	36.51	0.02	48
<i>n</i> -Heptane	-90.56	138.62		54
Cyclohexane	-87.06	78.70		53
<i>n</i> -Octane	-56.76	180.00		54
Mercury	-38.8344 ^e	11.443	0.004	44 ⁱ
<i>n</i> -Decane	-26.66	199.87		54
<i>n</i> -Dodecane	-9.65	214.35		54
H ₂ O	0.01 ^e	335	0.6	43
Benzene	5.53	125.9		47
Cyclohexane	6.54	30.91		53
Diphenyl ether	26.87 ^d	101.15	0.10	46
<i>n</i> -Octadecane	28.24	238.76		55
Hexatriacontane	72.14 (crystal)	18.54		55
Hexatriacontane	73.84 (crystal)	59.59		55
Hexatriacontane	75.94	173.38		55
Benzoic acid	122.37 ^d	147.4	0.1	45
Indium	156.5985 ^e	28.57	0.17	43
Tin	231.928 ^e	60.6	0.2	43
Bismuth	271.442 ^d	53.07	0.58	43
Cadmium	321.108 ^d	55.09	1.4	44
Lead	327.502 ^d	23.1	0.3	43
Zinc	419.527 ^e	108	0.6	43 ^g
Tellurium	449.6	137.0	4	50, 51
Antimony	630.74 ^d	163.2	5.2	44 ^j
Magnesium	650	362	17	49 ^h
Aluminum	660.325 ^e	400.1	4.7	44 ^h
KBr	734.0	216.0	3.0	51
NaCl	801.0	480.0	10.0	51
Silver	961.78 ^e	104.4	3.9	44
Gold	1064.18 ^e	63.72	2.1	44
Copper	1084.62 ^e	205.4	6.6	44 ^{f,c}
Nickel	1455 ^d	297.6		44
Cobalt	1494 ^d	274.8	4.3	44 ^b
Iron	1538	253	7	49
Palladium	1554 ^d	165		

^a The table summarizes the best known temperatures and heats of melting for many standard materials. These values may be used for temperature and/or cell constant calibration of the TA Instrument's DSC or high temperature DTA.

^b Sample sublimes.

^c Sample oxidizes easily.

^d Temperature taken from the IPTS-1968. *Pure Appl. Chem.*, **22**, 557 (1971).

^e Temperature taken from the ITS-90. *Metrologia*, **27**, 3–10 (1990).

^f Reacts with alumina.

^g Amalgams with aluminum as low as 450 °C, do not heat above 430 °C.

^h Sample amalgams with platinum.

ⁱ Shelf-life 1 week at room temperature.

^j Amalgams with copper.

there are more than 30 standard materials, inorganic, metals and organic chemicals listed. The values cited in Table 1 can be used to establish the DSC cell constants. The latter converts measured values, for example, temperatures and heats of fusion and crystallization to accurate physical properties.

2.3 Sample Size

Thermal properties may be dependent on the specimen size and shape. A common sample size is from 1 to 10 mg. Replicates should be the same size to within 10%. Select the sample shape to ensure good contact

with the pan or container. A uniform size and shape is desirable.

2.4 Sample Preparation and Pan Selection

Heating through transitions erases thermal history at lower temperatures. Mechanical treatment of the sample may produce localized heating or stress in the sample. Cryogenic grinding in a freezer mill creates easily handled powders. The low temperature sampling minimizes treatment effects. Cutting it from the bulk sample with a razor blade or clipper can attain minimum stress on the sample. Minimum temperature and time exposure of the sample is accomplished by the latter techniques. Films can be heat pressed and then paper punched out. However, the effects of heating and oxidation must be considered.

DSC pan or container selection is dependent upon specimen size and shape. One must also consider the maximum temperature of the experiment, if the pan is chemically inert and whether it retains vapors or not. Other factors to consider when selecting an appropriate pan for use is whether it has a high thermal conductivity, low heat capacity, and low cost.

DSC pan types include aluminum, copper, gold, platinum, glass, carbon, stainless steel and mild steel. The form of the pan can also be varied. It can be crimped, hermetically sealed, and contain a molecular leak with a laser drilled pin hole, an autosampler pan and a center raised solid fat index pan to fit over a thermal sensor.

An as-received pan must be cleared in order to remove oils or lubricants used in manufacturing the pan. Organic oils and lubricants can be removed with xylene, acetone, dried with nitrogen gas and stored according to ASTM E-1858-97.⁽⁵⁶⁾

One supplier of aluminum pans used calcium carbonate as lubricant. Excess calcium carbonate confounded oxidative studies where organic oils decomposed to yield acids. The relative oxidative stability varied considerably.⁽⁵⁷⁾

Another vendor did not realize that when their supplier of aluminum pans stamped them out they were embedding small (less than 0.2 mm) particles of iron and copper. These metals are used to accelerate the oxidation of oils.^(58,59) These contaminants caused accelerated oxidation and a process that became out of control. The extraneous metals were only detected by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy, see Figure 4. Table 2 gives an elemental analysis. When the peak area ratio of iron and copper to chromium was greater than two, the relative oxidation rate (inflection point-first derivative of the exothermic heat flow versus temperature curve) was out-of-control. This particular problem was eliminated by returning to a source of new containers with a high standard of quality control.

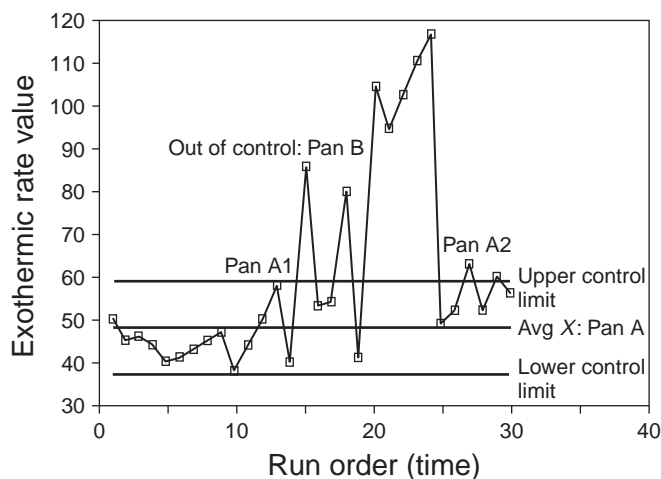


Figure 4 Out-of-control process: exothermic value versus time. □, oxidation rate (MW/min); —, average oxidation rate.

Table 2 Elemental analysis of pan surface

Al pan	Fe	Cr	Cu	Fe/Cr
Poor	414	135	173	3.1
Fair	328	103	136	3.2
Good	315	235	157	1.3

2.5 Differential Scanning Calorimetry Curve and Sample Analysis

A DSC or DTA baseline plot should be flat. The latter can be achieved through calibration with empty pans and application of the electronic correction. All samples have a baseline with an endothermic slope caused by the increasing specific heat capacity of the sample with increasing temperature, see Figure 5.

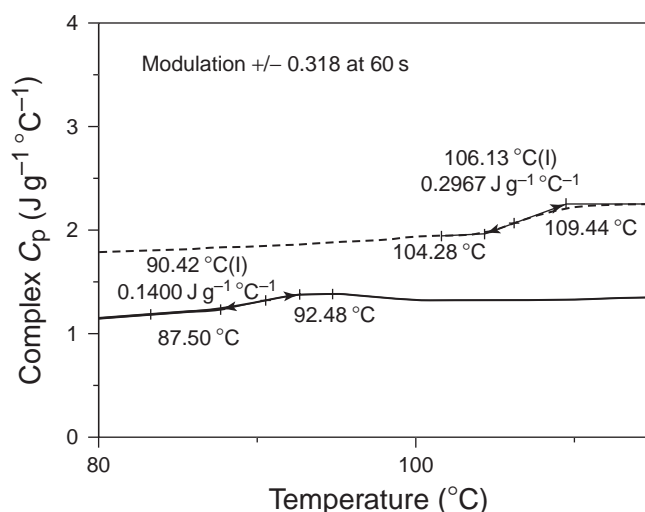
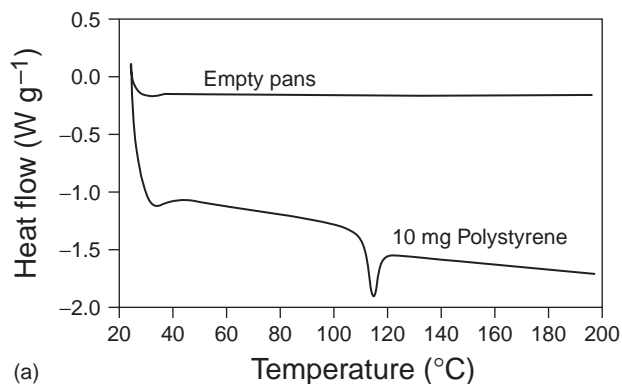
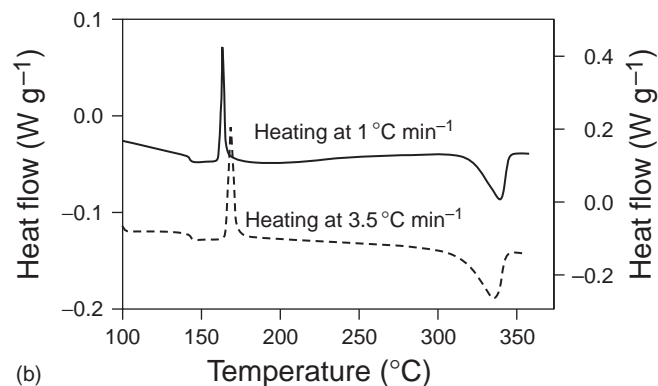


Figure 5 Specific heat capacity increases with temperature. —, general grade polystyrene (PS) and - - -, 900000 MW PS standard.



(a)



(b)

Figure 6 (a) DSC baseline slope. (b) DSC baseline curvature.

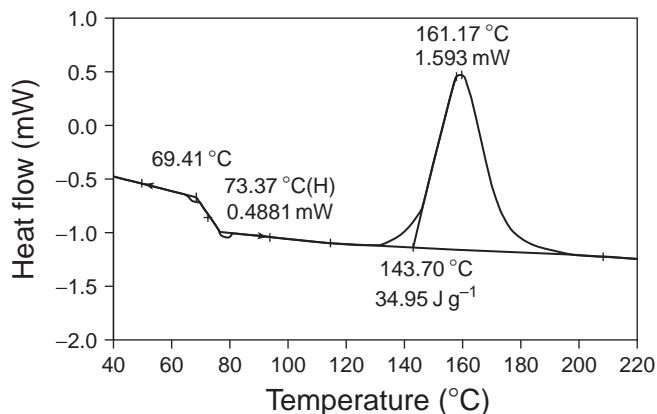
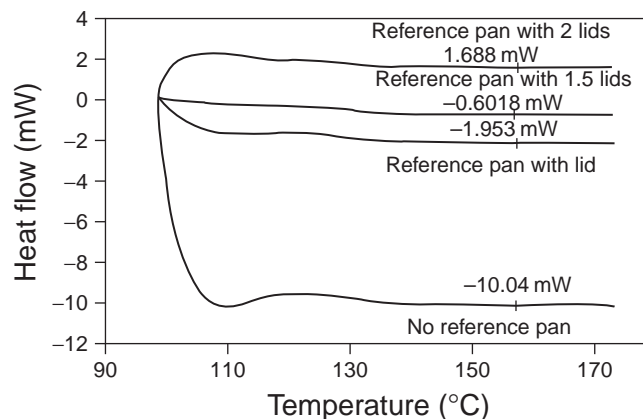
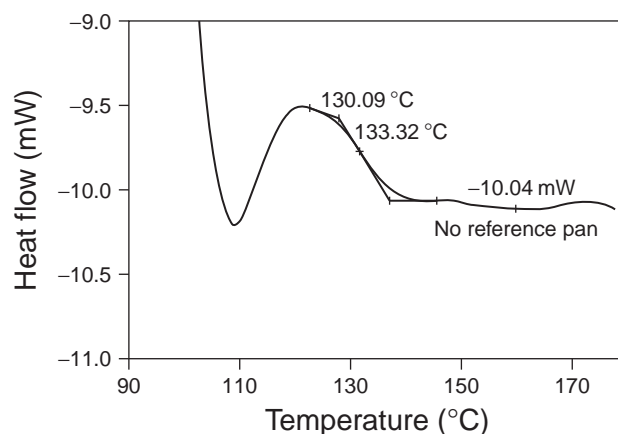
DSC baseline curvature cannot normally be corrected by calibration. However, if necessary, it can be eliminated by baseline subtraction, see Figure 6. Baseline slope and curvature can cause an error if integrating peaks over a broad temperature range and can make detection of a weak glass transition temperature, T_g , difficult, Figure 6(a) and (b).

Samples should be kept thin to minimize heat transfer problems. It is better to cut out a representative sample rather than crush it. Stresses could be imparted to the sample prior to thermal analysis. Typical sample mass in DSC is 10–15 mg for polymers. A goal is to achieve a change of 0.1–10-mW heat flow in going through a transition, see Figure 7. Use the lightest, flattest pan possible.

If the sample contains volatiles, put one or more pinholes in the lid of the pan before crimping in order to permit a continuous evaporation process.

2.6 Effect of Sample Specific Heat

Minimize differences in specific heat between the sample and the reference by adding aluminum to the reference pan. This improves the overall baseline; see Figures 8–10. Initiate a DSC analysis 2–8 min before the temperature of interest, depending on the heating rate, for example,

**Figure 7** Heat flow change during a transition.**Figure 8** Effect of reference pan weight. Epoxy sample of approx. 10 mg, heating rate $20^\circ\text{C min}^{-1}$.**Figure 9** Start up hook and T_g with no reference pan.

5°C min^{-1} or $20^\circ\text{C min}^{-1}$. That is about 40°C before the temperature of interest ($2 \times 20^\circ\text{C min}^{-1} = 40^\circ\text{C}$ and $8 \times 5^\circ\text{C min}^{-1} = 40^\circ\text{C}$).

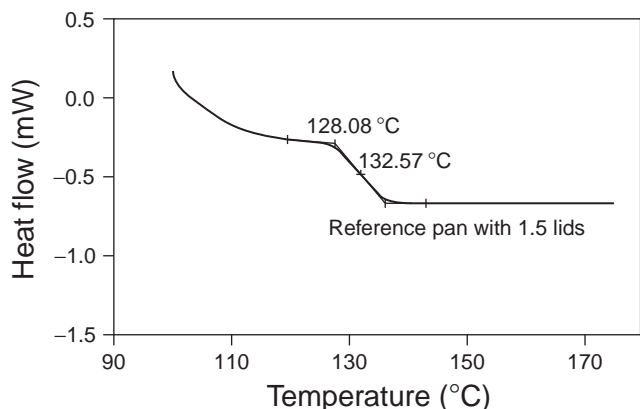


Figure 10 Start up hook and T_g with heat capacity of reference matched to sample.

2.7 Differential Scanning Calorimetry Sensitivity and Resolution

Adjust sample weight, heating rate and purge gas if necessary to improve sensitivity or resolution, see Table 3 and Equation (2)

$$\frac{dQ}{dT} = C_p \times \frac{dT}{dt} + f(T, t) \quad (2)$$

where heat flow = heat capacity \times heating rate + kinetic component, and the kinetic component is a function of temperature and time.

2.8 Pressure Differential Scanning Calorimetry

A special pressure cell is needed for both high-pressure as well as low-pressure studies in nitrogen, air or oxygen. The sample of 1–3 mg, is weighed into an open pan as per the ASTM standard test method E-1858 for oxidation induction time (OIT).⁽⁵⁶⁾ In the OIT method, the sample, a drug, oil or polymer is heated to an isothermal temperature, 175 °C at 35-MPa oxygen and 195 °C at 14 kPa of air or oxygen. The extrapolated onset temperature is defined as the OIT. A second method, ASTM E-2009, oxidation onset temperature (OOT) is based on a DSC or PDSC.⁽⁵⁷⁾ The OOT is defined as the extrapolated onset temperature in a plot of heat flow versus temperature. A thermogravimetric analyzer (TGA) coupled with a differential thermal analyzer, TGA/DTA, has also been

Table 3 Basic heat flow Equation (2); parameters, sensitivity and resolution

Parameters	Increase sensitivity	Increase resolution
Sample weight	increase	decrease
Heating rate	increase	decrease
Purge gas	nitrogen	helium

used to determine the OOT of hydrocarbons in air. In this study, the sample size was 10 mg, the flow rate of air was 250 mL min⁻¹, heating rate was 10 °C min⁻¹, and the sample pans were aluminum or platinum.^(60,61)

2.9 Differential Scanning Calorimetry Method and Thermoplastics

When analyzing thermoplastics with a standard DSC, the experimental program should include a heat-cool-heat cycle at 10 °C min⁻¹.^(62,63) The first heat results are a function of material and an unknown thermal history. The cool cycle gives the sample a known thermal history. These results can be used to compare polymer crystallization properties. Finally, the second heat results are a function of material and a known thermal history. They will be useful for comparison of materials, for example polymers, see Figures 11–13.

2.10 Differential Scanning Calorimetry Method and Thermosets

When analyzing thermoset polymers by conventional DSC, the experimental program should include an annealing

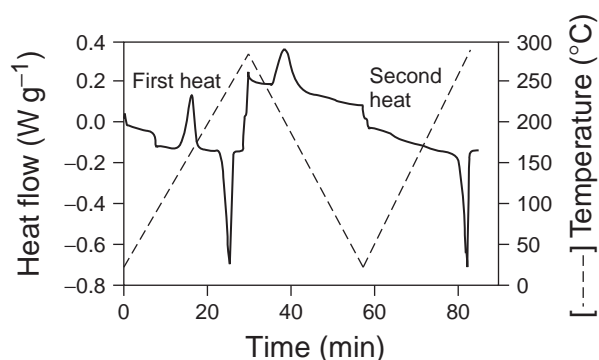


Figure 11 Thermoplastic: heat-cool-heat.

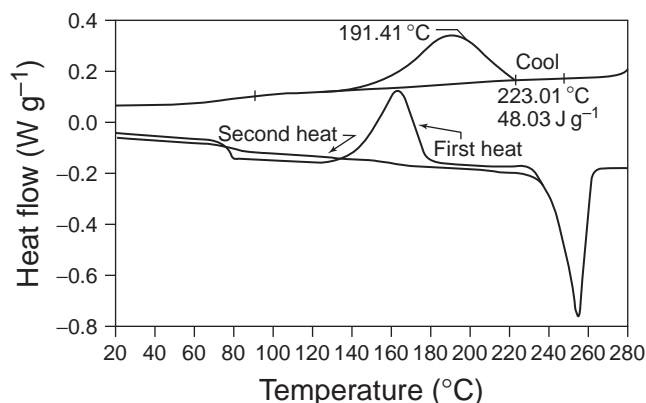


Figure 12 Thermoplastic: heat flow versus temperature.

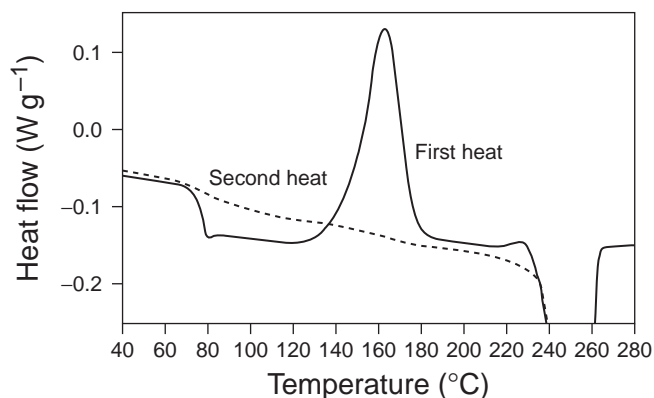


Figure 13 Comparison of first and second heating runs.

period, then heat, quench cool and finally heat at a rate of $10\text{--}20\text{ }^{\circ}\text{C min}^{-1}$. Anneal at approximately $25\text{ }^{\circ}\text{C}$ above the T_g onset to eliminate effects of enthalpic relaxation. The heat portion of the program is to measure the T_g and any residual cure (exothermic polymerization). Do not heat through the decomposition onset temperature; halt the experiment before decomposition occurs. Quench the sample, usually with liquid nitrogen or a dry ice–acetone slurry in a cooling can. This process will give the sample a known thermal history. During the final heating the T_g of the fully cured sample can be measured, see Figures 14–16.

Select an end temperature that does not cause decomposition of the sample in the calorimeter. Degradation products can condense in the cell and cause either corrosion of the cell or baseline problems. Use sealed glass ampoules or stainless steel pans that can take high pressure, $>70\text{ MPa}$, in order to study decomposition by DSC. The use of aluminum hermetically sealed pans can minimize corrosion and destruction of the cell liner. However, knowledge of the onset of degradation assists in lengthening the longevity of a DSC cell.

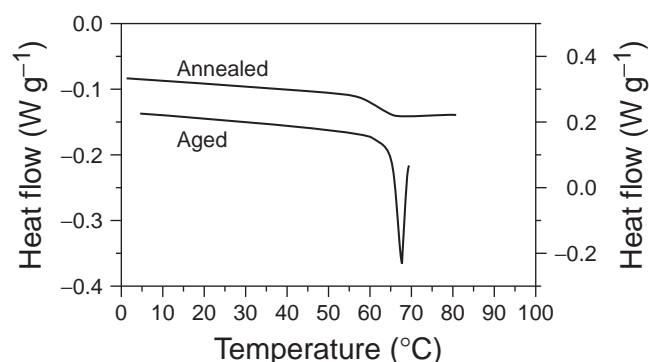


Figure 14 Effect of annealing on shape of glass transition.

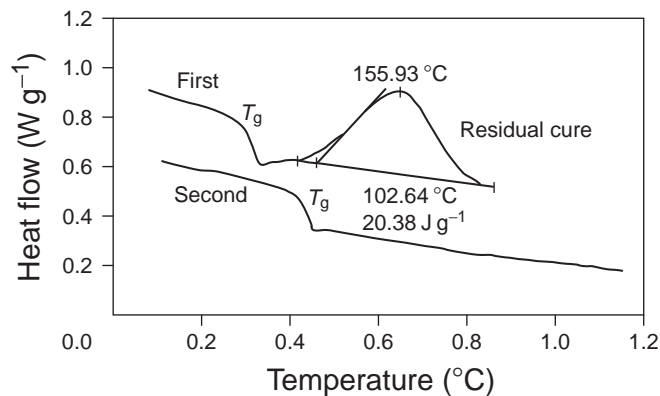


Figure 15 Thermoset: comparison of first and second heating runs.

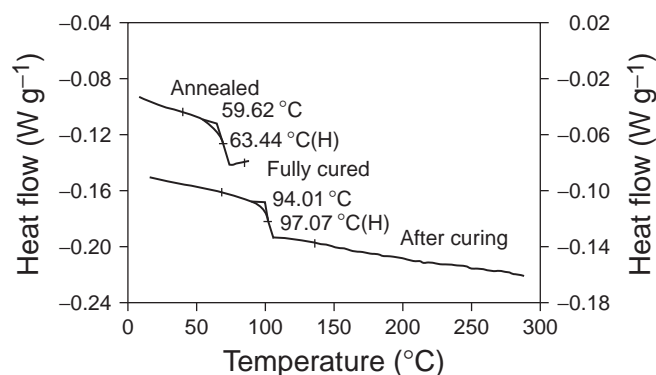


Figure 16 Shift in T_g as a result of curing.

2.11 Differential Scanning Calorimetry Method and an Unknown

When examining an unknown sample, first test the sample by thermogravimetric analysis (TGA). Determine if the sample contains any volatiles and its decomposition temperature. If you do not have a TGA, weigh the sample before and after each DSC run. A 1% weight loss will often show up in the thermal curve as an endothermic peak unless the run is taking place in either air or oxygen where oxidation shows up as an exothermic peak.

2.12 Internal Melting Point Standard

Use an internal melting point standard; see Table 1, to verify transition temperature accuracy. Place the sample in a DSC pan. Invert the lid and crimp it in place or force it into the pan so that good contact is achieved on the top and bottom of the sample. Weigh the internal standard, for example, indium metal, into the inverted lid. Record the DSC thermal curve. The melting profile of indium will be superimposed on the curve, Figure 17.

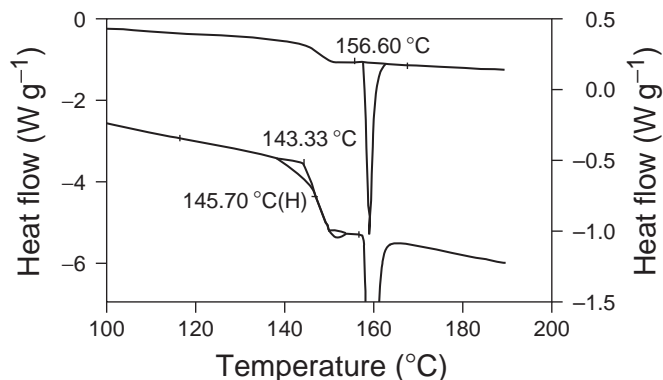


Figure 17 Use of internal melting point standard. Polycarbonate (PC) sample of approx. 10 mg with 1 mg indium, heating rate $5^{\circ}\text{C min}^{-1}$.

2.13 Modulated Temperature and Conventional Differential Scanning Calorimetry

How does MTDSC differ from conventional DSC? DSC measures the difference in heat flow between a sample and an inert reference. MTDSC measures the same total heat flow. A DSC thermal curve records the data as a function of a linear change in temperature. A MTDSC thermal curve represents the change in temperature as a function of both a linear and a sinusoidal change. The linear change in temperature provides the same information, total heat flow, in both MTDSC and DSC. The sinusoidal change in temperature permits the measurement of heat capacity effects simultaneously with the kinetic effects.

The DSC heating rate can vary from isothermal to $20^{\circ}\text{C min}^{-1}$. The MTDSC heating rate or ramp ranges from isothermal to $5^{\circ}\text{C min}^{-1}$. The MTDSC temperature of modulation amplitude can range from 0.01 to 10°C . The modulation period can vary from 10 to 100 s or 10–100 mHz in frequency.

In order to compare the two methods, MTDSC and DSC, poly(ethylene terephthalate) (PET) will be examined by the two methods. An MTDSC procedure is:

1. Equilibrate at 0°C .
2. Modulate 1°C every 40 s.
3. Maintain isothermal at 0°C for 5 min.
4. Ramp at $5^{\circ}\text{C min}^{-1}$ to 280°C .

A corresponding DSC protocol is:

1. Equilibrate at 0°C .
2. Maintain isothermal at 0°C for 5 min.
3. Ramp at $20^{\circ}\text{C min}^{-1}$ to 280°C .

DSC records only the total heat flow in the sample. The modulated heat flow contains all thermal events

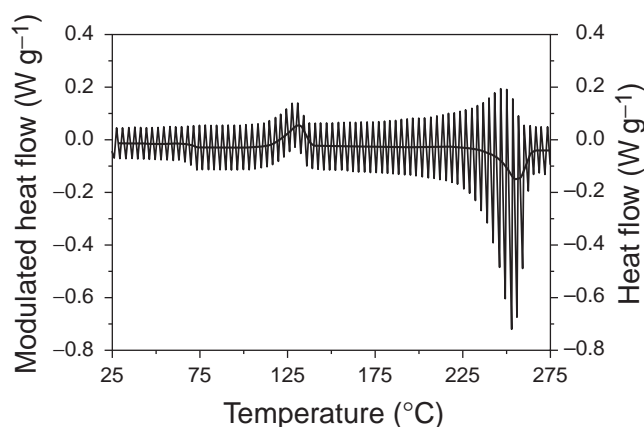


Figure 18 Total heat flow from MTDSC raw signals calculated as the average value of the modulated heat flow signal.

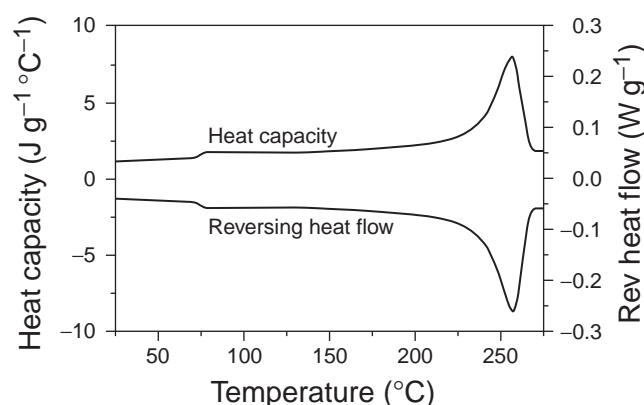


Figure 19 Reversing heat flow from MTDSC raw signals.

occurring in the sample. Fourier transformation analysis of the modulated heat flow signal is used to calculate its average signal continuously. Total heat flow is the same in both techniques at the same average heating rate. The reversing heat flow is the heat capacity component of the MTDSC total heat flow. The nonreversing heat flow is the kinetic component of the heat flow, Figures 18–20.

2.14 Examples of Modulated Temperature Differential Scanning Calorimetry Characteristics

The MTDSC of an as-received molded blend of a PET/acrylonitrilebutadiene terpolymer (ABS) is represented in Figure 21. The total heat flow thermal curve indicates a T_g at about 60°C and an exothermic event at about 97°C . The total heat flow T_g is the PET glass transition temperature. The exothermic event is the cold crystallization of PET. The cold crystallization event masked the ABS T_g . However, the reversing heat flow thermal curve clearly differentiates the ABS and PET T_g values. The ABS T_g (e), the

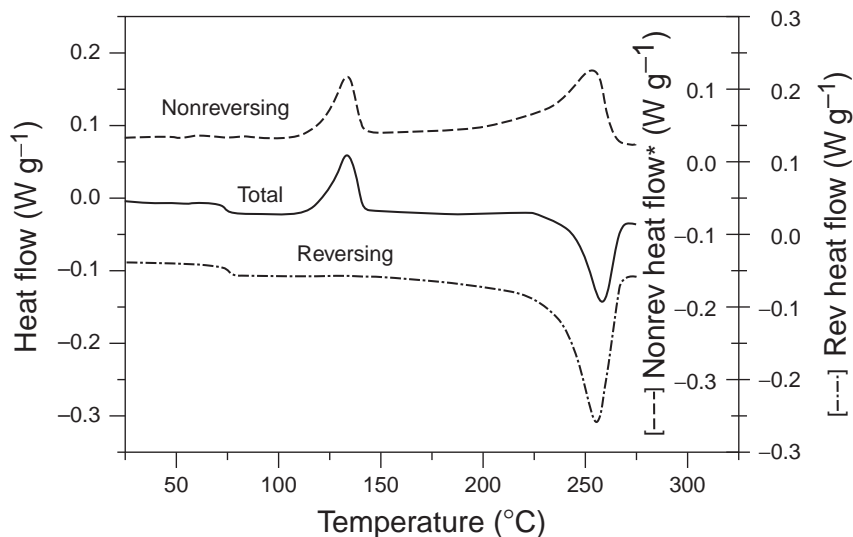


Figure 20 Quench cooled PET/MTDSC.

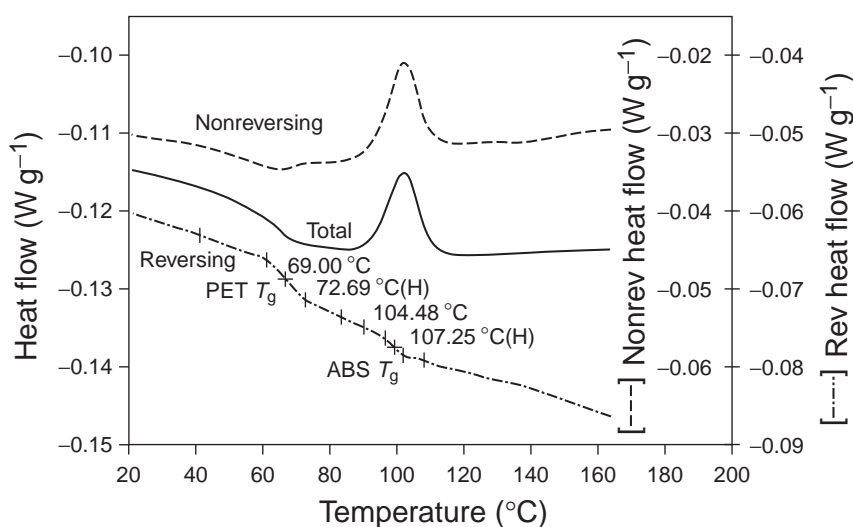


Figure 21 PET/ABS blend “as received” MTDSC.

extrapolated onset T_g , is 104.5 °C and the PET $T_g(e)$ is 67.0 °C.

The T_g values and melt temperature of another polymer blend are clearly delineated in their first heat by MTDSC, see Figure 22. This blend contains PET, PC, and high-density polyethylene (HDPE). Overlapping thermal events confound the total heat flow curve. The exothermic PET cold crystallization overlaps the melting peak of HDPE. The reversing heat flow ($W g^{-1}$) thermal curve for reversible processes has a PET T_g at approximately 72 °C, a peak melt temperature for HDPE at 123 °C and a PC T_g at approximately 138 °C. The nonreversing heat flow, which is representative of nonreversible processes, shows an enthalpic relaxation endotherm at

approximately 70 °C and the PET crystallization peak at ca. 115 °C.

2.15 Modulated Temperature Differential Scanning Calorimetry Experiments and the Glass Transition

Next, is a review of the MTDSC experimental factors that affect T_g properties of a thermoplastic and two elastomers. Also determined was the difference between glass transition temperature of elastomers by MTDSC and conventional DSC.

Aubuchon reported that “the frequency effect seen in MTDSC data is the effect that (occurs when) the heat

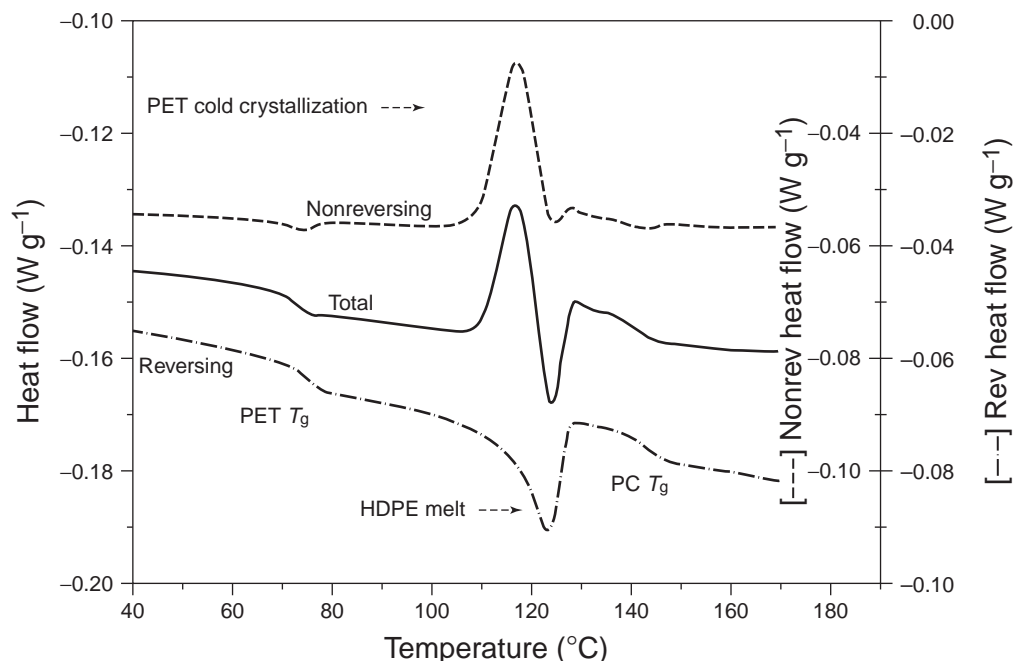


Figure 22 Polymer blend characterization by MTDSC.

capacity and reversing signals shift to higher temperatures with shorter periods (higher frequencies) of temperature modulation.⁽⁶⁴⁾ The total heat flow signal does not show any frequency dependence". Both in dynamic mechanical analysis (DMA) and dielectric thermal analysis (DETA) the temperature shifts are accompanied by orders of magnitude change in frequency. The nonreversing heat flow signal is calculated from the difference of the total heat flow minus the reversing heat flow. Therefore, the nonreversing signal is also dependent on the frequency or period.

The MTDSC has two simultaneous ramps or heat rates. One is the average underlying heating rate (ramp) and the other, the instantaneous heating rate (amplitude). These ramp rates vary with the temperature modulation period and the amplitude. A shift in the extrapolated onset glass transition temperature, $T_g(e)$, of PS with frequency was observed. In the heating cycle, the $T_g(e)$ decreased by 1.3 °C with an increase of frequency from 25 to 100 s. In the cooling cycle, the $T_g(e)$ decreased by 3.4 °C with the same increase in frequency. The effect of the amplitude or instantaneous heating rate (0.1, 0.2, and 0.4 °C) on the T_g at a constant heating rate of 1.5 °C min⁻¹ showed a variation of 103.7, 103.9 °C (cooling cycle) and 104.4, 104.8 °C (heating cycle). Within experimental error, the T_g did not vary with amplitude for PS. Aubuchon noted that a four-fold increase in frequency (10–40 mHz) or decrease in period (100–25 s) increased the T_g by 3.0 °C. A four-fold increase in amplitude (instantaneous heating rate) increased the $T_g(e)$ by 0.3 °C.

There is a great interest in how the amplitude, heating rate or ramp and period affect the T_g of polymers, for example, polybutadiene (PBD) and polystyrene-cobutadiene (SBR). A two to the third (2³) factorial designed experiment⁽⁶⁵⁾ examined PBD, SBR and a National Institute of Standards and Technology (NIST) high molecular weight PS. The following are the three MTDSC experimental variables and the low and high levels:

- Amplitude, 0.312 and 0.796 °C
- Period, 25 s (40 mHz) and 60 s (17 mHz)
- Ramp, 2.0 and 5.0 °C min⁻¹.

Two sets of experimental variables are considered optimum for MTDSC⁽⁶⁶⁾

1. amplitude, 0.312 °C; period, 60 s (0.017 Hz); and ramp, 2.0 °C min⁻¹
2. amplitude, 0.796 °C; period, 60 s (0.017 Hz); and ramp, 5.0 °C min⁻¹.

The run order for this study was randomized. The following physical properties associated with the glass transition temperature were measured in the reversing mode of the MTDSC for the eight runs and the three polymers (see Figure 23):

- $T_g(e)$, the extrapolated onset glass transition temperature (°C)
- $T_g(i)$, the inflection temperature of the sigmoid-shaped T_g curve (°C)

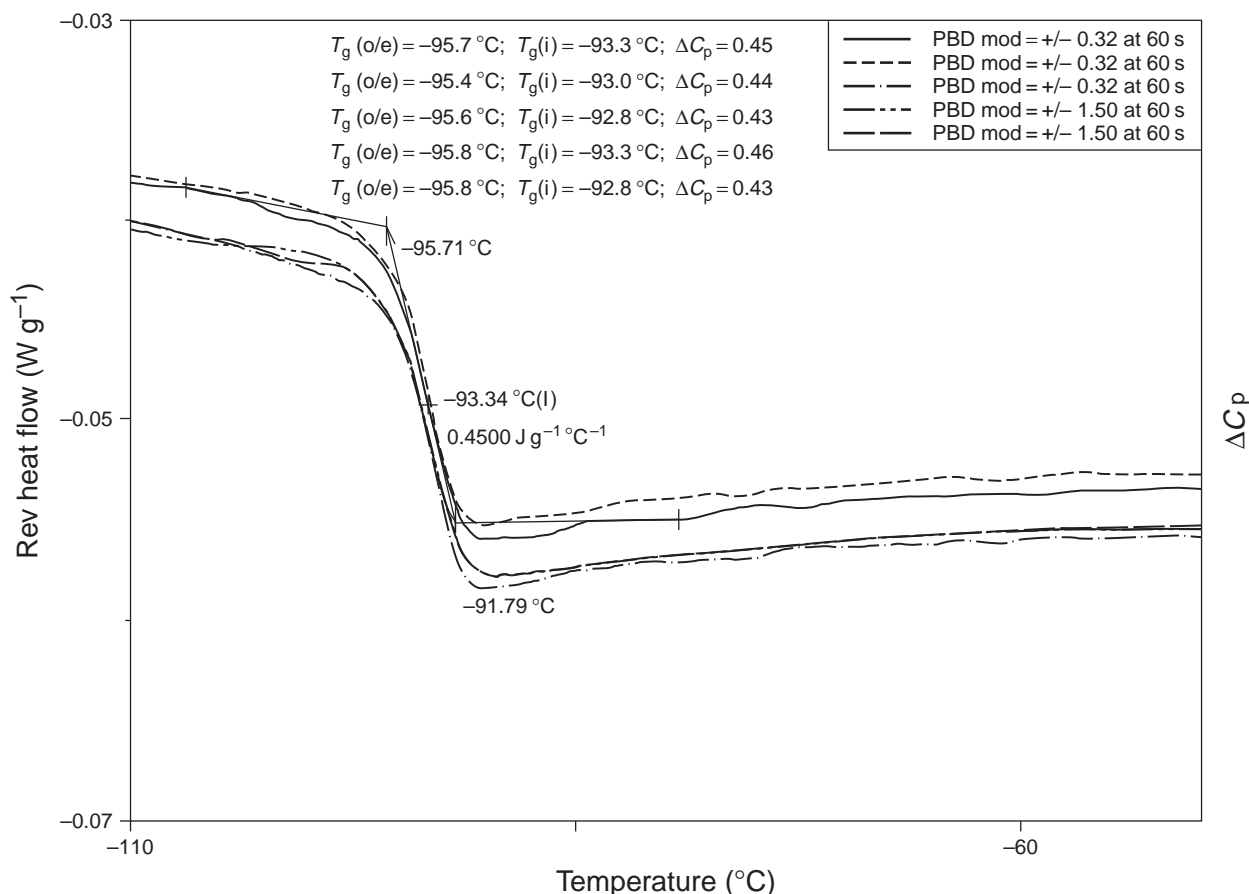


Figure 23 PBD: MTDSC amplitude variation.

- ΔC_p at T_g , the change in heat capacity at the T_g (J g⁻¹ °C⁻¹) (y-axis change at T_g)
- ΔT at T_g , the change in temperature at the T_g , measured as the T_g (end) minus the T_g (e) (°C) (x-axis change at T_g), Figure 24.

Statistical and graphics analysis of the data was accomplished with JMP 3.2.⁽⁶⁶⁾ A least squares fit model was used and the significance of the data was ranked by the *t*-test.

The most important MTDSC polymer property studied was the glass transition temperature, T_g (e) or T_g (i). Employing the *t*-test to evaluate the measured variations in the factorial design the absolute variation of the T_g was <2 °C and this variation was not significant, Table 4. The interactive variables heating rate and period, heating rate and amplitude and period and amplitude also exhibited small variations in T_g (<2 °C). The standard deviation of the T_g (e) at the 95% confidence level was ± 3 °C for the polymers studied. The standard deviation of the T_g (i) at the 95% confidence level was ± 2 °C. Wide variations in the MTDSC variables, heating rate, amplitude and period did not significantly affect the value of T_g .

However, variation of the period from 25 to 60 s did significantly affect the PS properties, the change in heat capacity at T_g (ΔC_p at T_g) and the change in temperature at T_g (ΔT at T_g). The ΔC_p at T_g varied by 30% and the ΔT at T_g by 25%. Variation of the period also caused similar changes in the ΔC_p at T_g for SBR and PBD.

The *t*-test⁽⁶⁸⁾ for all four glass transition properties of PS varied significantly with the changes in the period (inverse frequency). The properties of the elastomers studied were not affected by the variables, except for the period.

A comparison between the T_g properties of PS as determined by MTDSC and conventional DSC is given in Tables 4 and 5 and Figure 24. The MTDSC values in the total heat flow mode were selected from the experimentally designed study and compared to an ASTM DSC test.⁽⁶⁹⁾ The ASTM method calls for a heating rate of 10 °C min⁻¹. The T_g of PS at MTDSC heating rates of 2 and 5 °C min⁻¹ were compared to standard DSC heating rates of 5, 10 and 20 °C min⁻¹.

There was a small difference (0.7 and 1.0 °C, respectively) between the T_g (e) and T_g (i) for PS when examined by MTDSC at 2.0 and 5.0 °C min⁻¹. The T_g (e) found by MTDSC and DSC both at 5.0 °C min⁻¹ were 101.6 °C and

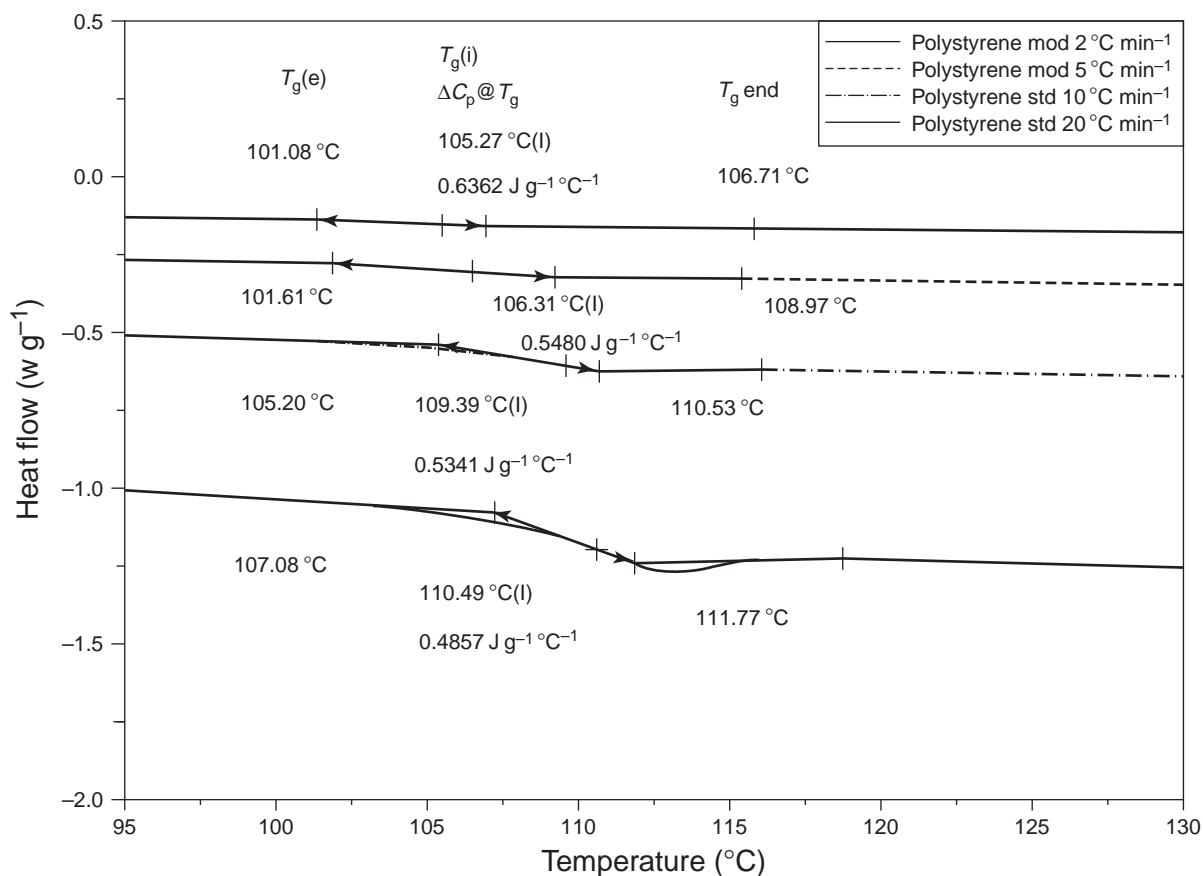


Figure 24 PS standard 900 000 MW: MTDSO plotted against standard DSC.

104.0 °C, a difference of 2.4 °C. The standard DSC $T_g(e)$ increased with increasing heating rate, 5–20 °C min⁻¹, 104.0–107.1 °C. The optimum MTDSO conditions at 2 °C min⁻¹ yields a $T_g(e)$ at 101.1 °C and the ASTM standard DSC test at 10 °C min⁻¹ had a $T_g(e)$ of 105.2 °C. Therefore, when trying to compare $T_g(e)$ or $T_g(i)$ by MTDSO to the T_g by standard DSC, a 3–4 °C difference should be expected.

The ΔC_p at T_g and ΔT at T_g values were higher for MTDSO than DSC. Based on total heat flow, PS had a ΔC_p at T_g value of 0.54 J g⁻¹ °C⁻¹ and ΔT at T_g of 5.5 °C. In the MTDSO test the ΔT at T_g for PBD and PS were <6 °C, while the copolymer SBR had a value of 12–15 °C. It appears that MTDSO can distinguish between copolymers and homopolymers. Examining a number of standard thermoplastics substantiated the observation that copolymers have a larger ΔT at T_g than homopolymers.

The MTDSO variables do not significantly affect the measurement of the glass transition temperatures of the polymers studied. The period (frequency) did affect the T_g properties of PS. Only the heat capacity change at T_g was affected by the period variation for PBD and

SBR. The MTDSO T_g (reverse heat flow mode) value is more accurate than the standard DSC T_g (total heat flow) measurement. There will be a 3–4 °C higher T_g value when measured by standard DSC compared with the MTDSO value.

2.16 Power Compensated Differential Scanning Calorimetry Experimental Procedures

Next, is a brief review of the power compensated DSC experimental procedures. The optimum experimental conditions for dynamic differential scanning calorimetry (DDSC), DSC and DTA using a Perkin Elmer DSC is 1–75 mg, depending on the sensitivity required.^(70,71) The heating rate is 0.1–100 °C min⁻¹ depending on the application. A standard heating rate is 20 °C min⁻¹. The experimental conditions for a DDSC are 5–30 mg depending on the sensitivity required. 10 mg is a good default. The repeat pattern is 30 s heat up by 2 °C, 30 s cool down by 1 °C. A wide range of other values works too, but this is a good starting point and one that leads to specific heats within a few percent without any special calibration. A power compensated DSC is

Table 4 Fundamental characteristics of the PS glass transition temperature by MTDSC

Factorial design run order in MTDSC	Experimental variables			Amplitude (+/- °C)	Measured properties (reversed heat)				
	Standard order	Heating rate	Frequency × 10 ³ s ⁻¹ (period, s)		T _g (e) (°C)	T _g (i) (°C)	ΔC _p @ T _g (J g ⁻¹ °C ⁻¹)	ΔT@ T _g (°C)	
3 (optimum)	1	2	17(60)	0.318	106.1	108.1	0.34	4.5	
	1				103.5	107.7	0.29	5.8	
	1				105.6	108.0	0.32	4.2	
5	2	5	17(60)	0.318	<i>105.1</i>	<i>107.9</i>	<i>0.32</i>	<i>4.8</i>	ave
	2				104.0	108.0	0.36	6.0	
	2				103.5	107.8	0.38	6.4	
2	3	2	40(25)	0.318	<i>103.8</i>	<i>107.9</i>	<i>0.37</i>	<i>6.2</i>	ave
	3				106.5	107.6	0.24	5.5	
	3				106.8	107.6	0.23	4.2	
1	4	5	40(25)	0.318	<i>106.7</i>	<i>107.6</i>	<i>0.24</i>	<i>4.9</i>	ave
	4				108.4	110.0	0.15	2.5	
	4				108.9	110.1	0.13	2.0	
8	5	2	17(60)	0.796	108.2	110.1	0.19	3.3	
	5				<i>108.5</i>	<i>110.1</i>	<i>0.16</i>	<i>2.6</i>	
	5				104.9	108.5	0.38	5.7	
6 (optimum)	6	5	17(60)	0.796	105.2	108.0	0.38	5.7	
	6				<i>105.1</i>	<i>108.3</i>	<i>0.38</i>	<i>5.7</i>	
	6				105.7	108.4	0.35	5.8	
4	7	2	40(25)	0.796	105.1	109.0	0.37	6.0	
	7				<i>105.4</i>	<i>108.7</i>	<i>0.36</i>	<i>5.9</i>	
	7				106.6	110.0	0.25	5.6	
7	8	5	40(25)	0.796	106.1	110.0	0.28	6.4	
	8				<i>106.4</i>	<i>110.0</i>	<i>0.27</i>	<i>6.0</i>	
	8				107.2	110.0	0.24	5.1	
					107.3	110.1	0.25	5.3	
					<i>107.3</i>	<i>110.1</i>	<i>0.25</i>	<i>5.2</i>	ave
average (C)					<i>106.0</i>	<i>108.8</i>	<i>0.29</i>	<i>5.0</i>	
standard deviation +/-					sigma	1.5	1.0	0.08	1.3
2 × standard deviation +/-					2 × sigma	3.0	2.0	0.19	2.6
% standard deviation +/-						1.5	0.9	27.5	25.0

Table 5 Fundamental characteristics of the PS glass transition temperature by MTDSC and conventional DSC

Sample number	Ramp (°C min ⁻¹)	Method	MTDSC T _g properties				
			Measured properties (heat flow)				
			T _g (e) (°C)	T _g (i) (°C)	ΔC _p @ T _g (J g ⁻¹ °C ⁻¹)	ΔT@ T _g (°C)	
A3	2	MTDSC (heat flow)	101.1	105.3	0.64	5.6	
		MTDSC (reversed heat flow)	<i>101.1</i>	<i>105.3</i>	<i>0.64</i>	<i>5.6</i>	
A6	5	MTDSC (heat flow)	101.6	106.3	0.55	7.4	
		MTDSC (reversed heat flow)	<i>101.4</i>	<i>105.8</i>	<i>0.60</i>	<i>6.5</i>	
B	5	Standard DSC (heat flow)	104.0	107.3	0.50	4.7	
C	10	Standard DSC (heat flow)	105.2	109.4	0.53	5.3	
D	20	Standard DSC (heat flow)	107.1	110.5	0.49	4.7	
Std DSC average (C)			<i>105.4</i>	<i>109.1</i>	<i>0.51</i>	<i>4.9</i>	ave
standard deviation +/-			1.6	1.6	0.02	0.3	
% standard deviation +/-			1.5	1.5	4.1	7.1	
DSC and MTDSC average			<i>103.1</i>	<i>107.1</i>	<i>0.56</i>	<i>5.7</i>	ave
standard deviation +/-			2.4	2.1	0.06	1.0	
% standard deviation +/-			2.3	1.9	11.1	17.2	

described in Figure 25. A DDSC thermal profile is given in Figure 26.

2.17 Quantitative Differential Scanning Calorimetry and Differential Thermal Analysis

DSC and DTA are used to determine a wide range of physical properties of materials, including the glass transition temperature, melting temperature and solid–solid transition. To quantify these, transition temperatures instrument calibration is necessary with known standard materials. Therefore, calibration of DSC and DTA from -100 to 600 °C consists of heating the calibration material at a controlled rate in a controlled atmosphere through a region of known thermal transition.^(72,73) The temperature and the heat flow difference in a heat flux DSC are continuously monitored, that is, between the calibration material and a reference material. A transition is marked by the absorption of energy by the specimen resulting in an endothermic peak in the heating mode of the thermal curve.

For a two-point temperature calibration, select a pure material in the temperature range of interest, see Table 1. The DSC or DTA can be calibrated with some degree of confidence with indium and zinc and the temperature correction factor can be extrapolated 100 °C or from about 50 to 500 °C. However, in order to report transition temperatures in a journal article or in an internal communication, the temperature calibration is best when it is very close to the temperature that needs to be measured. As a minimum, two temperature standards that bracket the temperature of interest should be used.

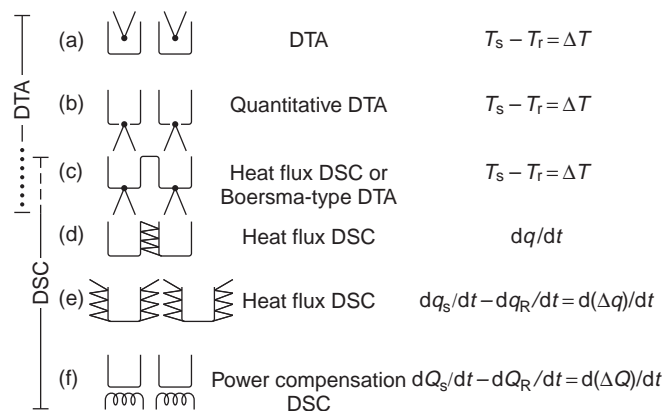


Figure 25 Comparison of DTA, power compensation DSC and heat flux DSC. S is the sample, R is the reference, T is the temperature and q is the heat.

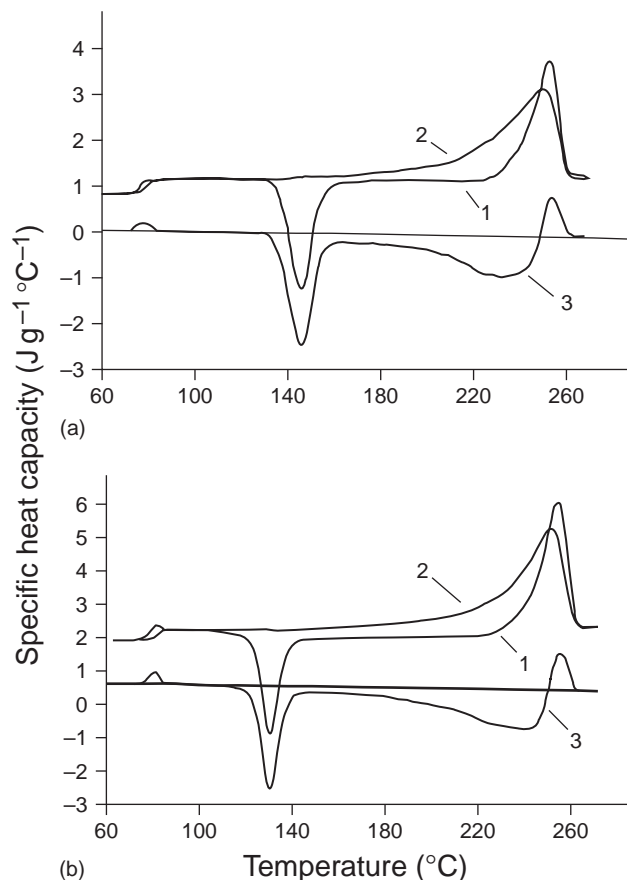


Figure 26 Measured curves of PET ($\beta_0 = 5 \text{ K min}^{-1}$, $T_a = 1 \text{ K}$, $t_p = 30 \text{ s}$). (a) Measured with a heat flux DSC. (b) Measured with a modified Perkin–Elmer DSC-7. Calculated from: 1, the underlying heat flow; 2, reversing component; 3, nonreversing component.

2.18 Low-temperature Quantitative Analysis

Low-temperature calibration with mercury is valid. However, mercury is toxic and most researchers prefer to use the melting temperature of spectroscopic grade organic chemicals, for example, octane, -58 °C, decane, -30 °C or dodecane at -10 °C.

DSC specimen containers are typically solvent cleaned aluminum or alumina pans. The pans can also be crimped with a lid or hermetically sealed to preserve the standard material. DTA specimen containers are typically thin walled glass capillaries with a flat bottom. Specimen containers must not react with a standard or sample material or melt in the temperature range of interest. Purge gases, like nitrogen or helium, are used at a flow rate of ca. 50 mL min^{-1} . The mass of the standard is measured to the nearest 0.1 mg . The melting temperatures of calibration materials are given in Table 1. The most common melting temperature standards are indium at 156.6 °C, tin at 231.9 °C and zinc at 419.5 °C.

Table 6 Sapphire specific heat capacity literature values^{a,b}

Temperature (°C)	(K)	Specific heat (J g ⁻¹ °C ⁻¹)	Temperature (°C)	(K)	Specific heat (J g ⁻¹ °C ⁻¹)
-183.15	90	0.0949	296.85	570	1.0876
-173.15	100	0.1261	306.85	580	1.0932
-163.15	110	0.1603	316.85	590	1.0987
-153.15	120	0.1968	326.85	600	1.1038
-143.15	130	0.2349	336.85	610	1.1089
-133.15	140	0.2739	346.85	620	1.1137
-123.15	150	0.3134	356.85	630	1.1183
-113.15	170	0.3526	366.85	640	1.1228
-103.15	170	0.3913	376.85	650	1.1271
-93.15	180	0.4291	386.85	660	1.1313
-83.15	190	0.4659	396.85	670	1.1353
-73.15	200	0.5014	406.85	680	1.1393
-63.15	210	0.5356	416.85	690	1.1431
-53.15	220	0.5684	426.85	700	1.1467
-43.15	230	0.5996	446.85	720	1.1538
-33.15	240	0.6294	466.85	740	1.1604
-23.15	250	0.6579	486.85	760	1.1667
-13.15	260	0.6848	506.85	780	1.1726
-3.15	270	0.7103	526.85	800	1.1783
0.00	273.15	0.7180	546.85	820	1.1837
6.85	280	0.7343	566.85	840	1.1888
16.85	290	0.7572	586.85	860	1.1937
26.85	300	0.7788	606.85	880	1.1985
36.85	310	0.7994	626.85	900	1.2030
46.85	320	0.8188	646.85	920	1.2074
56.85	330	0.8373	666.85	940	1.2117
66.85	340	0.8548	686.85	960	1.2159
76.85	350	0.8713	706.85	980	1.2198
86.85	360	0.8871	726.85	1000	1.2237
96.85	370	0.9020	746.85	1020	1.2275
106.85	380	0.9161	766.85	1040	1.2312
116.85	390	0.9296	786.85	1060	1.2348
126.85	400	0.9423	806.85	1080	1.2383
136.85	410	0.9545	826.85	1100	1.2417
146.85	420	0.9660	846.85	1120	1.2451
156.85	430	0.9770	866.85	1140	1.2484
166.85	440	0.9875	886.85	1160	1.2516
176.85	450	0.9975	906.85	1180	1.2548
186.85	460	1.0070	926.85	1200	1.2578
196.85	470	1.0161	976.85	1250	1.2653
206.85	480	1.0247	1026.85	1300	1.2724
216.85	490	1.0330	1076.85	1350	1.2792
226.85	500	1.0409	1126.85	1400	1.2856
236.85	510	1.0484	1176.85	1450	1.2917
246.85	520	1.0557	1226.85	1500	1.2975
256.85	530	1.0627	1276.85	1550	1.3028
266.85	540	1.0692	1326.85	1600	1.3079
276.85	550	1.0756	1376.85	1650	1.3128
286.85	560	1.0817			

Source: D.A. Ditmars et al., *Res. Natl. Bur. Stand.*, **87**(2), 159–163 (1982).

^a Specific heat capacity measurements by DSC require the use of a well-characterized reference material (usually sapphire) to obtain results. This table summarizes specific heat capacity data (literature values) for sapphire as a function of temperature. These values can be used in the required calculations.

^b The values in the table were determined by Ginnings and Furukawa of the National Bureau of Standards on aluminum oxide in the form of synthetic sapphire (corundum). The sapphire pieces passed a #10 sieve but were retained by a #40 sieve, and had 99.98–99.99% purity by weight. Heat capacity values below the experimental range were obtained by extrapolation of the Debye equation fitted to the experimental value at the lowest temperature. The units (J g⁻¹ mol⁻¹) are absolute joules per degree per gram mole (molecular weight, 101.9613) at a constant pressure of 1 atm (100 Pa).

For a comprehensive list of available standards, see Table 1.

2.19 Specific Heat Capacity by Differential Scanning Calorimetry and Modulated Temperature Differential Scanning Calorimetry

There is an ASTM method, E-1269-95, that covers the determination of specific heat capacity, C_p , by conventional DSC.⁽⁷⁴⁾ It is applicable to thermally stable solids and liquids. The normal operating range of the test is from -100 to 600 °C. The total DSC heat flow of an empty sample and reference pan is measured. The C_p is determined from the empty pan heat flow profile and the sample heat profile from the thermal curve. Subtraction of these two thermal curves, sample minus the empty pan, will give C_p as a function of temperature. A sapphire standard is used as the calibrant. It is best to evaluate the multiple heat flow responses to sapphire, in order to determine the precision and accuracy of this method, see Table 6.

Measurements of the C_p by the MTDSC method are direct; that is, the specific heat varies linearly over the desired temperature range.^(75,76) When determining C_p by MTDSC, calibrate the cell with sapphire every 10 °C and correct the reversing heat flow output (the calorimetric portion of the total heat flow). A high-molecular weight NIST PS standard is used to verify the sapphire calibration. The repeatability of the C_p measurement is 2–5% of the value at a specific temperature.

3 APPLICATIONS

Some of the DSC and DTA applications reviewed are based on physical and chemical properties of materials. Melting temperature and heat of fusion, crystallization temperature and heat of crystallization, specific heat capacity of polymers, and curing will be included.

3.1 Alkane Structure–Property Relationships by Differential Scanning Calorimetry, Thermal Microscopy and X-ray Diffraction Analysis

DSC and thermal microscopy helped define a commercial product composed of normal alkanes that was involved in a major law suit.⁽⁷⁷⁾ The solid-state structures of a number of alkanes have unique crystal structures. These alkanes melt and crystallize below room temperature at more than 60 °C below zero, see Figures 27 and 28. Mixtures of specific alkanes have attributes of pure chemicals, the X-ray diffraction structure (XDS) was very similar,

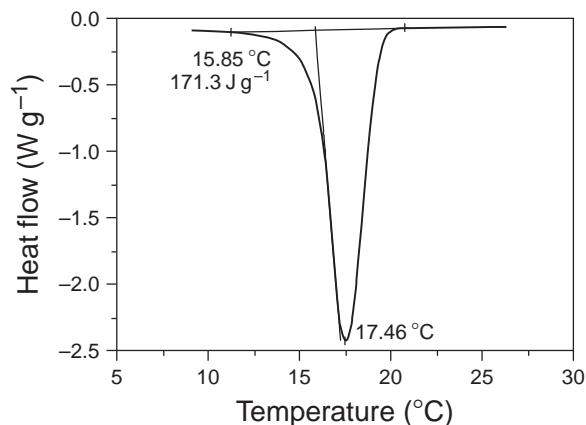


Figure 27 DSC of hexadecane at low temperatures, 2 °C min^{-1} .

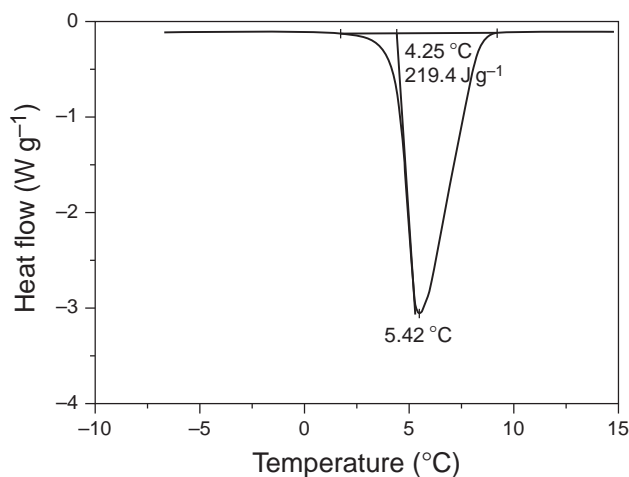


Figure 28 DSC of tetradecane at low temperatures, 2 °C min^{-1} .

but the melting and crystallization temperatures were statistically different from those expected, see Table 7. The XDS, Miller Index d (002) of a number of even carbon number normal alkanes was linearly related to the corresponding melting and crystallization temperatures, see Figure 29.

3.2 Oxidative Behavior of Materials by Standard and Pressure Differential Scanning Calorimetry: Polymers and Engine Oils

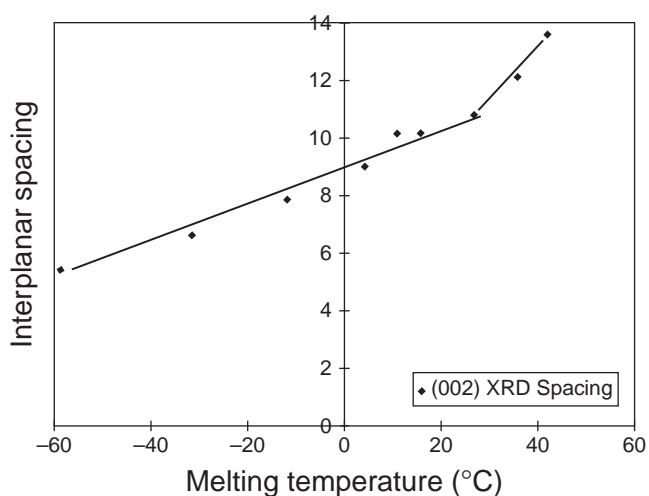
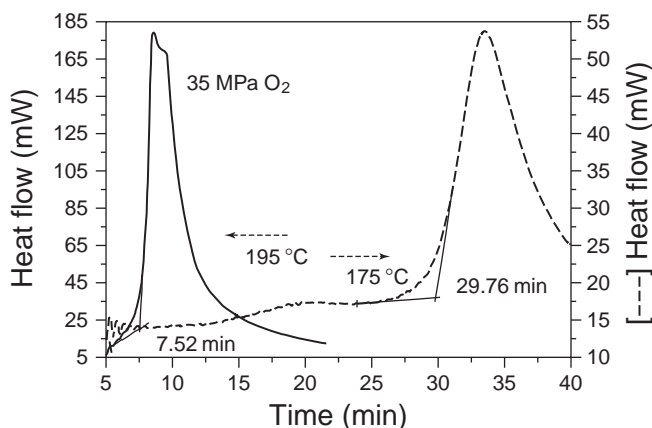
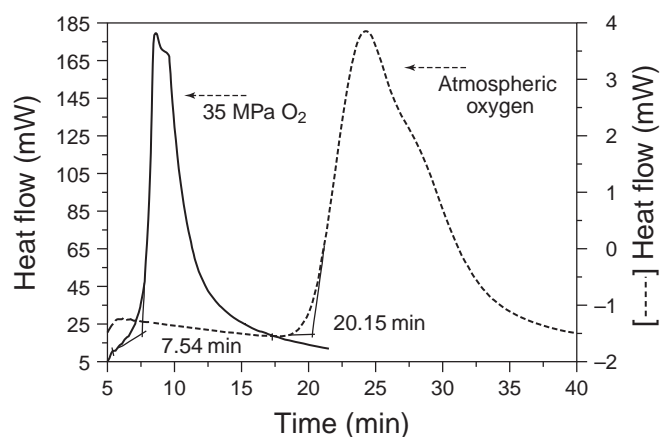
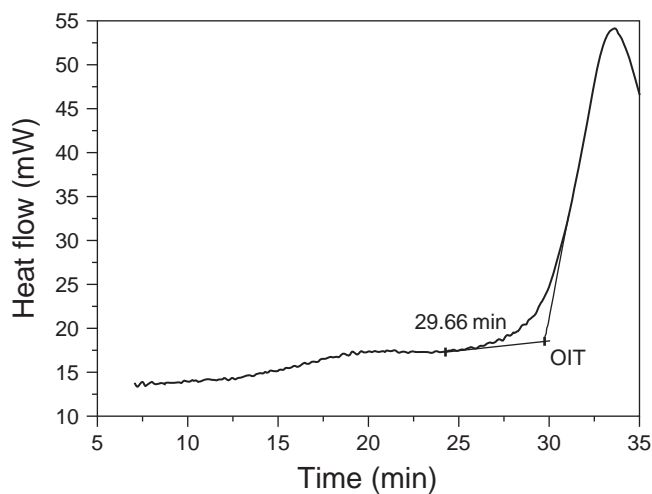
Fundamental knowledge of the oxidative properties of commercial oils is necessary to predict the stability of these fluids. A primary tool to determine the oxidation of fully formulated motor oils, greases, diesel oils, transmission fluids and vegetable oils is DSC and PDSC.⁽⁶⁰⁾ A diluted motor oil was used to establish experimentally designed relationships between the DSC variables and the OIT,

Table 7 Melt and crystallization properties of *n*-alkanes by DSC

Normal alkanes		Temperature (°C)			Heat of transition (J g ⁻¹)		
		<i>T</i> _m	<i>T</i> _n	<i>T</i> _m (lit)	Δ <i>H</i> _m	Δ <i>H</i> _c	Δ <i>H</i> _m ^a
1. Octane	C ₈ H ₁₈	-59	-59	-56	176	181	
2. Decane	C ₁₀ H ₂₂	-32	-33	-32	177	177	
3. Dodecane	C ₁₂ H ₂₆	-12	-13	-12, -10	182	188	
4. Tetradecane	C ₁₄ H ₃₀	4.2	4.3	5.5	220	221	
5. Mixture	C ₁₄ -C ₁₆ (10:90)w	11	11	17 ^a	180	178	178 ^a
6. Hexadecane	C ₁₆ H ₃₄	16	16	18, 16	174	172	
7. Octadecane	C ₁₈ H ₃₈	27	27	28	177	175	
8. Eicosane	C ₂₀ H ₄₂	36	36	38	199	201	
9. Docosane	C ₂₂ H ₄₆	42	43	43	196	197	

^a Calculated value based on property additivity of C₁₄H₃₀ and C₁₆H₃₄.

*T*_m = melt temperature based ASTM E794-97; *T*_n = nucleation/crystallization temperature based on ASTM E794-97; Δ*H*_m = heat of fusion; Δ*H*_c = heat of crystallization; lit = literature values.

**Figure 29** XRD interplanar distance ♦ (002) plotted versus DSC melt temperature.**Figure 30** OIT at constant pressure and variable temperature.**Figure 31** OIT at constant temperature and variable pressure.**Figure 32** OIT by PDSC.

ASTM E-1858, by PDSC and DSC, see Figure 4 and Figures 30–32.

The variables used to develop this protocol were temperature, pressure, heating rate, sample mass, gas flow

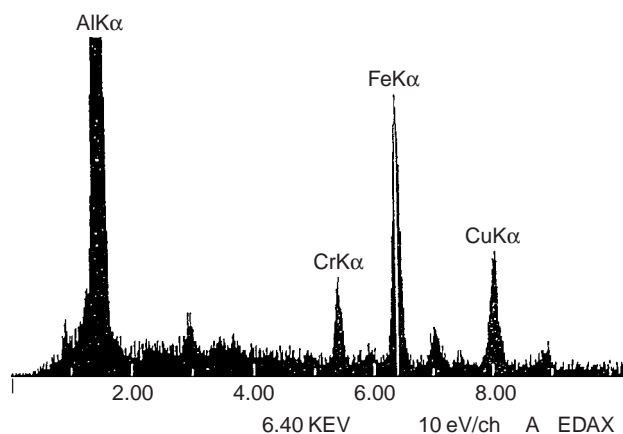


Figure 33 SEM–EDS (Energy Dispersive Spectroscopy) of aluminum pan with Fe.

rate, and gas type, air or oxygen. The DSC pan metallurgy played a statistically significant role in the measured OIT. Quality control charting of the DSC oxidation process discovered an out-of-control problem that was related to the impurities in the aluminum pans, see Figure 33 and Table 8. Iron impurities caused a decrease in the OIT of the reference fluid, while the presence of chromium stabilized the oxidation process. A costly engine test can be predicted when a new fully formulated oil blend is examined by PDSC using the OIT protocol, see Figure 34 and Table 9.

Oxidative behavior of commercial engineering plastics, polyolefins and elastomers were evaluated by DTA, TGA and PDSC.⁽⁶¹⁾ There is a good correlation between the measured stability by PDSC in oxygen (ASTM E-1858, OIT) and DTA/TGA (ASTM E-2009, OOT) in air for olefin polymers, see Figures 35–39. The thermooxidative properties of the polymers studied were reliable and precise.

3.3 Inorganic Reactor Deposits by Differential Thermal Analysis, Thermogravimetric Analysis and X-ray Diffraction Analysis

Ash deposits on heat exchange tubes were characterized by DTA, TGA and X-ray diffraction methods.⁽⁷⁸⁾ The

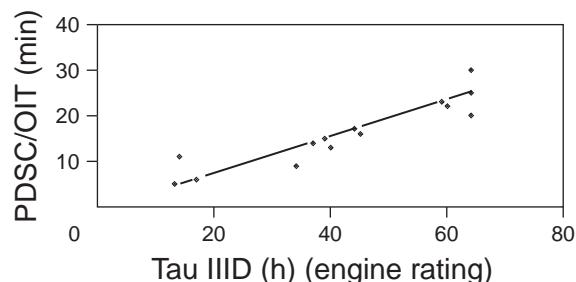


Figure 34 Engine test sequence IID Tau plotted against PDSC/OIT at 185 °C.

Table 9 Comparison of PDSC/OIT engine ratings and performance: effect of base oils with the same lubricant additive package

Base oil	PDSC/OIT (min)	OIT Predicted ^a viscosity @ 64 h	Observed sequence IID viscosity @ engine test time
A	42	Pass	Pass @ 64 h
B	35	Pass	Pass @ 64 h
C	35	Pass	Pass @ 64 h
D	36	Pass	Pass @ 56 h
E	22	Borderline fail	Fail @ 64 h
F	14	Fail	Fail @ 48 h
G	8.2	Fail	Fail @ 16 h

^a OIT predicted = PDSC at 175 °C and 35 MPa oxygen. OIT predicted viscosity = <20 min, fail; OIT predicted viscosity = 20–25 min, borderline fail; OIT predicted viscosity > 25 min, pass.

ash samples were deposited at different locations in the atmospheric fluidized bed combustor system at the TVA Shawnee Steam Plant, Paducah, KY (Figure 40). DSC aided in the identification of the endothermic and exothermic behavior of the deposits and helped develop the mechanism that promotes deposits. The major compound in the deposits from the convention pass inlet, superheater and multiclone inlet was calcium sulfate, CaSO₄. The predominant minor component was calcium oxide, CaO. The combined thermal and X-ray techniques are useful for profiling and identifying an unknown ash sample.

Table 8 Effect of pan surface metallurgy on PDSC/OIT and SEM/EDS elemental analysis

PDSC ^a	Elemental analysis					
	OIT (min)	Iron	Copper	Chromium	Fe/Cr	Ratios Fe + Cu/Cr
Poor	12	414	173	135	3.1	4.3
Fair–Poor	17	328	136	103	3.2	4.5
Good	26	315	157	235	1.3	2.1

^a PDSC = ASTM E 1858, interlab study in aluminum pans.

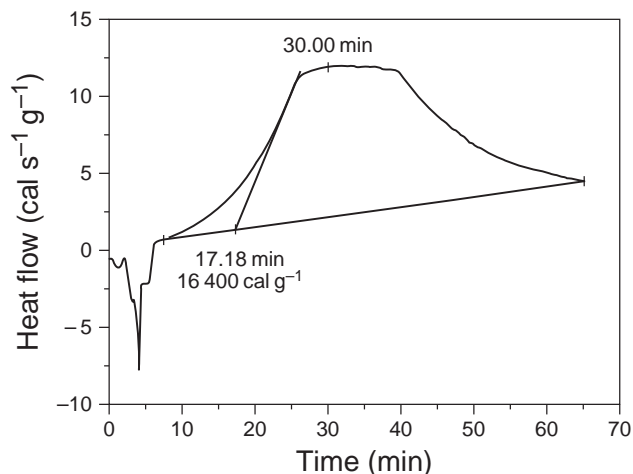


Figure 35 PDSC of low-density polyethylene (LDPE) in oxygen.

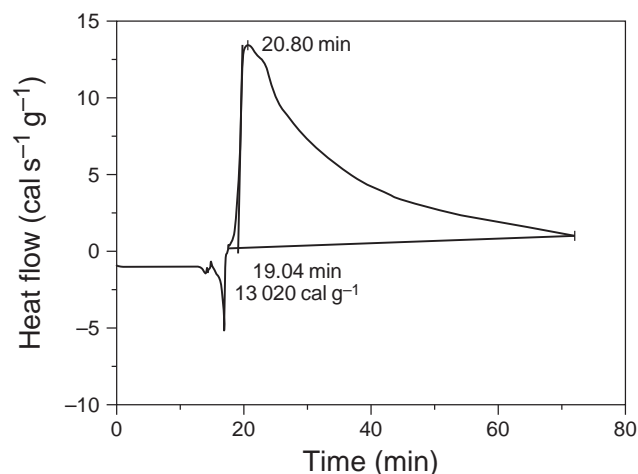


Figure 38 PDSC of PP plus CaCO₃ in oxygen.

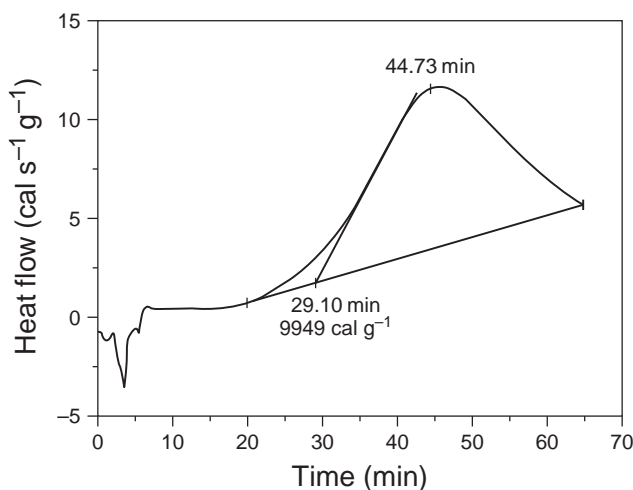


Figure 36 PDSC of polyethylene-covinyl acetate (EVA) in oxygen.

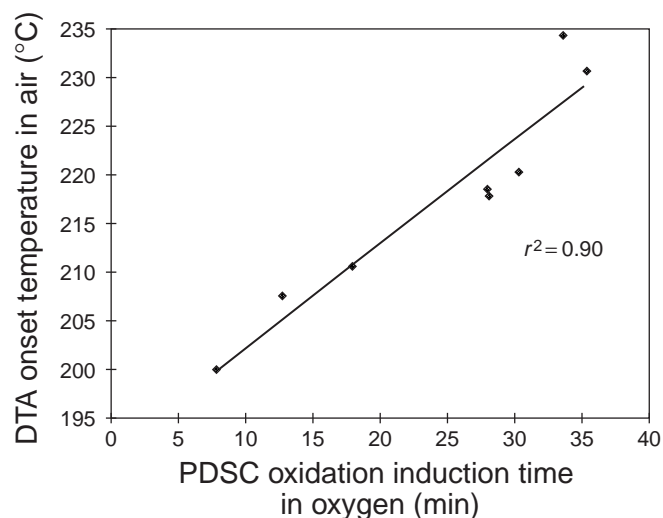


Figure 39 OOT by DTA plotted against OIT by PDSC.

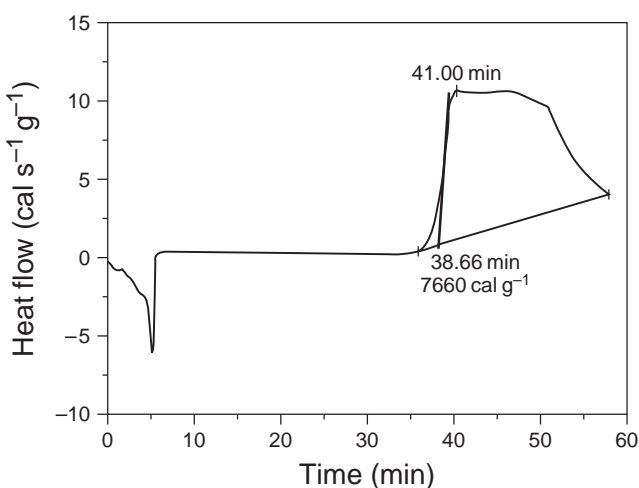


Figure 37 PDSC of polypropylene (PP) in oxygen.

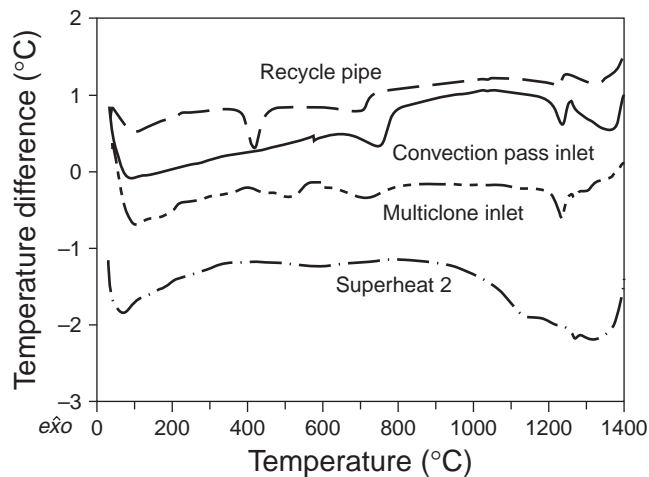


Figure 40 Comparison of DTA curves of four deposits heated to 1490 °C.

Table 10 Characterization of polymers by DSC, DTA and TMA^a

Polymer	RK#	Transition temperature (°C)					COE
		DSC Set A T_m, T_{oc}	DTA T_m, T_p	TMA			
				T_g, T_{oc}	T_i, T_{oc}	T_m, T_{oc}	
1. HDPE	25	121	123			127	120
2. MDPE	49	na	121			126	115
3. LDPE	24	91	93			99	136
4. EVA	34	84	88			87	93
5. PP	27	145	147			154	
6. PP copolymer	26	133	137			147	
7. PP + flame retardant	38	na	151			153	
8. PP + talc	44	na	152			154	
9. PP + calcite	45	na	153			154	
10. PP + mica	46	na	151			153	
11. PS-general purpose	1			90	136		54
12. PS-medium impact	2			90	140		56
13. PS-high impact	3			84	140		57
14. ABS-medium impact	6			96	142		55
15. ABS-high impact	7			92	141		52
16. SAN-copolymer	4			98	144		53
17. SB-copolymer	8			68	111		103
18. Acetal	31			42			91
19. Acetal-copolymer	32			65			80
20. Acetal-copolymer	32			64			78
21. Nylon 6	16			51			34
22. Nylon 66	15			44			30
23. Nylon 6 + glass	47			40			13

^a All data collected in 1996.

RK#, resin kit sponsored by the Society of Plastics Engineers, Inc.; Set A, resin kit, 1979; Set B, resin kit, 1994; T_g , glass transition temperature, °C; T_m , melting temperature, °C; T_i , transition temperature, marked change in COE, °C; COE, coefficient of linear expansion ($\text{mm mm}^{-1} \text{ } ^\circ\text{C}^{-1}$); T_{oc} , extrapolated onset temperature, °C; T_p , peak temperature, °C; na, not available. MDPE, medium-density polyethylene.

3.4 Polymer Characterization by Thermogravimetric Analysis, Differential Thermal Analysis/Differential Scanning Calorimetry, Thermomechanical Analysis, Fourier Transform Infrared and X-ray Diffraction Analysis

A diverse set of commercial polymers were characterized by TGA/DTA, DSC, thermomechanical analysis (TMA), Fourier transform infrared (FTIR) spectroscopy and

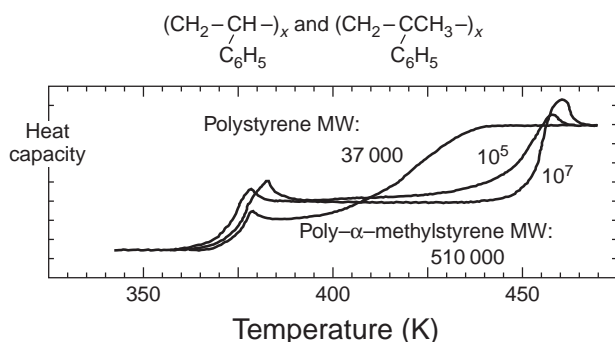


Figure 41 Change of breadth of T_g in copolymers (Wunderlich).

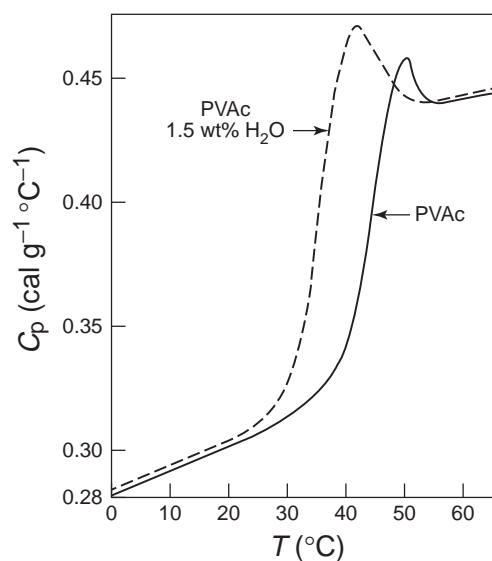


Figure 42 C_p versus T showing plasticizing effect on PVAc's T_g (Bair).

X-ray diffraction analysis.⁽⁷⁹⁾ The DSC and DTA were used to document the polymer melting temperature.

Polyolefin melt temperatures by DSC, DTA and TMA were very comparable, see Table 10.

3.5 Assignment of the Glass Transition Temperature

Assignment of the glass transition temperature was the focus of an ASTM conference and special technical publication.⁽⁸⁰⁾ R. Seyler, who was the editor and conference chairperson, lead the discussion on the T_g . His observations on DSC and DTA are summarized here: a consistently assigned T_g will vary because of differences in heating rate; composition, both chemical and physical, will cause the T_g to vary; diluent and fillers in a specimen

usually affect the T_g , moisture is particularly troublesome in T_g measurements. There were many calorimetric contributions to the assignment of the T_g of polymers.

3.6 Copolymer T_g and Molecular Weight

Wunderlich⁽⁸¹⁾ pointed out that the breadth of the T_g in copolymers varies with molecular mass, see Figure 41.

3.7 Polymer T_g and Moisture

Bair⁽⁸²⁾ demonstrated the effect of water on the T_g of polyvinyl acetate (PVAc); the T_g was lower with the addition of 1.5 wt% water, Figure 42.

3.8 Effect of High-pressure Gases on the Polymer T_g

Some representative calorimetric curves for PS and ethylene, C_2H_4 , under various pressures can be seen in Figure 43.⁽⁸³⁾

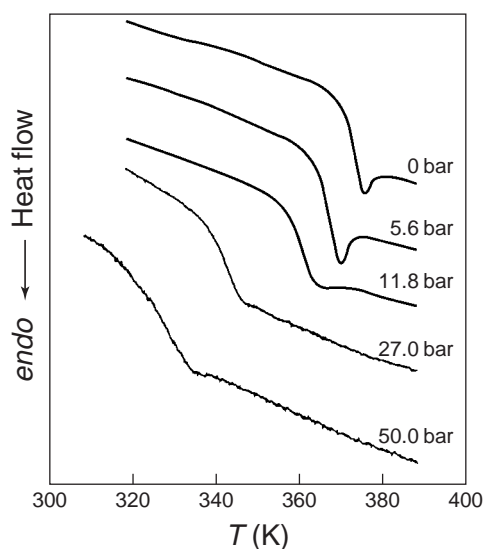


Figure 43 Some representative calorimeter outputs for PS- C_2H_4 scanned under various pressures (O'Neill).

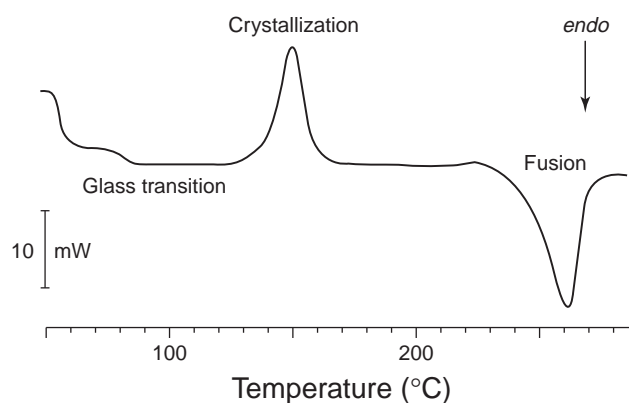


Figure 44 DSC curve of the T_g , crystallization and fusion of a PET sample quenched in liquid nitrogen (Wiedemann).

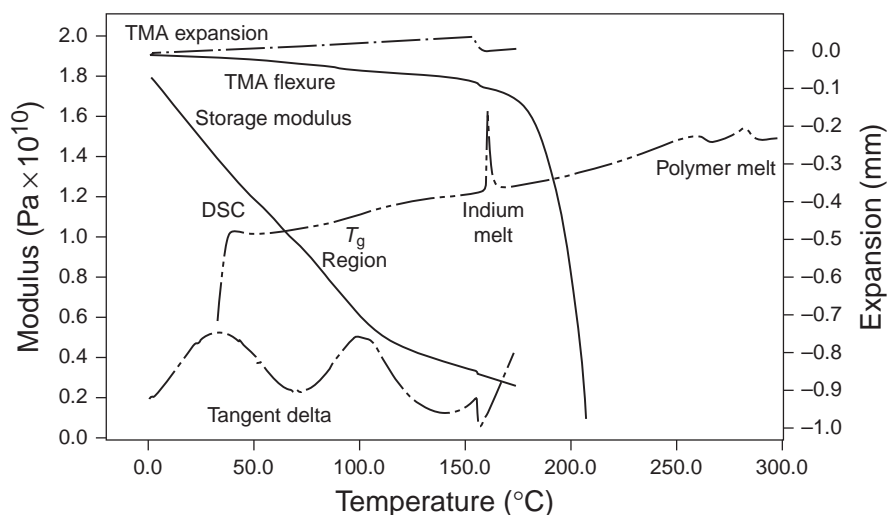


Figure 45 Thermal curves of a copolyester liquid crystal polymer, showing the use of indium as an internal standard (Cassel and Riga).

3.9 Polymer T_g , Crystallization and Fusion

Wiedemann⁽⁸⁴⁾ presented various thermal techniques in measuring the T_g in polymers, including a DSC curve of the T_g , crystallization and fusion of PET quenched in liquid nitrogen, Figure 44.

3.10 Liquid Crystal Polymer T_g and Internal Reference

Cassel and Riga⁽⁸⁵⁾ contributed a thermal curve of a copolyester liquid crystal polymer, showing the use of indium as an internal reference standard, Figure 45.

3.11 Polymer Film T_g and Thermal History

Moscato and Seyler⁽⁸⁶⁾ studied PET films oriented uniaxially without constraint: see Figure 46, first thermal cycle and second thermal cycle.

3.12 Effect of Inhibitors on Vinyl Monomer Polymerization

DSC^(87,88) has been used to study the polymerization of vinyl monomers, acrylamides and acrylates and the effect of free radical inhibitors. Selection of the optimum inhibitor and concentration was based on the exothermic autopolymerization of the monomers. The autopolymerization temperature was proportional to the concentration of a given inhibitor, for example, *para*-methoxyphenol or *t*-butyl pyrocatechol, Figure 47.

3.13 Differential Scanning Calorimetry "Fingerprint" Curve Identifies Unknown

If you have an unknown material, a polymer or an excipient and drug mixture, DSC can give you vital

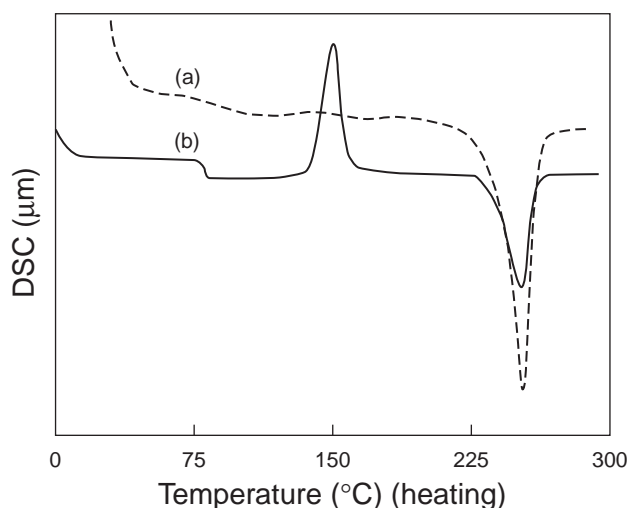


Figure 46 DSC curve of PET film oriented uniaxially with constraint (a) first thermal cycle and (b) second thermal cycle (Moscato and Seyler).

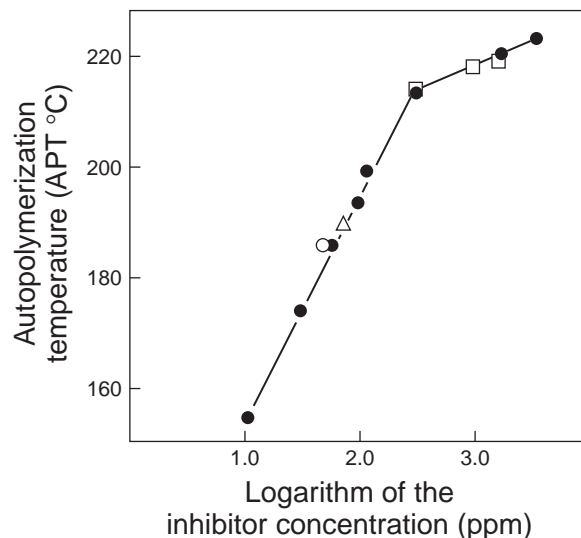


Figure 47 Effect of inhibitor concentration on the autopolymerization temperature of esters of acrylic acid. ● = isodecyl acrylate + *p*-methoxyphenol, □ = isodecyl acrylate + 2,6-di-*t*-butyl-*p*-cresol, △ = *n*-butylacrylate + *p*-methoxyphenol, ○ = 2-ethylhexylacrylate + *p*-methoxyphenol.

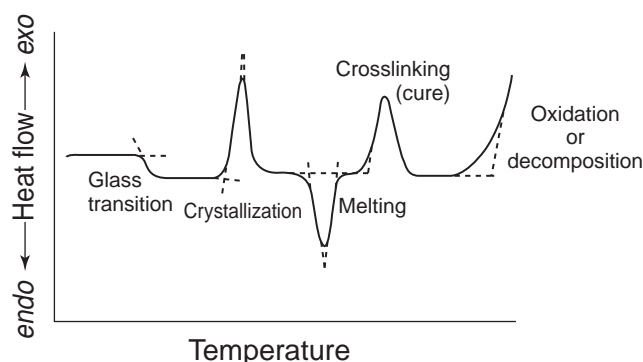


Figure 48 Schematic DSC thermal curve.

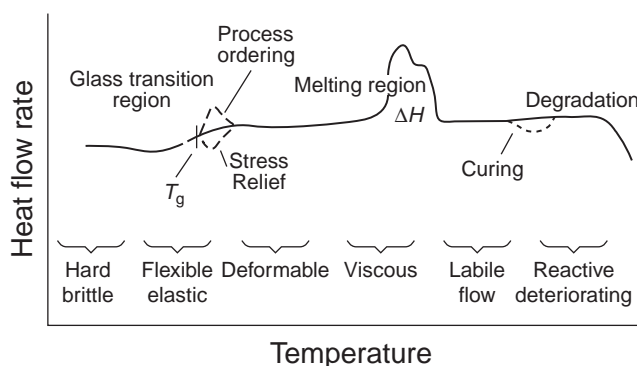


Figure 49 Polymer characterization by DSC.

physical and chemical information about it. In general, a DSC curve has many clues that will lead you on

a path to identification or a better understanding of your material. The DSC, in summary, can supply the T_g , crystallization temperature, heat of fusion and/or crystallization, crosslinking (cure) and oxidation or decomposition, Figure 48.

If you have a failed polymer, a DSC curve can reveal the T_g and melt temperatures, but can also suggest prior history of the part, Figure 49.

Endothermic process ordering or exothermic stress relief can be obtained from data surrounding the T_g . From low temperatures, below the T_g , a material is hard and brittle and above the T_g flexible and elastic. Upon further heating, the polymer is deformable, viscous and finally it reactively deteriorates or degrades. The T_g of thermoplastics, PS and PC are distinguishable from the elastomeric T_g of PBD and SBR, Figure 50. Two immiscible polymers, with a T_g difference between the two homopolymers or copolymers of greater than 10°C , have two T_g values, Figure 51.

3.14 Curing and Polymerization of Thermoset Polymers

Incomplete polymerization of an epoxy resin, thermoset polymer, can yield a lower than expected T_g , for example, 77.1°C , Figure 52. However, continued heating of the polymer reveals an exothermic polymerization at 149°C

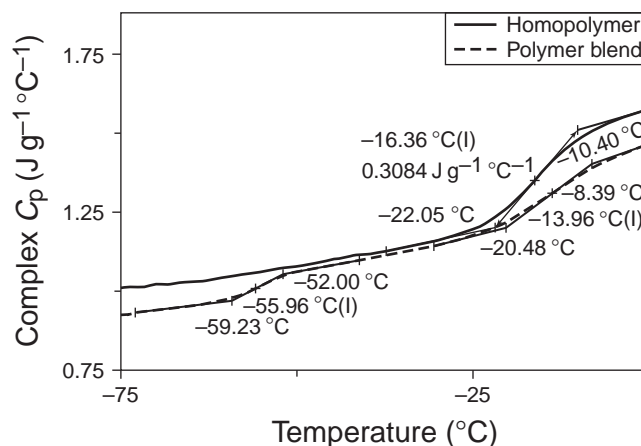


Figure 51 Immiscible polymer blend versus homopolymer by MTDSC.

with an exothermic heat of 20.4 J g^{-1} . Upon cooling and reheating the epoxy had a higher T_g at 110.5°C .⁽⁸⁹⁾ The glass transition temperature of another thermoset polymer varied with cure time and temperature, Figure 53. It is obvious from the plot that the polymer is cured in 20–40 min (plateau in the T_g versus cure time curve) at 175°C , and does not reach cure even at 70 min at 140°C .

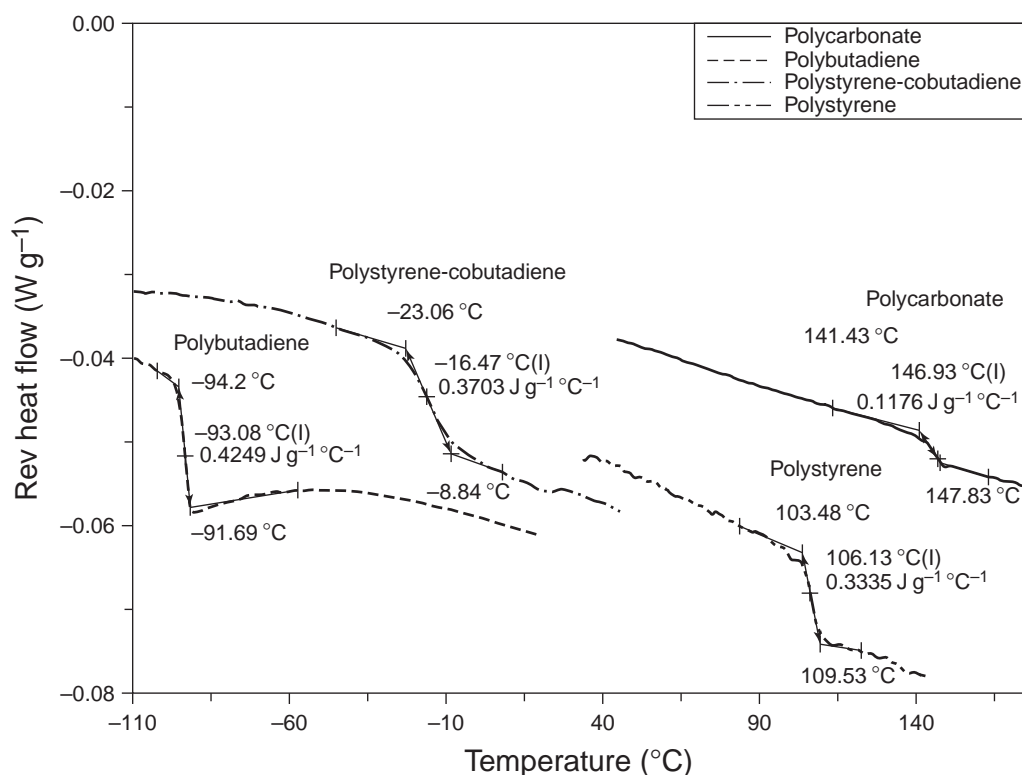


Figure 50 Polymer glass transition temperature by MTDSC.

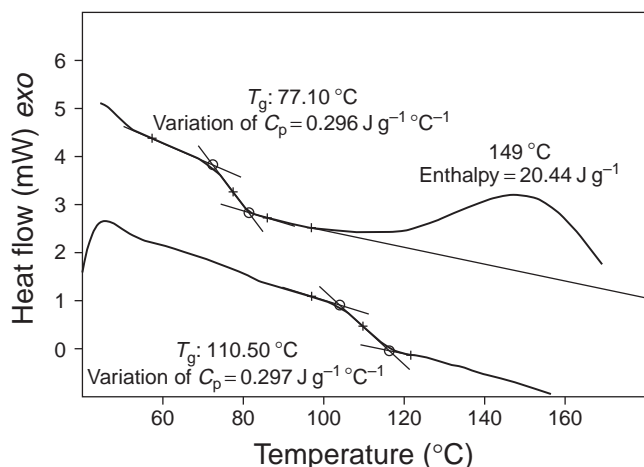


Figure 52 T_g and polymerization of an epoxy resin.

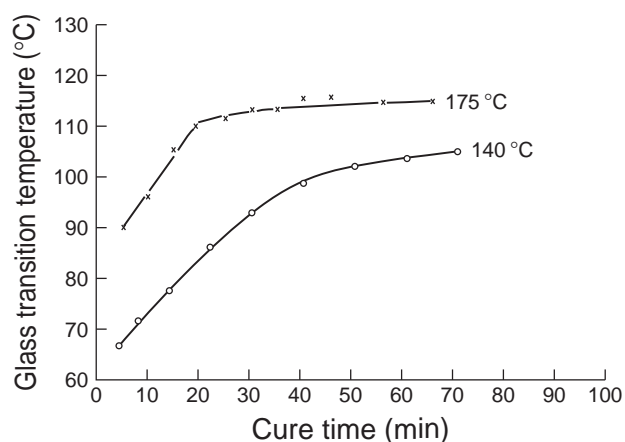


Figure 53 Variation of glass transition temperature with cure time and temperature.

3.15 Polymer Fabrics Identified by Differential Scanning Calorimetry

Hall and Cassel⁽⁹⁰⁾ identified fabric material by DSC. Rayon, cotton and wool underwent dehydration and degradation reactions at different temperatures. The DSC “fingerprint” curves clearly distinguished a polyester, polyester–cotton blend and cotton, Figure 54.

3.16 Pharmaceutical Applications: Purity, Polymorphism, Excipients and Lubrication

The DSC is also a problem-solving tool in pharmaceutical applications.⁽⁸⁹⁾ First, the purity of $C_9H_9BrO_3$ is determined from the melting peak and software using the Van’t Hoft melting depression equation. This chemical was found to be 99.43% pure, heat of fusion was $90.9 J g^{-1}$ and the melting temperature was $114.8 ^\circ C$, Figure 55. ASTM E-0928 is the standard test method for mole percent impurity by DSC.⁽⁹¹⁾ This protocol which is based

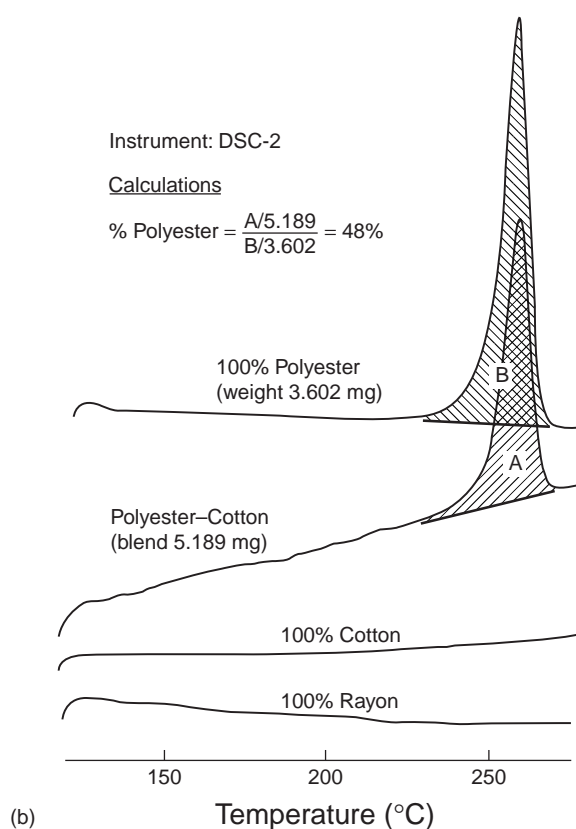
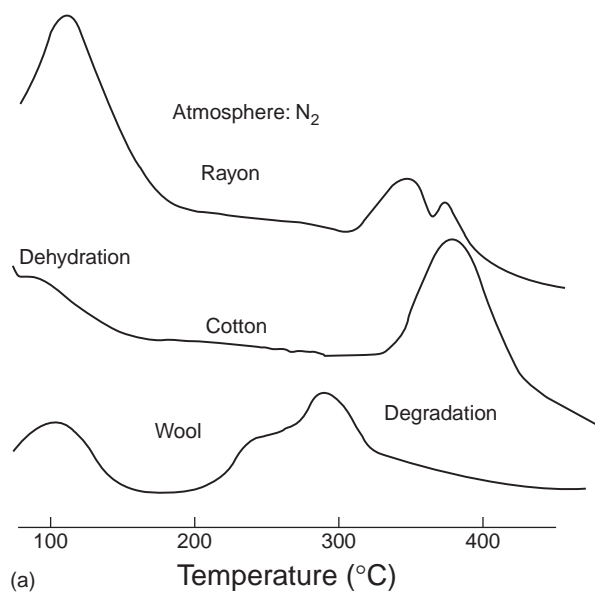


Figure 54 Identification of (a) fabric materials by DSC and (b) blend samples. (After Cassell and Hall.⁽⁸⁷⁾)

on the melting temperature range of a compound, broadens as the impurity level rises. Results obtained from this method include sample purity (in mol%), enthalpy of fusion (in $J mol^{-1}$) and the melting temperature (in Kelvin) of the pure form of the major component. The

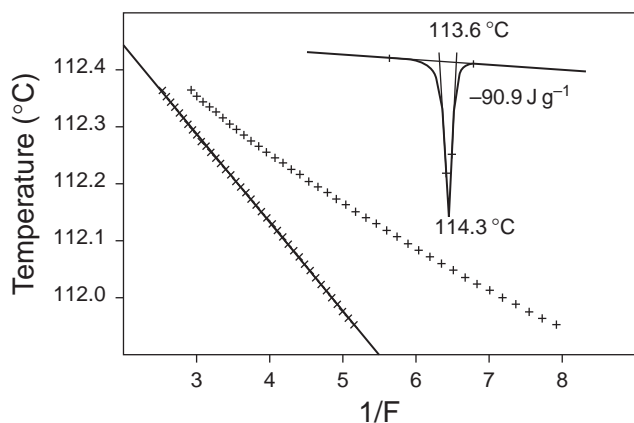


Figure 55 Determination of purity of $C_9H_9BrO_3$.

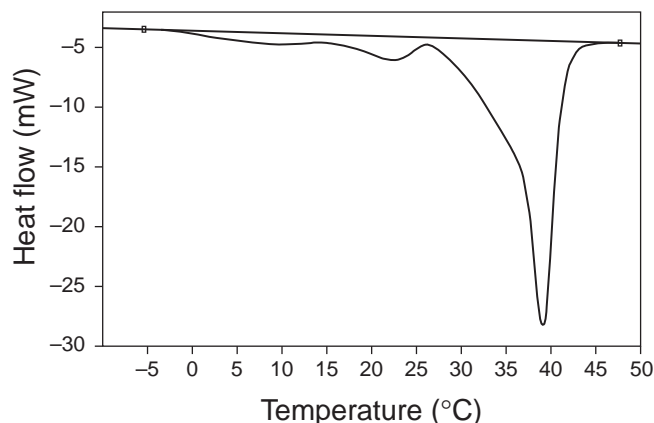


Figure 57 Melting of suppository excipient.

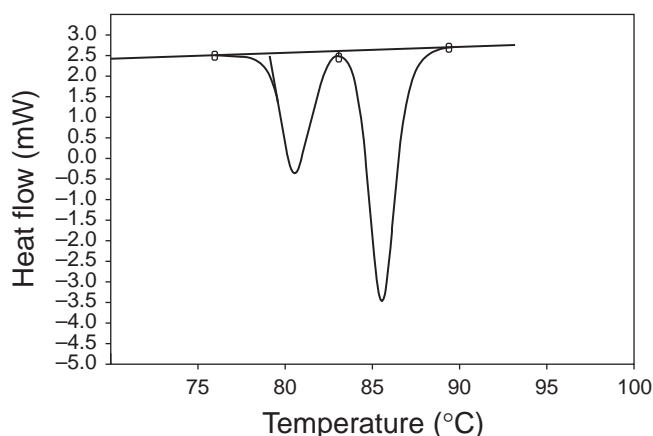


Figure 56 DSC separation of pharmaceutical polymorphs.

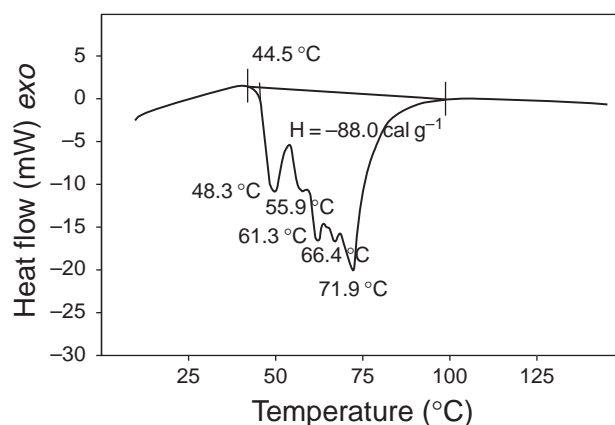


Figure 58 DSC analysis of pharmaceutical lubricants.

single instrument repeatability of purity at a 95% confidence level is that two results should be considered suspect if they differ by more than 0.19 mol%. The multiple instrument reproducibility at a 95% confidence level is that two averages should be considered suspect if they differ by more than 0.72 mol%.

Another pharmaceutical DSC application is the separation of polymorphs.⁽⁸⁹⁾ A 4.8-mg sample was heated at 2°C min^{-1} from room temperature to 100°C . Two endothermic peaks are seen at 80°C and 85°C corresponding to the transition of each polymorph. The enthalpy of polymorph 1 is 141.0 J g^{-1} and polymorph 2 is 78.2 J g^{-1} , Figure 56. The approximate composition of the mixture is 64% polymorph 1 and 36% polymorph 2. The actual composition was 52% polymorph 1.

The melting of a pharmaceutical suppository excipient (42.3 mg) was measured from -20 to 55°C at 2°C min^{-1} .⁽⁸⁹⁾ The thermal curve shows a very broad endothermic peak of melting from 0 to 45°C . The multiple peaks are due to the melting of the different fatty

compounds in the composition of the suppository excipient, see Figure 57.

DSC analysis of a pharmaceutical lubricant is seen in Figure 58. The sample, Sterotex, with a mass of 7.40 mg was heated from ambient to 150°C at $10^\circ\text{C min}^{-1}$. A broad endothermic peak occurred from 44 to 100°C with an enthalpy of fusion of 88 cal g^{-1} . Superimposed on the broad peak were five additional peaks corresponding to at least five melting phenomena. The melting peaks at 48, 56, 61, 66, and 72°C correspond to melting of different fatty compounds in the lubricant. If the components were paraffin in nature then the melt temperatures correspond to compounds with greater than 30 carbon atoms or a molecular mass of about 400 g mol^{-1} .

3.17 Food Application: Cocoa Butter

A food application of DSC is the melting analysis of cocoa butter, Figure 59.⁽⁸⁹⁾ An 11.1-mg sample was first heated to 50°C at $10^\circ\text{C min}^{-1}$, then cooled to -10°C at 5°C min^{-1} and finally heated to 60°C at 5°C min^{-1} . This DSC scheme of heating-cooling and reheating

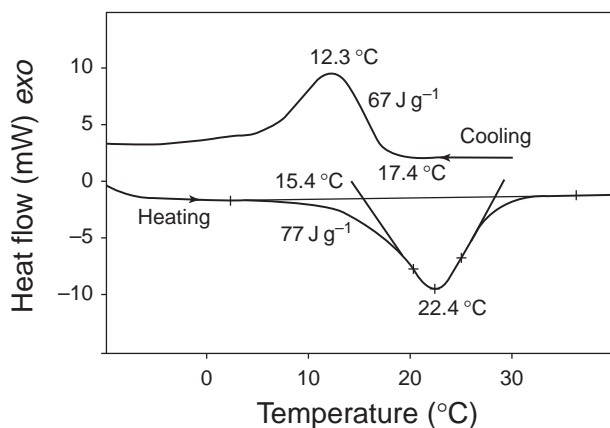


Figure 59 Analysis of cocoa butter by DSC.

was to impart a known thermal history to the cocoa butter. The cooling experiment shows an exotherm of crystallization, 67 J g^{-1} at $17.4\text{--}12.3^\circ\text{C}$. The final heating cycle had a melt range of $15.4\text{--}22.4^\circ\text{C}$ with a 77 J g^{-1} heat of fusion. The cocoa butter slightly supercooled based on different melt and crystallization temperatures. The melting crystallization is almost reversible with the heats of crystallization and fusion being 67 and 77 J g^{-1} , respectively. Melting and crystallization heats and temperatures have been observed to be the same, approaching equilibrium values, when the ramp rate is $\cong 1.0\text{--}2.0^\circ\text{C min}^{-1}$.⁽⁷⁷⁾

3.18 Biochemical Application: Ribonuclease

A biochemical use of DSC is the denaturation of ribonuclease, Figure 60.⁽⁸⁾ The sample is ribonuclease A from bovine pancreas. A solution of 2% of the ribonuclease is prepared in 0.2 mol L^{-1} of glycine and 0.2 mol L^{-1} of NaCl. The sample mass is 17.7 mg and scanned at $0.3^\circ\text{C min}^{-1}$ from 25 to 95°C . The

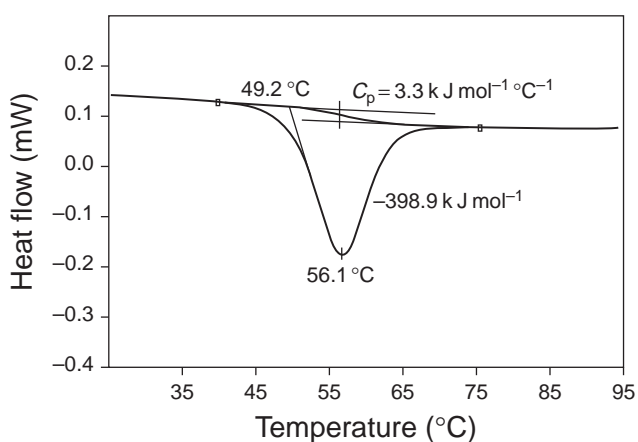


Figure 60 Denaturation of ribonuclease.

endothermic denaturation starts at 49.2°C with a peak maximum at 56.1°C and an enthalpy of reaction of 389 kJ mol^{-1} . The specific heat capacity variation measured before and after the denaturation is $3.3 \text{ kJ mol}^{-1} \text{ }^\circ\text{C}^{-1}$.

3.19 Hazardous Material: Aromatic Nitro Compound

Decomposition of an aromatic nitro compound is easily detected by a DSC curve, Figure 61.⁽⁸⁹⁾ A stainless steel container was used with a 5.4-mg sample. The ramp rate was $2.0^\circ\text{C min}^{-1}$ from ambient to 330°C . The nitro compound melts below 50°C and exothermically decomposes from 200 to 273°C . The kinetics of decomposition can be estimated when the ramp rate is varied. An ASTM test method, E-0698 can be used to determine Arrhenius kinetic constants for thermally unstable materials by DSC or DTA.⁽⁹²⁾ The Arrhenius parameters combined with the general rate law and the exothermic heat of reaction can be used for the determination of thermal explosion hazards. The accuracy of the kinetic constants is checked by an isothermal aging procedure. A difference of less than 10% relative between predicted and observed results, can be considered a reasonable test of accuracy.

3.20 Characterization of Inorganic Compounds

The dehydration of calcium sulfate hydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ can be resolved by DSC, Figure 62.⁽⁸⁹⁾ A 34.7-mg sample is heated in a closed pan and lid system. The sample is heated at 5°C min^{-1} from ambient to 250°C . The dehydration occurs in two steps. In the first step $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$, hemihydrate is formed with the loss of 1.5 mol of H_2O . In the second step, CaSO_4 , anhydrite is formed with the loss of $1/2 \text{ mol}$ of H_2O . TGA of mass loss as a function of temperature or time, can further study this application.

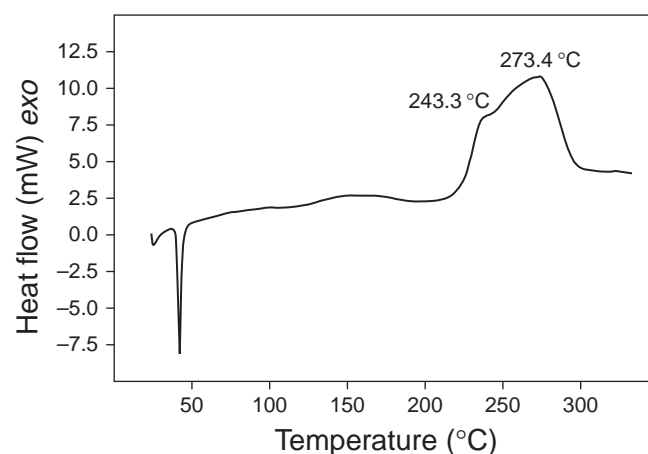


Figure 61 Decomposition of an aromatic nitro compound.

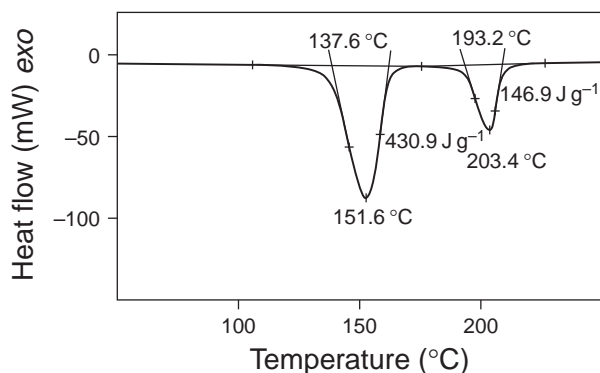


Figure 62 Dehydration of calcium sulfate dihydrate by DSC.

4 SUMMARY

DSC and DTA are invaluable research, quality control and performance measuring tools. It is easy to run a DSC or DTA experiment and interpretation is usually straightforward. There is an increase in the use of thermal analytical instruments in undergraduate and graduate college and university laboratories. This will result, eventually, in an increased use of DSC, MTDSC and DTA in industrial applications.

5 RESOURCES

The North American Thermal Analysis Society and the International Congress on Thermal Analysis and Calorimetry are resources for scientists seeking a high level of understanding and use of the many thermal analysis methods. ASTM Committee E-37 on Thermal Measurements is the source of standardized thermal analysis procedures, as well as new method development.

6 AMERICAN SOCIETY FOR TESTING AND MATERIALS METHODS USED IN DIFFERENTIAL SCANNING CALORIMETRY AND DIFFERENTIAL THERMAL ANALYSIS

- **D-3417**, 08.02, Standard Test Method for Enthalpies of Fusion and Crystallization of Polymers by DSC – This test method covers the determination of heat of fusion and heat of crystallization of polymers by DSC. It is applicable to polymers in granular form or to any fabricated shape from which appropriate specimens can be cut. The normal operating temperature range is from the cryogenic region to 600 °C.

- **D-3418**, 08.02, Standard Test Method for Transition Temperatures of Polymers by Thermal Analysis – This test method covers determination of transition temperatures of polymers by DTA and DSC. First-order transition temperatures or melting points of semicrystalline polymers may also be determined or approximated by the procedures found in D-2117 and D-789. The normal operating temperature range is from cryogenic region to 600 °C.
- **D-4591**, 08.03, Test for Temperatures and Heats of Transitions by DSC (fluoropolymers) – This test method defines conditions for the use of DSC with fluoropolymers: polytetrafluoroethylene, polyvinylidene difluoride, PCTFE and PVF and their copolymers. This test method is applicable to the analysis of powders as well as samples taken from semifinished or finished products.
- **D-5028**, 08.03, Test for Curing Properties of Pultrusion Resins by DSC – This test method covers determinations of curing parameters of pultrusion resins by DSC. The normal operating temperature range is from 0 to 200 °C.
- **D-3895**, 08.02, Test for OIT of Polymeric Materials by DSC – This test method outlines a procedure for the determination of the OIT of polymeric materials by DSC. It is applicable to polyolefin resins that are in a fully stabilized/compounded form.
- **D-4816**, 05.03, Test for Specific Heat Capacity of Aircraft Turbine Lubricants by DSC.
- **D-5483**, 05.03, Test for OIT of Lubricating Greases by PDSC.
- **D-4419**, 05.02, Test for Transition Temperatures of Petroleum Waxes by DSC.
- **E-0472**, 14.02, Standard Practice of Reporting Thermoanalytical – This practice is for general use in reporting experimental information from DTA, TGA, evolved gas analysis or detection and TMA studies. It incorporates laboratory practice with some of the specific needs in thermal analysis. These specific needs account for possible variations of the observed curve with the several parameters reported. Without changing the observed data, reporting in full the conditions under which the data were taken will enable another worker to reconcile differences that may be apparent in another study.

Accompanying each TMA record should be: identification of substances, a statement of source of all substances, a statement of the temperature environment of the sample, identification of the sample atmosphere, statement of geometry, dimensions and materials of sample holder and identification of the abscissa scale in terms of time or temperature.

- **E-0473-94**, 14.02, Standard Definitions of Terms Relating to Thermal Analysis – This standard is a compilation of definitions used in thermal analysis. A definition is a single sentence with additional information included in the notes. It is reviewed every five years.
- **E-0537**, 14.02, Thermal Stability by DTA and DSC.
- **E-0698**, 14.02, Test for Arrhenius Kinetic Constants of Thermally Unstable Materials using DTA and DSC.
- **E-0793-95**, 14.02, Standard Test Method for Heats of Fusion and Crystallization by DSC – This test method covers the determination of the enthalpy (heat) of fusion (melting) and crystallization by DSC. This method is applicable to solid samples in granular form or in any fabricated shape from which an appropriate specimen can be cut, or to a liquid sample that crystallizes within the range of the instrument. The normal operating range is from -120 to 600°C . This method is applicable to thermally stable materials with well-defined endothermic or exothermic behavior.
- **E-0794-95**, 14.02, Standard Test Method for Melting and Crystallization Temperature by Thermal Analysis (DSC and DTA) – This test method covers the determination of melting and crystallization temperatures of pure materials by DSC and DTA. It is applicable to thermally stable materials with well-defined melting temperatures.
- **E-0928**, 14.02, Standard Test Method for Mole Percent Impurity by DSC – This method covers the determination of purity by use of DSC and evaluation of the results using the van't Hoff equation. Determination of purity by this method is only applicable when the impurity dissolves in the melt and is insoluble in the crystal.
- **E-0967**, 14.02, Standard Practice for Temperature Calibration of DSC and DTA analyzers – This practice covers the temperature calibration of DSC and DTA analyzers over the temperature range -40 to $+2500^{\circ}\text{C}$.
- **E-0968**, 14.02, Standard Practice for Heat Flow Calibration of DSC – This practice covers the heat flow calibration of differential scanning calorimeters over the temperature range from -130 to $+800^{\circ}\text{C}$.
- **E-1142**, 14.02, Terminology Relating to Thermophysical Properties – This is a compilation of terms and corresponding definitions commonly used in the study of thermophysical properties. Terms that are generally understood or defined adequately in other readily available sources are either not included or their sources are identified.
- **E-1269-95**, 14.02, Test Method for Determining Specific Heat Capacity by DSC – This method covers the determination of specific heat capacity by DSC. It is applicable to thermally stable solids and liquids. The normal operating range of the test is from -100 to 600°C .
- **E-1356-95**, 14.02, Test Method for Glass Transition Temperatures by DSC or DTA – This method covers the determination of the glass transition temperature, T_g , of materials using DSC or DTA. It is applicable to amorphous materials or to partially crystalline materials containing amorphous regions that are stable and do not undergo decomposition or sublimation in the T_g region.
- **E-1782-96**, 14.02, Test Method for Determining Vapor Pressure by Thermal Analysis – This method covers a procedure for the determination of the vapor pressure of pure liquids or melts from boiling measurements made using DTA or DSC instrumentation operated at different applied pressures. It may be used in the temperature range 273 – 773 K (0 – 500°C) and for pressures between 5 and 2 MPa.
- **E-1858-97**, 14.02, Test Method for Determining OIT of Hydrocarbons by DSC (PDSC) – This test method covers the procedure for determining the oxidative properties of hydrocarbons by DSC or PDSC and is applicable to hydrocarbons that oxidize exothermically in their analyzed form.

This standard reviews two test methods: A, a DSC is used at ambient pressure, for example, about 100 kPa of oxygen and B, a PDSC is used at high pressure, for example, 3.5 MPa (500 psig) oxygen.

The test specimen in an aluminum pan and the reference aluminum pan are heated to a specified constant test temperature in an oxygen environment. Heat from the specimen is monitored at an isothermal temperature until the oxidative reaction is manifested by heat evolution on the thermal curve. The OIT, a relative measure of the oxidative stability at the test temperature, is determined from data recorded during the isothermal test. The OIT measurement is initiated upon reaching the isothermal test temperature.
- **E-1860-97**, 14.02, Test Method for Elapsed Time Calibration of Thermal Analyzers – This method covers the calibration or performance confirmation of the elapsed time signal from thermal analyzers.
- **E-1952-98**, 14.02, Test Method for Thermal Conductivity and Deriving Thermal Diffusivity by Modulated Temperature DSC.
- **E-2009-99**, 14.02, Test OOT of Hydrocarbons by DSC – This method covers the procedure for

determining the oxidative properties of hydrocarbons by DSC or PDSC and is applicable to hydrocarbons which oxidize exothermically in their analyzed form. In test method A, a DSC is used at ambient pressure, for example, 0.1 MPa or 1 atm of oxygen. In test method B, a PDSC is used at high pressure, for example, 3.5 MPa (500 psig) oxygen.

ABBREVIATIONS AND ACRONYMS

ABS	Acrylonitrilebutadiene Terpolymer
ASTM	American Society for Testing and Materials
DDC	Dynamic Differential Calorimetry
DDSC	Dynamic Differential Scanning Calorimetry
DEA	Dynamic Enthalpic Analysis
DETA	Dielectric Thermal Analysis
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EVA	Ethylene Vinyl Acetate Copolymer
FTIR	Fourier Transform Infrared
HDPE	High-density Polyethylene
ISO	International Standardization Organization
LDPE	Low-density Polyethylene
MTDSC	Modulated Temperature Differential Scanning Calorimetry
NIST	National Institute of Standards and Technology
OIT	Oxidation Induction Time
OOT	Oxidation Onset Temperature
PC	Polycarbonate
PBD	Polybutadiene
PDSC	Pressure Differential Scanning Calorimetry
PET	Poly(ethylene terephthalate)
PP	Polypropylene
PRT	Platinum Resistance Thermocouple
PS	Polystyrene
PVAc	Polyvinyl Acetate
QDTA	Quantitative Differential Thermal Analysis
SBR	Polystyrene-cobutadiene
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analyzer
TMA	Thermomechanical Analysis
XDS	X-ray Diffraction Structure

RELATED ARTICLE

Thermal Analysis (Volume 15)
Thermal Analysis: Introduction

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