

NE 125 L

Title Page

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Experiment Number:	3
Experiment:	Determination of Specific Heat Capacity (C_p) of Materials by Differential Scanning Calorimetry (DSC)
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1. Introduction

The main purpose of this experiment is to learn the basic concepts of the differential scanning calorimeter and to illustrate its importance to materials science and engineering. We do this by using the calorimeter to determine the specific heat capacity (C_p) of silicon and low-density polyethylene at given temperatures.

The heat capacity of a material is defined as the amount of heat required to raise the temperature of a given substance or material by 1 °C, or equivalently, 1 K. The *specific* heat capacity is the heat capacity per unit mass. This relationship can be described mathematically:

$$Q = mC_p\Delta T \quad (1.1)$$

The subscript p in C_p is an indication that the specific heat capacity was obtained under isobaric (constant volume) conditions. For isochoric (constant volume) conditions, we would denote the specific heat capacity with C_v . For ideal gases, C_p and C_v are related by the equation $C_p - C_v = R$, where R is the universal gas constant.

Differential Scanning Calorimetry (DSC) is a thermal analysis technique used to measure temperature and heat flow associated with important transitions in materials as a function of time or temperature. Some measurements that can be made with the DSC are:

- Glass transition temperature
- Melting point
- Latent heat of melting
- Latent heat of crystallization
- Endothermic and exothermic natures of transitions
- Degree of Crystallinity
- Phase changes
- Specific heat capacity

In this lab, we will be using the Q10 differential scanning calorimeter to determine the specific heat capacity of elemental silicon and low density polyethylene (LDPE). We will also determine the melting point of LDPE and the enthalpy (latent heat) associated with this change.

We subject the sample to some source heat and measure the heat flow between the sample and a reference pan placed beside the sample pan. We then plot this data as a function of temperature to obtain the thermal profile for our sample. We can then perform many qualitative and quantitative observations from this graph. An example thermal profile would look the following, although not all features will be observed on all DSC plots:

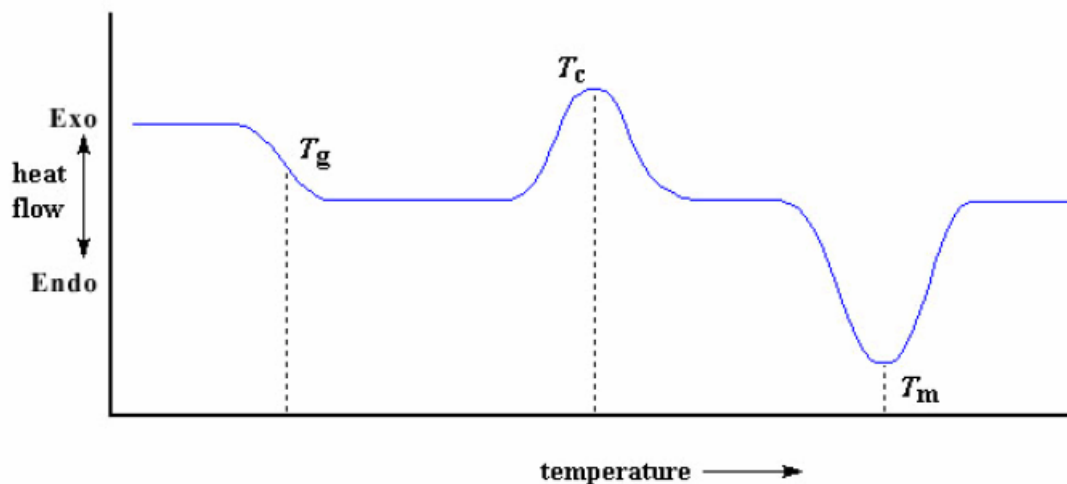


Figure 1 DSC Curve of Quenched PET

2. Materials and Equipment

1. Analytical balance
2. Q10 differential scanning calorimeter with mass flow control
3. Computer and data acquisition system
4. Data processing software
5. Sapphire (~25.0 mg)
6. Silicon (~10.0 mg)
7. Low density polyethylene – LDPE (~5.0 mg)

3. Procedure

The Q10 Differential Scanning Calorimeter used nitrogen as purge gas and the mass flow control has been set to 50 ml/min for the sample purge.

Modified Heating Procedure

The heating procedure involved many steps for running different trials. The first step involved the testing of empty pans to measure background heat flow. The second step was to find the calibration constant k . The last and final step was to run each of the samples of interest through the calorimeter to determine the heat flow at a specific temperature and to calculate C_p at that temperature.

1. Empty Pan
 - a. Create thermal method as follows

- i. Equilibrate at 40.0 °C.
 - ii. Isothermal for 5.0 min
 - iii. Ramp 20.0 °C/min to 200.0 °C
 - iv. Isothermal for 5.00 min
 - b. Run empty pans to determine background heat flow to be subtracted from following trials.
2. Determine the value of *k* (instrumental calibration constant) using sapphire standard
- a. Heat sapphire disc (*C_p* standard) using above thermal procedure keeping in mind that *k* is temperature dependent
 - b. Calculate *k* at the temperatures of interest using the following equation:

$$k = C_p(mJ \cdot mg^{-1} \cdot ^\circ C^{-1}) \frac{H_r(^{\circ}C \cdot \text{min}^{-1}) \times M(mg)}{H[mW(mJ \cdot \text{sec}^{-1})] \times 60(\text{sec} \cdot \text{min}^{-1})} \quad (1.2)$$

3. Measure *C_p* of silicon sample
- a. Measure sample mass
 - b. Using same thermal procedure as above, measure heat flow at 87 °C
 - c. Calculate *C_p* by substituting *k* into the equation:

$$C_p = \frac{k \times H \times 60}{H_r \times M} \quad (1.3)$$

4. Similarly, calculate *C_p* of LDPE at 67 °C
5. Analyze sources and magnitudes of error/uncertainty.
6. Return all samples and pans into their corresponding containers.

7. Results

We imported the raw data from the computer-aided data acquisition system into Microsoft Excel for processing. The raw data provided us with the temperature of the sample and the corresponding heat flow at that temperature. Our first task was to find the value of *k* for any given temperature using the data from the sapphire run. We used equation (1.2) for this purpose.

For example, *k* at 87 °C:

$$k = 0.885 \times \frac{20 \times 25.9}{7.15 \times 60} = 1.068$$

The heat-flow vs. temperature profile for all three samples were plotted and the following graph was obtained:

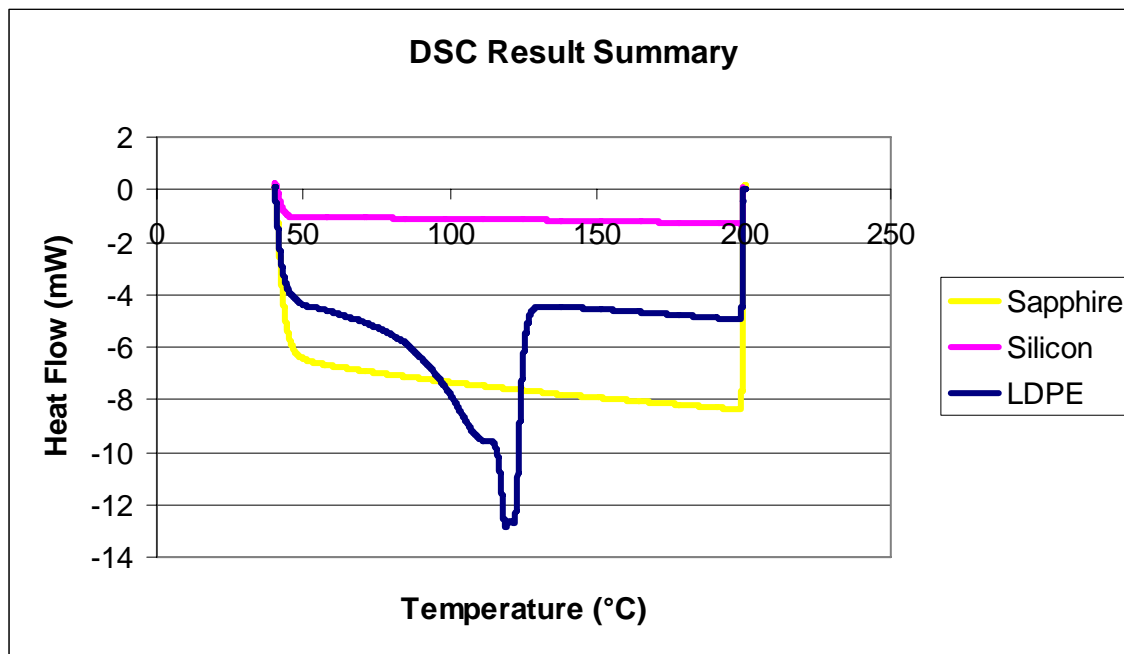


Figure 2 Comparison of DSC's of Silicon and LDPE against Sapphire standard

It is clear from the graph that only the LDPE curve has a dip in its thermal profile. In other words, this is the only sample that underwent melting. This split in the melting point dip is possible due to impurities in the sample, or more likely, due to the amount of branching in the LDPE polymer chain.

We do not observe a melting point dip in silicon's thermal profile because the melting point of silicon is 1400 °C, well above the maximum temperature at which we examined silicon (200 °C). Furthermore, we will never observe a glass transition for silicon as silicon is 100% crystalline. Only materials with amorphous regions will exhibit a glass transition.

8. Discussion

1. Calculate the specific heat capacities (C_p) of Si at 87 °C and 107 °C respectively.

Value of k at 87 °C = 1.068

Value of H for Si at 87 °C = 1.094 mW

$$\text{Using equation (1.3), } C_p = \frac{k \times H \times 60}{H_r \times M} = \frac{1.068 \times 1.094 \times 60}{20 \times 6.2} = 0.565 \text{ J/g/}^\circ\text{C}$$

Similarly for 107 °C, $k = 1.065$ and $H = 1.12$ mW.

Using equation (1.3), $C_p = \frac{1.065 \times 1.12 \times 60}{20 \times 6.2} = 0.577$ J/g/°C

2. *Calculate the specific heat capacities (C_p) of LDPE polymer at 67 °C, and determine the glass transition point, melting and crystallization temperatures if available.*

We use the same method as that used for silicon:

For 67 °C, $k = 1.085$ and $H = 4.919$ mW.

Using equation (1.3), $C_p = \frac{1.085 \times 4.919 \times 60}{20 \times 5.0} = 3.20$ J/g/°C

No glass transition points were observed in the thermal profile for LDPE. The temperature range at which the experiment was conducted was already well above the glass transition temperature for LDPE.

On the same note, no crystallization temperatures were observed either as our LDPE sample was subjected to a heating procedure only. We did not perform a cooling procedure.

A melting temperature for LDPE was observed at around 112.40 °C. The latent heat of melting (fusion) was estimated by the computer system (by integrating the DSC curve within the boundaries specified by us) to be around 116.7 J/g.

Sample: LDPE
Size: 5.0000 mg
Method: Cp determination

DSC

File: C:\TA\Data\DSC\ne125\3E\LDPE.001
Operator: Xie
Run Date: 20-Feb-2006 15:28
Instrument: DSC Q10 V9.4 Build 287

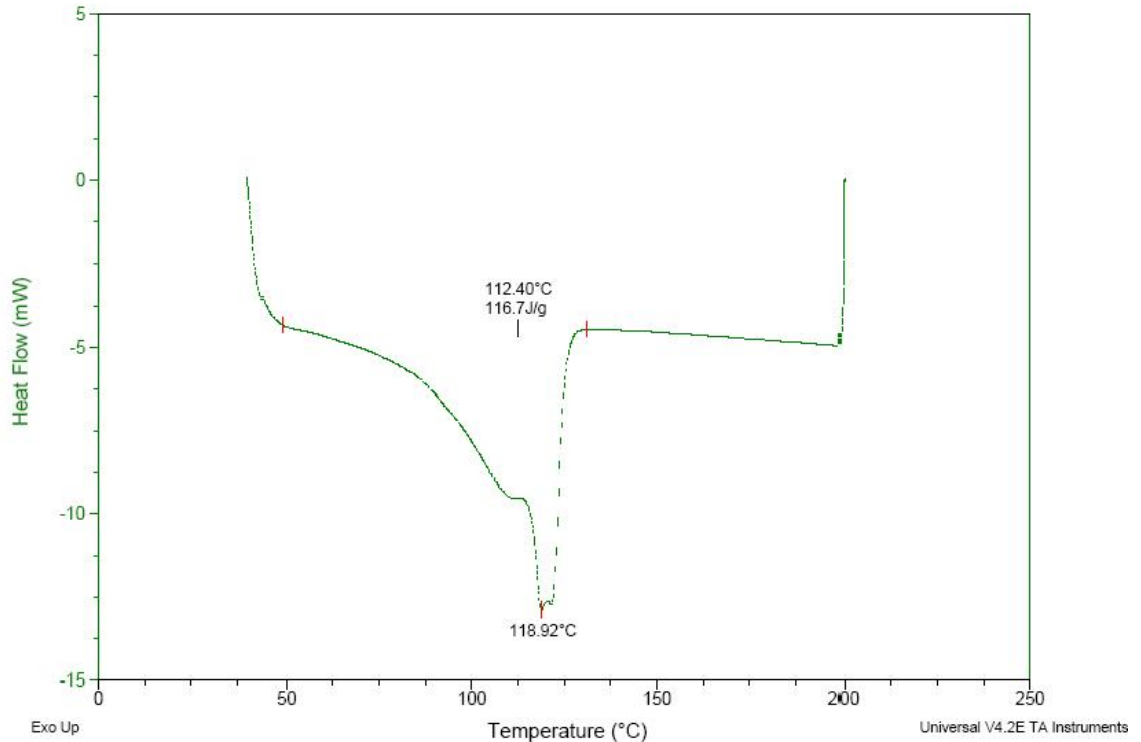


Figure 3 Thermal Profile for LDPE

We also note that the dip for LDPE is not a single distinctive peak because the crystallization of the polymer was non-uniformly distributed which leads to some parts melting faster than the others. Also, the existence of branching and sub-branching contribute to different dips in the melting point. Another major fact is that different arrangements and different molecular weights of the polymer can change the way the dips appear in the DSC profile.

9. Questions

1. *What were the sources and approximate magnitudes of uncertainties in your various experiments?*

We identified three different sources of uncertainty.

First, there is the natural uncertainty (both random as well as systematic) associated with any equipment. There is going to be some amount of uncertainty in the measured weight of the sample because of the analytical balance used. There is also some uncertainty in the heat flow measurements and the temperature measurements using the thermocouple.

Second, the LDPE we were provided with was not industrial-scale LDPE and therefore may not have been entirely LDPE. There could have been some impurities in them that could induce a modicum of uncertainty in the accuracy of our thermal profiles. These impurities could have also been present in the silicon/sapphire samples.

Third, we assumed that the LDPE polymer was a pure material and not a copolymer or a filled polymer of secondary variety. If this assumption is not correct, we have a source of error in our results and conclusions.

None of these uncertainties are truly large to interfere significantly with the conclusions drawn. The qualitative results drawn still hold true regardless.

2. *What are some of the drawbacks to the DSC method and the samples used in it?*

The biggest drawback to using the differential scanning calorimeter is the cost of instrumentation. The DSC method is also a tedious method and does not allow us to obtain the specific heat capacity of an unknown material quickly. We are required to calibrate the instrument every time of its usage because of changes in background heat flow. This could pose a problem when looking for quick and speedy approximations. Lastly, the material used to find the calibration constant k , sapphire, is expensive to purchase. This means that two labs with identical equipment but using a different calibration material other than sapphire may obtain unequal numerical results.

3. *State another technique that could be used to determine the degree of crystallinity of a polymer.*

A proposed technique that can be used to determine the degree of crystallinity of polymers is to exploit the characteristics of their mechanical properties versus changes in temperature. This analysis can be done by comparing the modulus of elasticity of an unknown sample to a known reference sample at certain temperatures.

Polymers can have different proportions of amorphous regions. In this analysis, a sample polymer of a known crystallinity can be selected to obtain the modulus of elasticity at different temperatures. Then the modulus of elasticity of an unknown sample can also be tested at these same temperatures and be compared to the known sample. Depending on the difference, another known sample can be used to generate a profile resembling the unknown sample. By successive trials, the range of crystallinity can be narrowed down and a certain value of crystallinity can be approximated for the sample.

If the experimentalist already has a pre-conceived idea about the range of crystallinity in the unknown sample, the number of temperatures at which the

comparisons are made can be reduced to two or three temperatures to make the process faster. However, for this test to be successful, one major assumption that is made is that the amount of cross-linking in the reference samples is the same because an increased amount of cross-linking can significantly change the profile of a sample with a given amount of crystallinity.

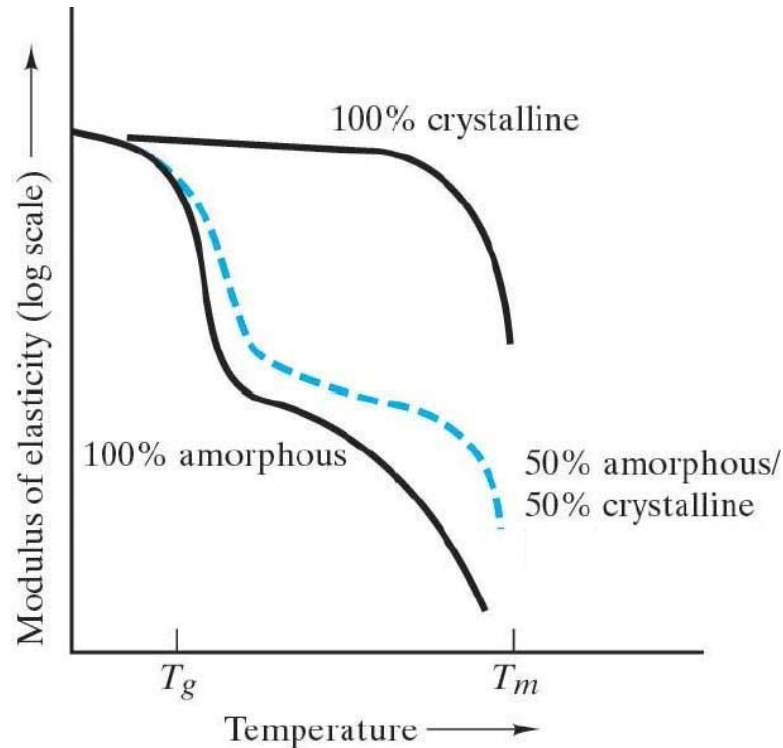


Figure 4 Relationship between Polymeric Crystallinity, Young's Modulus and Temperature (Shackelford, Fig. 6.45)

4. Using what you understand about the way polymer chains behave above and below T_g , why do you think glasses tend to be brittle whereas rubbers are not?

Above their glass transition temperatures (T_g), polymers have molecular chains that are disorganized. These polymers have an appreciable relative mobility above their T_g . At this stage, the polymers become more elastic. Above their glass transition, the secondary, non-covalent bonds between the polymer chains become even weaker, causing the polymer to become highly elastic and rubbery. This is the case of elastomers [4] and rubbers. At room temperature, these materials are found to be much above their glass transition temperatures and hence display high elasticity.

In contrast, ceramics and glasses (that also have also amorphous portions) demonstrate glass transition temperatures much higher than polymers. Below the glass transition temperature, the glass gains a crystal structure and loses its relative mobility. As a consequence, the crystal structure becomes brittle. Since

the crystal groups become strong and form grains, the chances of a fracture propagating through the material become much higher as opposed to when it is in a semi-liquid state. Heating glasses up to high temperatures provides them with elasticity and this phenomenon is used by glass blowers to shape glasses. Also, super cooling to temperatures close to absolute zero brings rubbers around or below their T_g and therefore makes them brittle.

10. Conclusion

From the above results and following discussion, we have seen how one could use a differential scanning calorimeter (DSC) to obtain the specific heat capacity of silicon and sapphire at two different temperatures. We were also able to obtain the melting point of low density polyethylene (LDPE) and the latent heat associated with this transition. We discussed why there was a split in the melting dip for LDPE (Figure 3); why no glass transitions were observed for either silicon or LDPE; why no peaks of crystallization were observed; and why no melting transition dip was observed for silicon.

More results were apparent upon further examination. We found that the specific heat capacity is a function of temperature. This specific heat capacity was found to change significantly after certain critical points in the material's phase cycle. We calculated the melting temperature for LDPE to be around 112.40 °C. The latent heat of melting was estimated to be around 116.7 J/g.

Further analysis revealed sources of error and uncertainty in our various experiments. We also analyzed specific drawbacks to the DSC method and the samples used in it. We discussed an alternative method to determine the degree of crystallinity in a polymer. Finally, we concluded the analysis on our understanding of polymer chains, brittle-to-ductile temperatures and glass transitions to explain why glasses tended to be brittle whereas rubbers were not.

Overall, the experiment was a success. We understood the basic working of a differential scanning calorimeter and discovered new relationships between heating rates and mechanisms of decomposition. This helped reinforce our knowledge on high temperature material decomposition and also provided insight into how scientific experimentation and testing was to be carried out.

11. References

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 - [5] Wikipedia contributors, "Glass Transition Temperature", *Wikipedia*. Retrieved March 13, 2006 from http://en.wikipedia.org/wiki/Glass_transition.
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