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# Application of IR Imaging during Temperature-Modulated Differential Scanning Calorimetry (TMDSC) Measurements

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## ABSTRACT

In a temperature-modulated differential scanning calorimetry (TMDSC) system, temperatures are measured by thermocouples under the sample and reference furnaces. TMDSC helps the researcher to establish a more realistic model to calculate heat capacity of various materials. This study examined the assumptions about temperature gradients in TMDSC characterization. An infrared camera was used to obtain surface temperature maps of DSC cells during temperature sweeps. TMDSC units from Perkin-Elmer and TA Instruments were studied using different heating and cooling rates. Temperature gradients exist between the top and bottom of the sample. IR images showed that temperature distributions within the sample and reference cells exist. Phase lags between the top and bottom temperatures were also observed.

**Keywords:** infrared imaging, calorimetry, TMDSC, indium, polyester

## 1. INTRODUCTION

Temperature Modulated Differential Scanning Calorimetry (TMDSC) is a recently introduced method in material studies. In a standard DSC test, a reference and a sample are placed side by side in a test cell. This cell is surrounded by a small furnace with multiple thermocouples instrumented to measure and control the temperature. The sample and reference both experience the same programmed heating and cooling cycles. Temperature measurements are crucial to the instrument accuracy. At steady state, the temperatures of the sample and reference are nominally the same. For a given temperature change,  $\Delta T$ , the sample and reference both approach the new temperature exponentially. For heat capacity tests, the small temperature gradient between the sample and reference during the approach can be neglected, because the measurements are conducted under a constant heating and cooling rate. TMDSC adds a small temperature oscillation on top of the normal heating and cooling scan. The rate-of-change of temperatures continuously alters. The temperature gradient between the sample and the reference becomes important.

When the test frequency is slow, the temperature gradient can be neglected. At higher frequencies, the temperature gradient causes a phase lag between the sample and reference. Understanding the temperature gradient and temperature distribution is key to obtaining the highest precision. To date, the most sophisticated TMDSC system uses thermocouple arrays to measure temperature. However, they are placed at the bottom of the cell and the measurements are contact by nature. An infrared (IR) imaging system provides surface temperature maps of the entire test cell [1], and the temperature gradient and distribution can be measured without contact. The IR temperature maps can also provide information of cross-talk (temperature transients) between the sample and reference during melting and crystallization. We utilized a high-speed,

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high-resolution IR camera in this study. Two different TMDSC systems, Perkin Elmer and TA Instruments, were studied. Standard and temperature modulated DSC tests were performed using indium metal and polymer films.

## 2. INTEGRATION OF IR IMAGING SYSTEM WITH TMDSC

Two commercial TMDSC systems were evaluated, a Perkin Elmer DSC 7 and a TA Instruments 2920. The infrared image system was a Raytheon, Radiance HS<sup>®</sup>, IR camera. The IR detector, InSb FPA, is sensitive to 3-5  $\mu\text{m}$  thermal radiations. At full frame, 256 x 256 pixels, the camera can take images at 141 frames per second. The 12-bit digital intensity readout gives a temperature resolution of 0.015 K near ambient. Using a 25 mm lens, the spatial resolution was about 120 to 150  $\mu\text{m}$  per pixel at full frame. The IR camera integration time was from 0.5 ms to 1.0 ms depending on the test temperature. A neutral density filter, NDI, was used for tests conducted above 100 $^{\circ}$  C.

Both TMDSC systems have enclosures to protect the furnace from heat loss. To allow the IR camera line of sight access to the specimen surface, the covers of the DSC were removed and replaced with a sapphire plate. In the Perkin Elmer system, two small sapphire discs replaced the platinum lids which cover the sample and reference furnaces, as shown in Figure 1. A larger sapphire plate replaced the aluminum block cover plate. In the TA system, only one sapphire plate was used to cover the furnace, which contains both the sample and the reference.

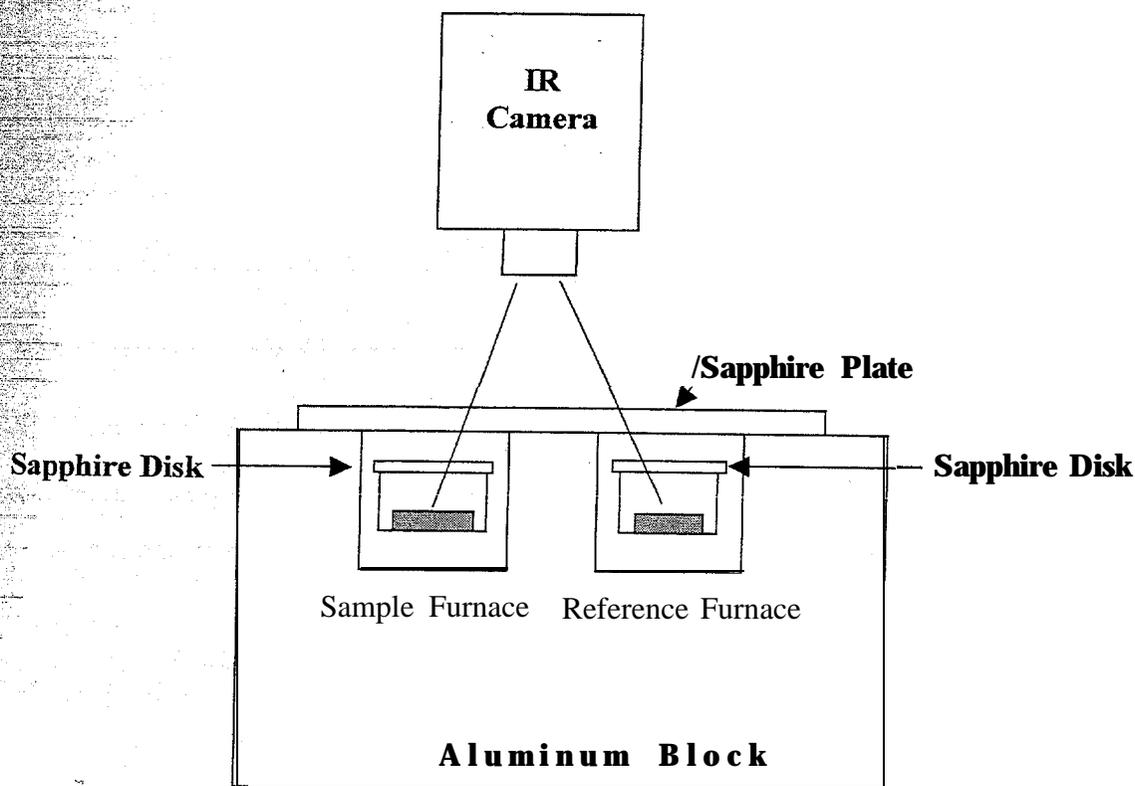


Figure 1. Integration of IR camera with the Perkin Elmer DSC 7.

### 3. IR IMAGING OF INDIUM MELTING IN A TMDSC SYSTEM

The IR camera was used to monitor the melting of indium in both standard DSC and TMDSC tests. The IR camera was calibrated (via the DSC thermocouples) for temperature measurements using the empty pans in the reference and sample position. Both the sample and reference pans were covered with aluminum lids and painted black. Since the melting temperature of indium is well known, the calibration was conducted from approximately 140°C to 160°C. Figure 2 is the calibration curve for both the reference and sample cells. Note the temperatures of the reference and sample cells are very close, and linear curve fits gave  $R^2$  values better than 0.999.

Figure 3 shows the temperatures of both the indium sample and the reference over a period of 40 seconds. The starting temperature was 136.65°C at which the DSC held the temperature steady for 3 minutes. Then the temperature increased at 10°C/minute. The IR camera started recording just below the melting temperature of indium. A few seconds after collecting data, the indium sample started melting at 157.30°C. The melting peak occurred at 158.87°C. The temperatures matched with DSC thermocouple recording very well indicating no significant temperature gradients. The reference temperature followed the programmed rate, but the sample temperature lagged behind during melting. It resumed the programmed rate after melting completed. The IR image in Figure 3 was taken during melting. The reference (left side) clearly showed higher temperature than the sample (right side). The size of reference seems bigger because the indium sample was not big enough to spread over the entire sample pan during melting. The IR camera not only recorded the temperatures but also provided temperature distribution maps that cannot be obtained otherwise.

The IR camera showed the ability to reproduce the function of thermocouples but in a non-contact fashion. As illustrated in Figure 4, the line profiles of the temperatures across the sample and reference cells showed an expected distribution where the center of the pans had the highest temperatures and the edges showed slightly lower temperatures. The sample cell had a smaller uniform temperature region compared to the reference cell, which was consistent with the IR image in Figure 3. There was as much as a 3°C temperature difference between the reference and the sample during melting. The area outside the pans had different IR intensity because the calibration was carried out using sealed aluminum pans sprayed with a thin (0.3 µm thick) graphite coating to reduce IR reflection. The surface of the furnace was not painted and had a different emissivity and was not calibrated.

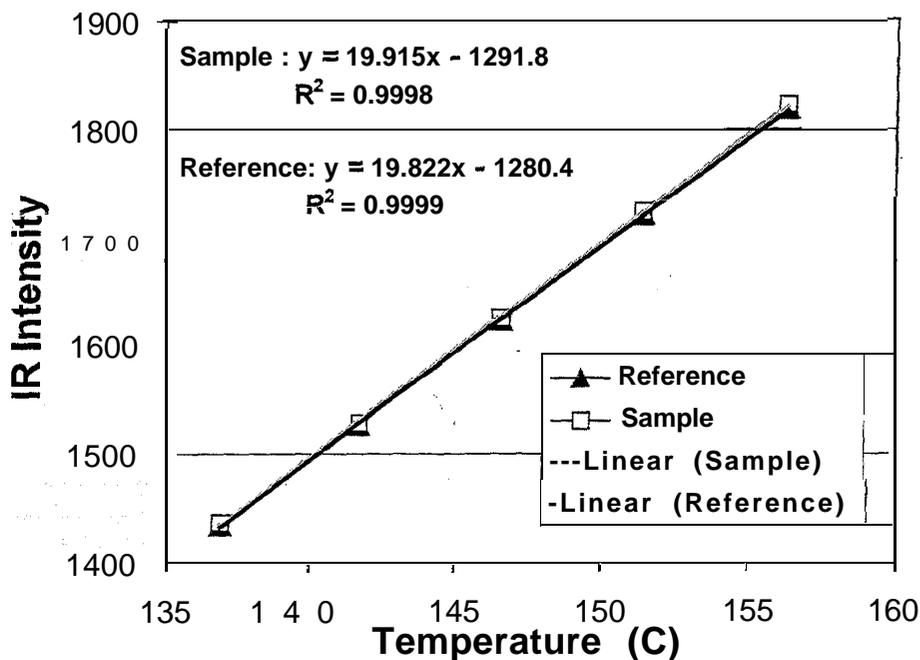


Figure 2. Temperature calibration on a TA TMDSC system.

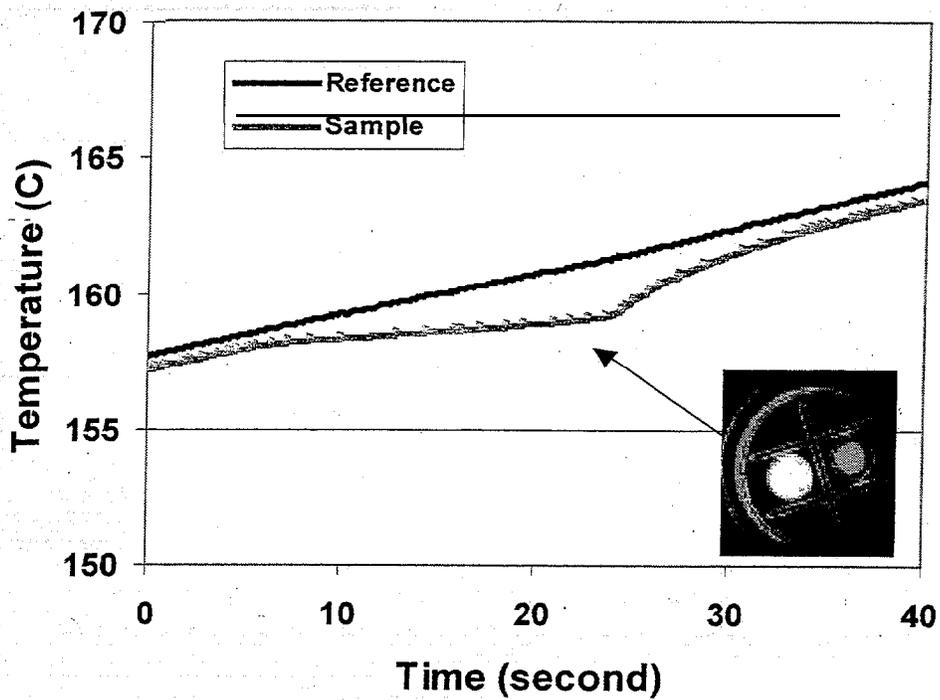


Figure 3. Temperature vs time plot for standard DSC during melting of indium obtained from IR imaging. The IR image taken at 20 seconds shows the temperature difference between the sample (right) and the reference (left).

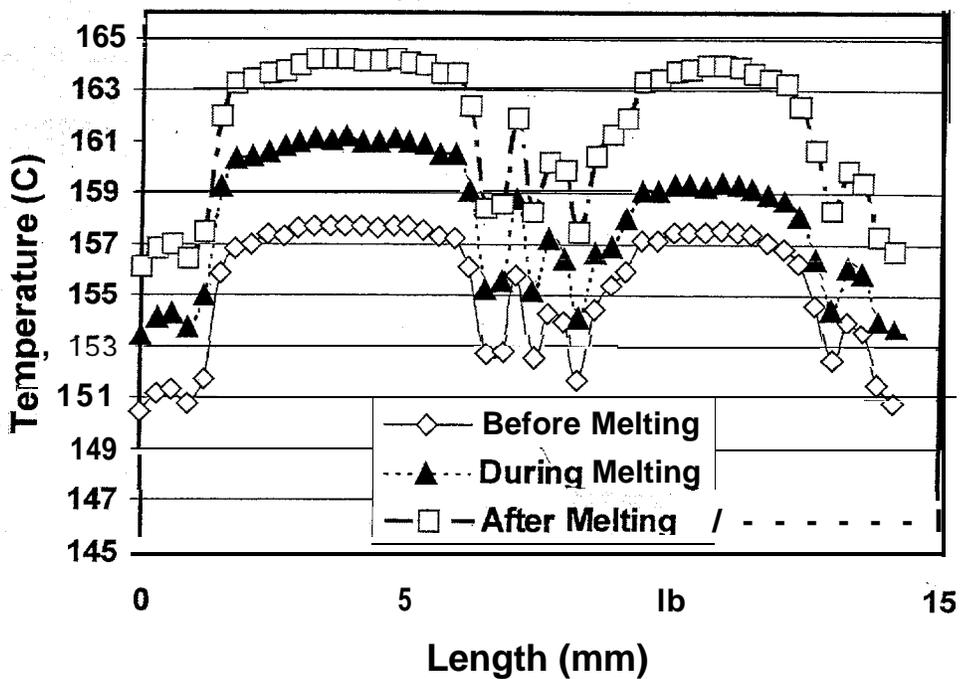


Figure 4. Temperature line profiles of the reference and sample cells before, during and after melting. The dips in the center were due to uncalibrated furnace bottom.

TMDSC was also performed for indium. The system was programmed to have an underlying heating rate of  $0.2^{\circ}\text{C}/\text{minute}$ . Temperature modulation of the modulated melting process was recorded at 120 frames per second. As shown in Figure 5, an IR camera captured more than 1.5 cycles. The peak sample temperature was  $0.6^{\circ}\text{C}$  to  $0.7^{\circ}\text{C}$  below the peak reference temperature. Towards the end of the cooling period, the sample temperature stayed  $0.5^{\circ}\text{C}$  above the reference. The shape of the sample temperature curve was also distorted from the programmed sine wave. There was a small phase lag between the sample and the reference.

Due to its power compensation mode, the Perkin Elmer system can be modulated with a maximum rate of change of temperature of  $48^{\circ}\text{C}/\text{minute}$  in an open-lid set up. In the meantime, the TA system can only be modulated up to  $2.4^{\circ}\text{C}/\text{minute}$ . Above this rate, the programmed heating and cooling could not be followed. This is mainly due to its heat flux controlled radiative furnace design. We performed TMDSC tests in a Perkin Elmer system on polymer samples.

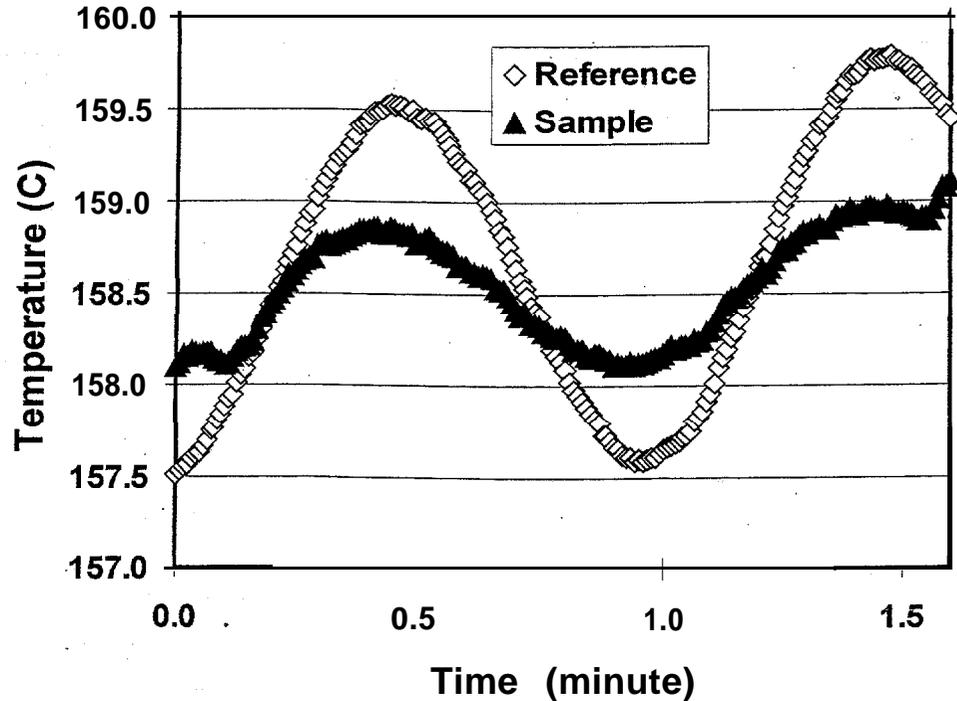


Figure 5. Temperatures measured by the IR camera in a TMDSC run during melting of indium. Conditions: Modulation  $1^{\circ}\text{C}/\text{minute}$ ; Underlying heating rate  $0.2^{\circ}\text{C}/\text{minute}$ .

#### 4. IR IMAGING OF POLYMER DURING TMDSC TESTS

Since metals have much higher thermal conductivity, they are expected to closely follow the temperature modulation during TMDSC. However, low thermal conductivity materials such as polymers cannot always follow the temperature modulation. Further, a temperature gradient is expected between the top and the bottom of the sample. This temperature gradient is a source of measurement error. This effect is more obvious in a first-order transition such as melting or crystallization of a single component polymer. The latent heat in the process can further distort the temperature gradient. These difficulties have long been recognized by many researchers [1-3]. Many instrumental and mathematical corrections have been implemented. But the use of IR imaging was not attempted until our first test in a Perkin Elmer DSC7 [1].

TMDSC tests were performed on commercial polyester [poly(ethylene terephthalate)] films. The film was 0.1 mm thick. Several discs were put in the sample pan for study of the effect of thickness. In the TA system, the melting and crystallization processes under standard DSC were performed. The melting process is illustrated in Figure 6. Similar to the

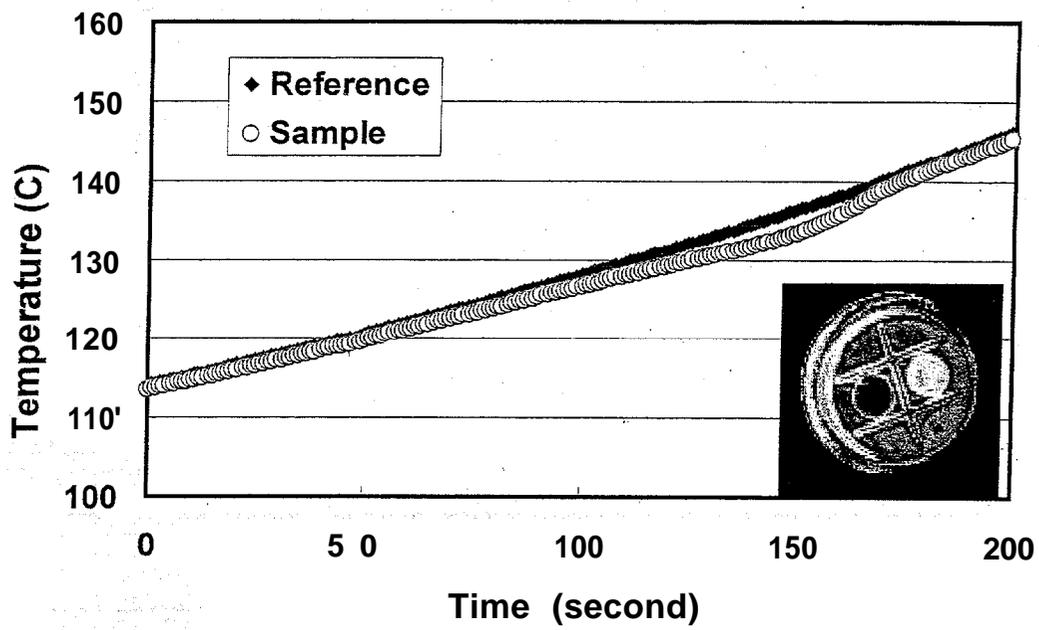


Figure 6. Melting of polyester in a standard DSC heating test. Insert shows IR image of reference (left) and sample (right) at t = 150 seconds. Heating rate: 10°C/minute.

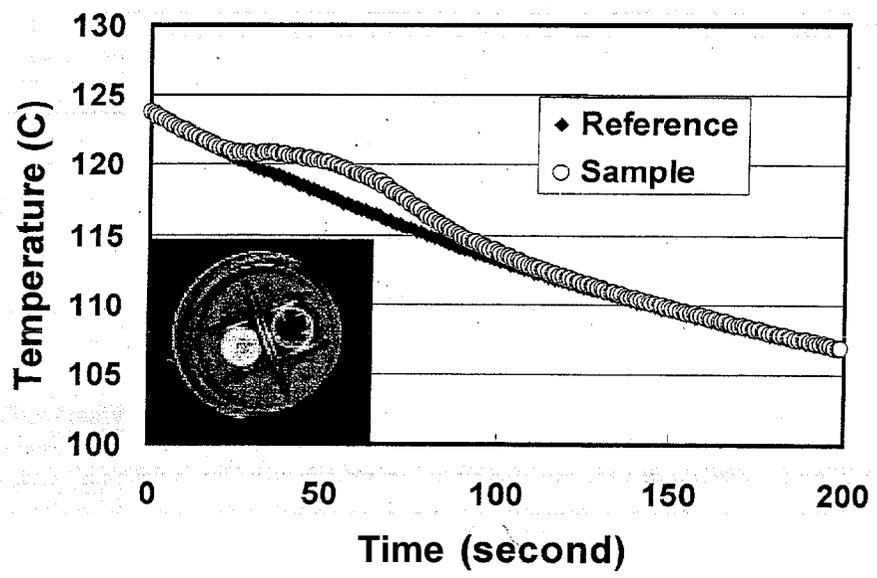


Figure 7. Crystallization of polyester in a standard DSC cooling test. Insert shows IR image of reference (left) and sample (right) at t = 50 seconds. Heating rate: 10°C/minute.

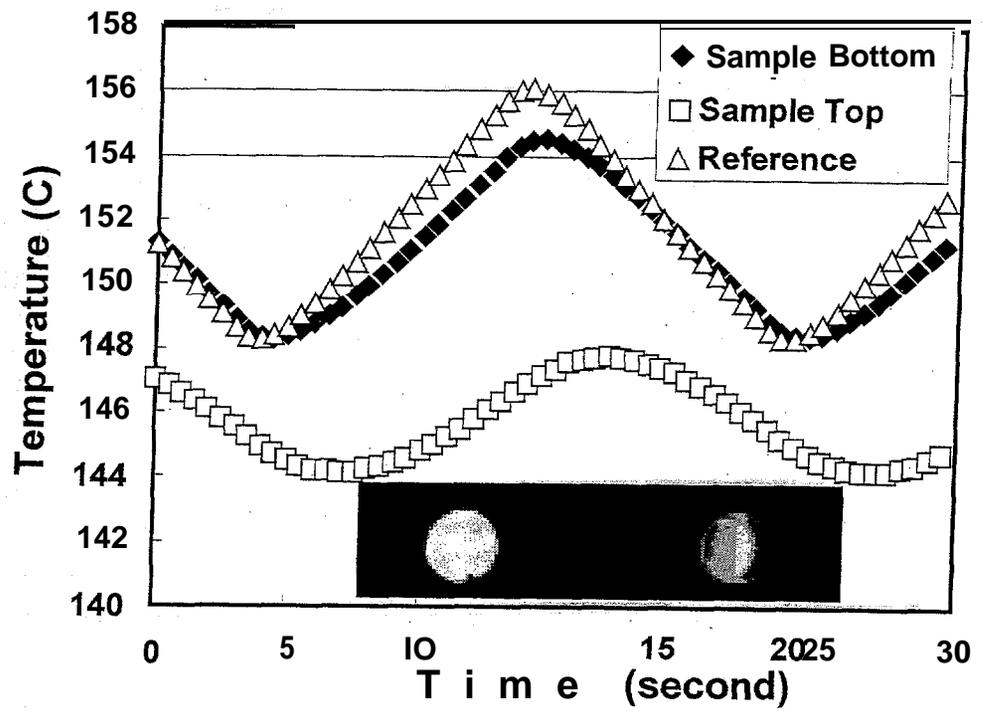


Figure 8. Temperature gradient and phase lags observed in a Perkin Elmer DSC 7. Sample: Thick PET; The highest heating rate = 48°C/minute; set up  $\pm 4^\circ\text{C}$ , period = 20 seconds, AT = 8.0°C. Reference (left); Sample (right).

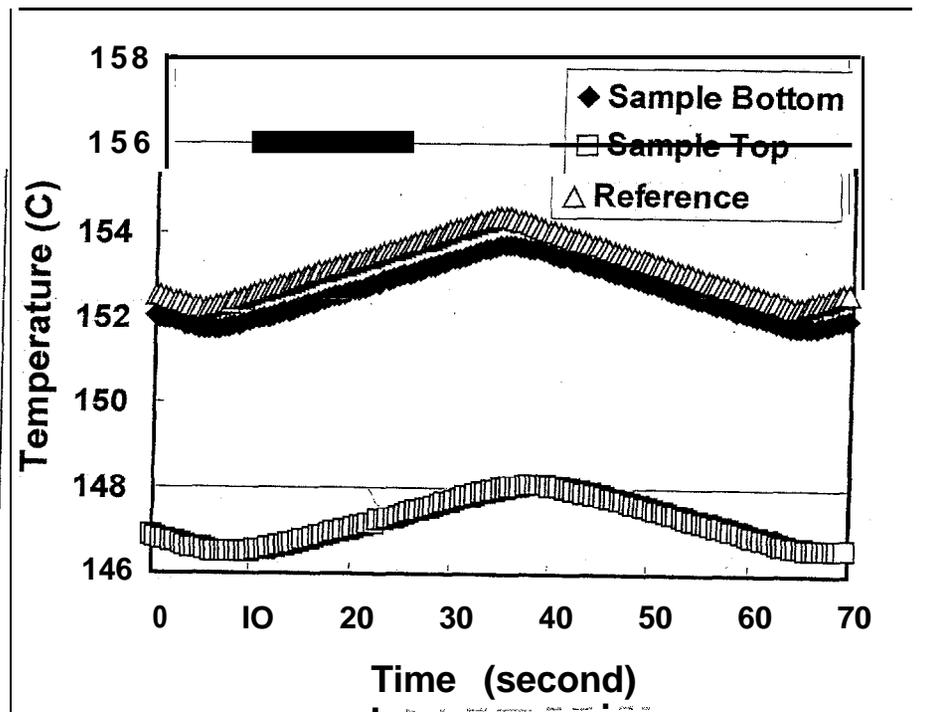


Figure 9. Temperatures obtained by the IR camera during a typical TMDSC test. Sample: Thick PET; The highest heating rate = 4°C/minute; set up  $\pm 1^\circ\text{C}$ , period = 60 seconds, AT = 2°C.

indium melting curves in Figure 3, the melting of the polymer was between 130°C and 140°C. The sample temperature stayed below the reference temperature due to latent heat. Figure 7 shows the sample specimen during cooling. The polymer crystallized between 120°C and 110°C. Opposite to melting, the sample temperature stayed above the reference temperature. This was due to the release of heat during crystallization.

Since the modulation range of the TA system was limited, TMDSC was performed on a Perkin Elmer DSC 7 unit. A polyester specimen was cut into a semicircle. It was placed in the sample pan without a lid. The bottom of the sample pan and polymer surface can be viewed simultaneously. The test temperature was above 140°C under quasi-isothermal condition. The polymer was then completely melted. The melt was viscous enough so that the black paint on the sample surface was not affected. Two TMDSC conditions were tested: 1) a fast rate of 48°C/minute and 2) the standard rate of 4°C/minute. The temperatures recorded under condition 1) is shown in Figure 7. The reference temperature followed the programmed rate nicely. The PET specimen bottom temperature showed a small phase lag. The biggest difference came from the top of the sample. The peak temperature was 8°C below the reference temperature and the modulation amplitude was only half of the programmed value. This is a good demonstration of the temperature gradient, although in a real test, the top of the sample is covered with an aluminum lid. The lid should help heat transfer from the bottom to the top be more efficient.

In the standard test condition 2), the temperature gradient was also observed, as shown in Figure 8. The top of the sample was still 6°C below, but the modulation magnitude was much closer to the programmed value. The phase lag was also smaller. Since heating in a Perkin Elmer unit is at the bottom of the sample and reference cell, the temperature gradient became more obvious. The TA system uses radiative heating. The surface-to-bottom temperature gradient was much smaller. But the TA system does not have a wide range of modulation flexibility. Understanding the temperature gradient and distribution of the TMDSC system can help researchers to correct the analytical model and improve accuracy of heat capacity measurements.

## 5. CONCLUSIONS

An infrared imaging system has been integrated with two TMDSC systems to obtain time dependent, temperature maps. The IR camera can be used to monitor temperatures in a TMDSC unit without contact. The melting of indium metal was used as an example. The IR camera was also used to monitor melting and crystallization of polymer specimens. Temperature differences between the sample and the reference were observed. In a Perkin Elmer system, the temperature gradient between the top and the bottom of the sample and phase lags were demonstrated.

## ACKNOWLEDGEMENTS

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