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Title: Comparing Single-Point and Multi-point Calibration Methods in
Modulated DSC

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Caleb Van Buskirk

*Comparing Single-Point and Multi-point Calibration
Methods in Modulated DSC*

UO Spring 2017

Dr. David Tyler



Abstract

Heat capacity measurements for High Density Polyethylene (HDPE) and Ultra-high Molecular Weight Polyethylene (UHMWPE) were performed using Modulated Differential Scanning Calorimetry (mDSC) over a wide temperature range, -70 to 115 °C, with a TA Instruments Q2000 mDSC. The default calibration method for this instrument involves measuring the heat capacity of a sapphire standard at a single temperature near the middle of the temperature range of interest. However, this method often fails for temperature ranges that exceed a 50 °C interval, likely because of drift or non-linearity in the instrument's heat capacity readings over time or over the temperature range. Therefore, in this study a method was developed to calibrate the instrument using multiple temperatures and the same sapphire standard.

Introduction

Polyethylene (PE), a simple organic polymer shown in figure 1, is used in a multitude of modern applications, from common materials such as water bottles and pen casings to high end applications such as blocking cosmic radiation¹. PE exists in many forms, but of interest for this study were high density PE (HDPE) and ultra-high molecular weight PE (UHMWPE). HDPE and UHMWPE both exhibit

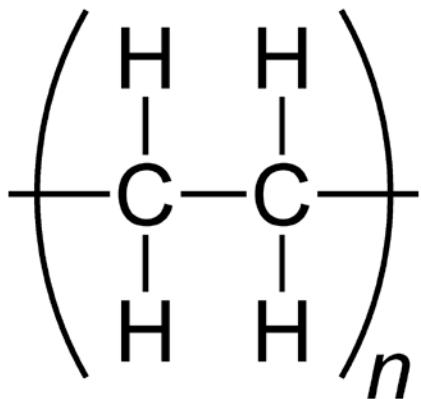


Figure 1: The basic polymeric structure for polyethylene.

semi-crystalline behavior; HDPE is a highly linear polymer that is generally 60-80% crystalline and UHMWPE can span from 40-75% crystallinity². In semi-crystalline polymers there are two domains, the chaotic non-ordered amorphous region and the highly ordered crystalline region. The goal of a larger study at Los Alamos National Laboratory is to understand how these domains, specifically the crystalline, change under mechanical stress. For semi-crystalline polymers, heat capacity is one property that is significantly influenced by the percent crystallinity in the sample. Thus, one of the first steps of this project was to look at the specific heat capacity of the as-received material as measured by modulated differential scanning calorimetry (mDSC). By comparing these values to theoretical specific heat capacity values for purely amorphous and purely crystalline PE, the relative crystallinity of HDPE and UHMWPE was compared. Additionally, a secondary study was undertaken to develop an improved method of calibrating with

sapphire, a standard with well-defined heat capacity values, at multiple temperatures. Previously, the TA instruments Q2000 mDSC used one calibration point for an entire temperature range, potentially not accounting for drift or non-linearity in the instrument's heat capacity readings over time or over the temperature range.

Experimental

Instrumental Method and Samples

Prior to heat capacity measurements, the instrument cell was cleaned with isopropyl alcohol and then baked out. The bake-out procedure involved ramping to 400 °C and holding for 55 minutes under nitrogen atmosphere, followed by 5 minutes at 400 °C under ambient air. Then the calibration wizard in the TA software was used to calibrate cell resistance, cell constant, and temperature using an indium standard. The cell constant was determined to be 1.018, meaning that the instrument was reading the melting temperature of indium to be a factor of 1.018 different from the literature value of 156.6 °C. Therefore, all readings were recorded with a factor of 1.018 applied to them. The mDSC experiments were performed with a TA instruments Q2000 mDSC with a ramp rate of 3 °C per minute, modulation rate of ± 0.95 °C per minute, and temperature range of -90 °C to 115 °C under nitrogen atmosphere. Heat capacity is calculated using the equation in figure 2, where KCp Rev is the reversing heat capacity constant as determined using one of the two calibration methods that follow.

UHMWPE and HDPE samples (~10 mg each) were cut from large blocks and placed in Tzero (TA instruments P/N 901683.901) hermetically sealed aluminum pans. Three replicates were run for each sample, each cut from a different section of the respective larger block. A sapphire verification was run before and after the three replicate runs as either verification that the instrument was holding calibration in the case of single-point calibration or to be used as the sapphire calibration in the case of multi-point calibration.

$$\text{Rev Cp} = \frac{\text{Heat Flow Amplitude}}{\text{Heating Rate Amplitude}} \times \text{KCp Rev}$$

where: KCp Rev = Calibration Constant for Reversing Cp

Figure 2: The equation for how the Q2000 calculates the reversing heat capacity (Rev Cp), where the heating rate amplitude and the heat flow amplitude (from the modulation) are measured by the instrument and the heat capacity constant (Kcp Rev) is calculated as explained in the text³.

Single Calibration Point

The instrument was then calibrated specifically for reversing heat capacity (Rev. Cp) by running a sapphire sample (TA instruments P/N 95079.902) in a hermetically sealed Tzero aluminum pan for the same temperature range and method as the samples and with the sapphire calibration constants set at one. Then the single-point calibration is determined by selecting a point in the middle of the temperature range and dividing the observed Rev. Cp by the literature heat capacity value⁴ at that temperature. For example, the data shown in figure 3 is the specific heat capacity for sapphire from the range of -70 °C to 105 °C; at 6.85 °C (about the middle of the range), the Rev. Cp was found to be 0.6654 $\frac{J}{g \text{ } ^\circ\text{C}}$, while the literature value is 0.7343 $\frac{J}{g \text{ } ^\circ\text{C}}$. This means the sapphire capacity constant (KCp Rev) is 1.103, and all capacity measurements will have this factor applied to them, as seen in the calculation for reversible heat capacity in figure 2. Sapphire is then run with the samples as verification. If the sapphire verifications have an error of greater than 3%, the experiment is repeated.

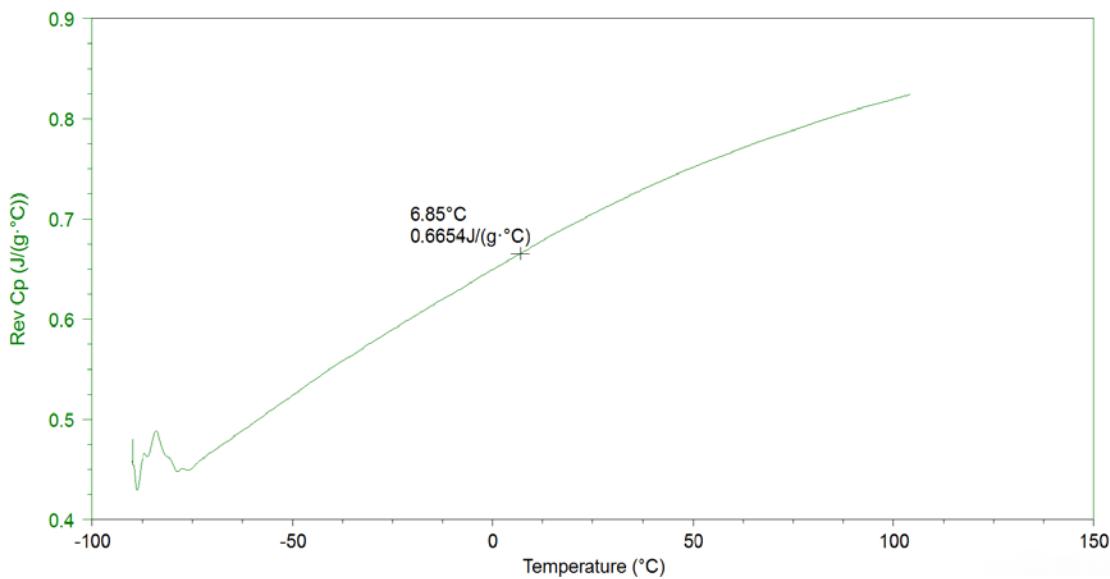


Figure 3: The reversing heat capacity for sapphire from -70 to 105 °C, marked with the single calibration point at 6.85 °C.

Multiple Calibration points

Calibrating with multiple points follows the same principle as single-point calibration in that it uses the equation in figure 2 to generate Rev. Cp values. As opposed to using one constant for the entire range, this method generates a constant for each individual sample data point based on the sapphire runs before and after the three replicate runs. An excel Visual Basic (VBA) code was generated by Jillian Adams (UO Alumni 2016) to determine the calibration constant for calculating reversing heat capacity (Kcp) for each data point generated. First, the code assigns a calibration constant for each sapphire data point. The literature data⁵ is reported in increments of 10 °C, whereas the instrument generated 3 data points per degree. Thus, the theoretical literature value for a given temperature must be interpolated in order to determine the constant. This first step is to find the literature data points that sandwich an observed temperature of interest, then the theoretical literature Rev. Cp for the temperature of interest is generated using equations 1-4.

$$\text{Interpolated literature Cp} = \left(\frac{\Delta y}{\Delta x}\right)x + b \quad (1)$$

$$\frac{\Delta y}{\Delta x} = \text{slope}$$

$$\Delta y = (\text{the upper literature Rev Cp}) - (\text{the lower literature Rev. Cp}) \quad (2)$$

$$\Delta x = (\text{upper literature temperature}) - (\text{lower literature temp}) \quad (3)$$

$$x = (\text{observed sapphire temperature}) - (\text{lower literature temp}) \quad (4)$$

$$b = \text{literature lower Rev. Cp}$$

The Kcp for the given observed sapphire data is then determined by taking the interpolated literature Rev. Cp and dividing it by the observed Rev. Cp (for a given temperature). After the Kcp is interpolated, it is applied to the sample data. Usually, the sample data and the sapphire data have slightly different temperatures as well; therefore, to apply the Kcp to the sample, a second linear interpolation is done to normalize the calibration constant to the sample data. Working similarly as above, the program finds the observed sapphire data points that sandwich the sample data point of interest, and the Kcp for the sample temperature of interest is interpolated using equations 5-8. The corrected Rev. Cp for the sample is then determined using figure 2 with its respective Kcp.

$$\text{Interpolated Calibration constant} = \left(\frac{\Delta y}{\Delta x}\right)x + b \quad (5)$$

$$\Delta y = (\text{the upper extrapolated}) - (\text{the lower literature Rev. Cp}) \quad (6)$$

$$\Delta x = (\text{upper observed sapphire temp}) - (\text{lower observed sapphire temp}) \quad (7)$$

$$x = (\text{observed sample temperature}) - (\text{lower sapphire temp}) \quad (8)$$

$$b = \text{lower extrapolated calibration constant}$$

Results/Discussion

Comparing Calibration Methods

TA Instruments recommends that the Kcp for sapphire fall between 0.8 – 1.2 and any data outside this range likely indicates an instrument error. Thus, for both calibration methods, the data was only used/generated (in the case of multipoint calibration method) if the associated sapphire calibration constant was between 0.8 – 1.2. In the case of single point calibration, the instrument needs to be initially calibrated and if this constant is outside the recommended range, this experiment will need to be re-done until the constant is achieved. Unlike the single point method, the multi-point calibration method does not require the initial heat capacity run to determine the calibration constant, but uses the sapphire heat capacity runs before and after the samples. Similarly, if the constants are outside the 0.8-1.2 range this experiment will need to be re-done, but since this method lacks the necessity for the initial sapphire heat capacity run (and its potential re-runs) it requires less time than the single point method. To ensure that this was a viable replacement for the single point calibration method it was compared to the traditional method (single point method) by applying both calibrations to the same sample, as can be seen in figure 4.

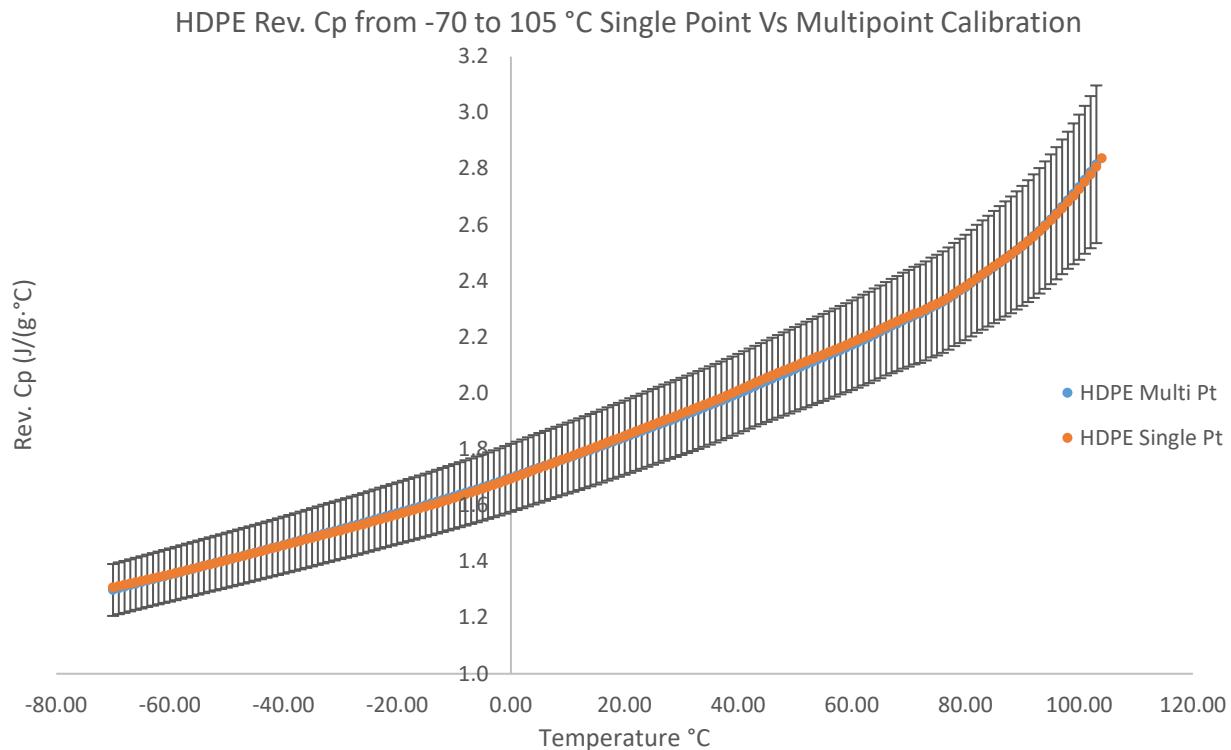


Figure 4: The single-point and multi-point calibration methods applied to HDPE Rev. Cp runs. Error bars represent standard deviation of the three replicate samples. The HDPE single-point data is in orange and the multi-point is in blue, directly underneath the single-point samples.

According to figure 4, the sample data overlaps almost perfectly, indicating that equivalent results are obtained with both methods of calibration. However, the multi-point calibration takes less time overall.

HDPE and UHMWPE

Heat capacity measurements were run on HDPE and UHMWPE from -70-115 °C. These values were compared to theoretical heat capacity values for perfectly amorphous and perfectly crystalline heat capacity data for polyethylene⁶. Because crystalline domains are more ordered and limited in vibrational and other molecular motions, materials with a higher percent crystallinity are expected to have a lower heat capacity. Conversely, amorphous domains are not ordered and can experience vibrational, rotational, and translational energy changes. Thus, the amorphous regions will consume more energy, resulting in a higher observed heat capacity. By collecting specific heat capacity values and comparing them to the theoretical values, the relative crystallinity of the UHMWPE and HDPE can be qualitatively assessed. This data can be seen in figure 5.

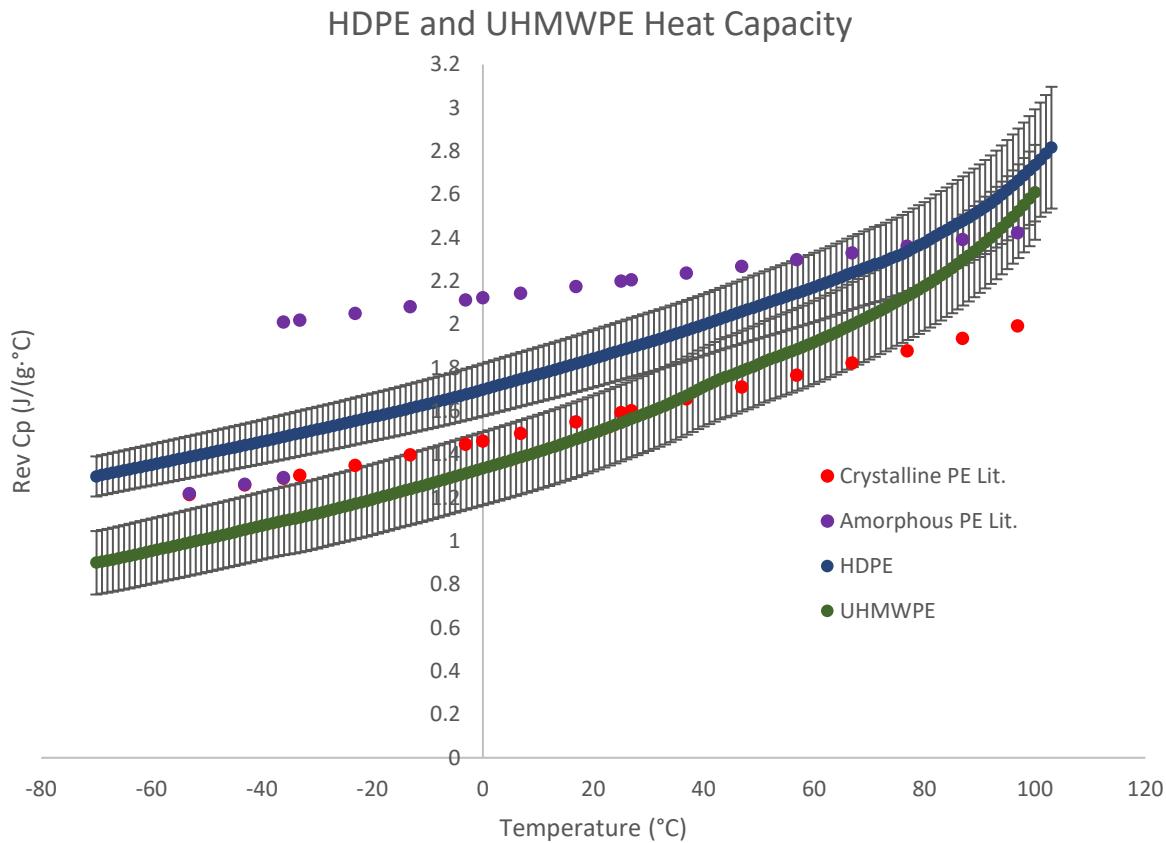


Figure 5: The Rev. Cp values as a function of temperature for UHMWPE (green) and HDPE (blue), compared to the theoretical values for crystalline and amorphous polyethylene⁶. Error bars represent the standard deviation of the 3 replicates.

As seen in Figure 5, the UHMWPE samples show heat capacity values that are below the theoretical values until about 0 °C. This could reflect an instrumentation error or an error in sample preparation. For example, the instrument readings are sensitive to sample size, sample contact to the pan, and pan contact to the heat flow cell. The signal-to-noise ratio in small samples is too low for accurate quantification, and the heat transfer is not uniform in samples that are too large resulting in the instrument observing the sample under multiple temperature conditions at once. Also in Figure 5, the error bars (which represent the standard deviation of three replicates) within each data set (UHMWPE or HDPE) are relatively high and start to overlap at around 20 °C. The high standard deviation is likely due to Instrument drift after the initial sapphire run. This is demonstrated in figure 6 where beginning sapphire data was used as calibration of all three replicates. As the replicates progressed (closest to furthest away from the when the calibration sapphire was run), the data drifted further away from the replicate that was run immediately after the sapphire. This could indicate that the instrument is drifting over time and suggests that more accurate calibration might be accomplished with sapphire runs immediately before each replicate.

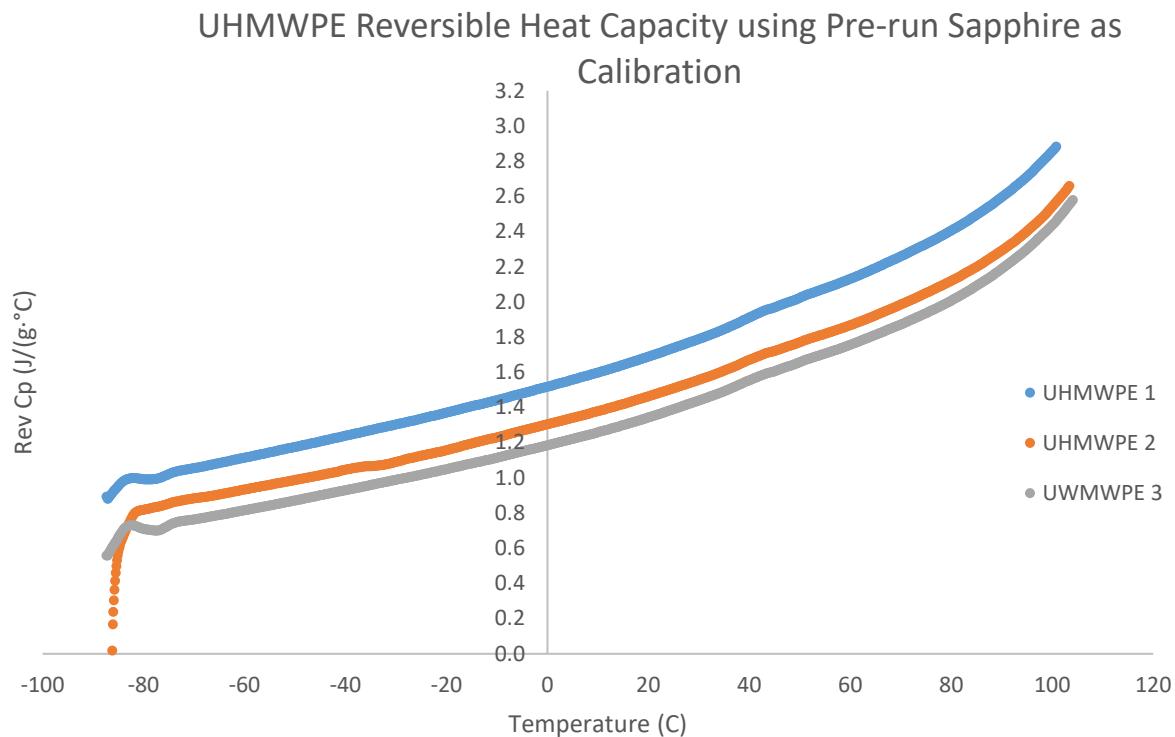


Figure 6: The Rev. Cp values as a function of temperature for three replicates of UHMWPE. 1 refers to the replicate that was directly after the sapphire run, 2 the next, and 3 being the last run on the instrument.

The last feature of this data is the relative crystallinity values of HDPE and UHMWPE. This data indicates that the UHMWPE is closer to the crystalline PE literature values. As mentioned above, UHMWPE spans a crystallinity range from 40-75% and HDPE from 60-80%. Thus, UHMWPE can have a higher % crystallinity than HDPE, but normal DSC runs for these UHMWPE and HDPE samples showed heats of fusion of 123.5 J/g and 200.7 J/g, respectively. Thus, the HDPE used in this study has a higher % crystallinity than the UHMWPE. Therefore, the heat capacity measurements shown above may not be indicating accurate relative crystallinity information.

Conclusions/Future Work

The multi-point calibration method lowers the time needed to collect data because it does not require an *initial* sapphire calibration (instead integrating the calibration into the experiments); thus, it will likely be used for all future heat capacity measurements on the Q2000 DSC. However, there does seem to be some drift in the data, indicating that the sapphire data being used to calibrate may be too far away from the sample data being collected. Due to the disagreement in relative crystallinity values between the conventional DSC and the modulated DSC and the drift being noticed in the data, it is likely that the heat capacity measurements will need to be run again with a sapphire calibration run before each sample. This allows for the sample to be calibrated by a sapphire calibration run that is as close as possible and should yield reproducible data. After the characterization of the thermal and crystal properties of UHMWPE and HDPE, the behavior of the crystal domains under mechanical stresses will be determined by heat capacity measurements and small-angle X-ray or neutron scattering on the deformed material, as well as Torsional Dynamic Mechanical Analysis (tDMA).

Acknowledgements

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