DSC - Differential Scanning Calorimetry

Investigation of the Thermal Properties of Polymers

Teaching assistant:
Annika Weiber
Introduction

In this lab you will measure and analyze transitions of the samples you produced in the processing lab by means of DSC. Moreover you will analyze runs on other type of samples.

Thermal analysis (TA) is the common term for measurements of the thermal properties of materials. The area called thermal analysis includes a number of different methods, of which Differential Scanning Calorimetry (DSC) is one of the most commonly used.

Differential Scanning Calorimetry

With a DSC-instrument you can study phase transitions or chemical reactions in a material when it is heated, held at a constant temperature or cooled. A DSC-instrument can schematically be described according to Figure 1.

![Schematic picture of a DSC equipment](image)

**Figure 1** Schematic picture of a DSC equipment

Two platforms are symmetrically positioned in a sample cell in the instrument. One platform is intended for an aluminum pan containing a sample and the other is intended for an empty reference pan. The sample cell is surrounded by a metal shield, which is thermally regulated.

During the measurement, heat flow, Q, is transferred to the sample and to the reference. The difference in heat flow, transferred to sample and reference in order to keep a certain temperature, is constant as long as the sample is not undergoing any transition. However, when the sample undergoes a transition, the heat capacity of the sample is changed. Consequently, the difference in heat flow also changes as the sample undergoes a transition. The heat flow difference is recorded in a computer as a function of temperature, or time, giving a curve, which is called a thermogram.
In a DSC instrument you can analyze samples in the shape of thin films, fibers, powder or fluids. To maintain good accuracy the contact surface between the sample and the aluminum pan should be as large as possible.

With a DSC-instrument you can study transitions in the polymer, such as melting, crystallization and glass transitions. Moreover polymerization and curing can be studied.

**Applications**

**Melting and crystallization**

Melting and crystallization are examples of phase transitions of the first order. This means a transition where the heat capacity as a function of time and temperature exhibits a discontinuity, which has the shape of a peak. The area under the peak in the thermogram is directly proportional to the energy that is emitted or absorbed during changes of state in the sample. The highest point in the peak reflects the temperature or time when the largest part of a sample is melting or crystallizing or when a polymerization or curing reaction occurs at its highest rate.

The crystallinity of a sample is calculated by dividing the enthalpy of melting (the area of the melting peak) with the enthalpy of melting for 100% crystallinity. The latter value can be found in “Polymer Handbook”. Care must be taken not to calculate the crystallinity with the total mass of the sample when additive such as a filler, plasticizer or another polymer is present in your sample.

The crystallinity is dependent on with which rate the sample was cooled during production. Moreover the time at which a polymer is held at its optimal crystallization temperature is important for the crystallinity of a polymer sample. The viscosity of a polymer sample affects the melting and crystallization temperature.

**Glass transition**

On a molecular level the glass transition can be interpreted as the temperature where large-scale motions between the chain segments in the amorphous regions begin. Heating above $T_g$ the material becomes leathery- and rubbery. When the temperature is around 100 °C above $T_g$ the material behaves as a highly viscous fluid.

As opposed to melting of a material, the glass transition is an example of a second order transition. The heat capacity, the temperature derivative of the enthalpy, is changed stepwise.

When heating, the glass transition occurs when the heat capacity of the polymer is increasing to a higher level. However, if the difference in heat capacity is not big enough for your equipment to detect it, one has to use some other type of technique like dynamical mechanical analysis (DMA) to identify the glass transition temperature of the polymer.

Another case where you might have problems in detecting the glass transition temperature is in semicrystalline polymers. In such polymers your glass transition might be broad. This is often due to that the amorphous part in the polymer contains chains that are differently constrained
between the crystals. Chains that have long amorphous parts between the crystals are moving much more easily when they reach a certain temperature whereas chains that are short and constrained between the crystals might need higher energy to reach their glass transition temperature. One way to overcome this is to heat your sample at a higher rate. Thus, the heat flow as function of time gets larger and you will get a more pronounced jump with a higher slope in your thermogram.

Which factors affect the glass transition temperature?
A number of polymer properties that influence $T_g$ have been concluded in Table 1. Moreover the rate at which a sample has been cooled affects the $T_g$.

Table 1

<table>
<thead>
<tr>
<th>Properties that increase $T_g$</th>
<th>Properties that decrease $T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Stiff main chain</td>
<td>- Flexible main chain</td>
</tr>
<tr>
<td>- Bulky/stiff side groups</td>
<td>- Flexible side groups</td>
</tr>
<tr>
<td>- High polarity</td>
<td>- Chain branching</td>
</tr>
<tr>
<td>- Crosslinking</td>
<td>- Addition of plasticizer</td>
</tr>
</tbody>
</table>
Assignments

The equipment used in this experiment is a TA Q2000. All DSC runs will be found under the folder “Polymerfysik”. Instructions of how to handle the computer software “Universal Analysis” will be given by the teaching assistant.

Hand in motivated answers of the assignments together with the analyzed DSC curves within one week to the teaching assistant.

1. Running the DSC equipment

Perform measurements on the samples you prepared in the processing lab. Discuss with the teaching assistant which heating rate, start- and end temperature etc. you should use in order to receive as much information as possible from your measurement.

a) Calculate the crystallinity of each sample. Does the filler or elastomer affect the crystallinity? How do the melt temperature- and crystallization temperature intervals differ for the different samples?

b) What about the crystallinity of EPR?

2. Curing of glue

Evaluate the curing reaction curves for epoxy (glue). Is the curing reaction endothermic or exothermic?

3. The effect of cooling rate on crystallinity

A sample of PET have been annealed and then cooled at different rates (10 °C/min or 200 °C/min). Evaluate the DSC curves and compare the crystallinity and crystallization behavior for the two samples. Explain the differences in relation to cooling rate.

4. The effect of molecular weight and viscosity on the melting temperature, crystallization temperature and crystallinity of PEO.

Poly(ethylene oxide) with different molecular weights, 750 g/mole and 5000 g/mole and 900 000 g/mole have been heated and held isothermally above the melting temperature prior to cooling and consecutive reheating at 10 °C/min.

Which sample has the highest viscosity at room temperature? How does the viscosity affect the melting- and crystallization temperature intervals and the crystallinity?
5. Study the glass transition temperatures for polystyrene in three different materials.

a) PS (Polystyrene)

b) HIPS (High Impact Polystyrene)

c) SIS (block copolymer of 80 weight% styrene-isoprene-styrene and 20 weight% polystyrene)

HIPS consists mainly of polystyrene but also of polybutadiene. Look at the picture of HIPS and combine it with the results of the DSC run.

How does the presence of an elastomer affect the glass transition temperature of polystyrene?

6. Investigate how the $T_g$ of the following polymers is affected by the molecular structure.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>PP (Polypropylene)</td>
<td><img src="image" alt="Polypropylene" /></td>
</tr>
<tr>
<td>b)</td>
<td>PS (Polystyrene)</td>
<td><img src="image" alt="Polystyrene" /></td>
</tr>
<tr>
<td>c)</td>
<td>PVC (Polyvinyl chloride)</td>
<td><img src="image" alt="Polyvinyl chloride" /></td>
</tr>
<tr>
<td>d)</td>
<td>PMMA (Polymethyl methacrylate)</td>
<td><img src="image" alt="Polymethyl methacrylate" /></td>
</tr>
</tbody>
</table>

How do the side groups affect the glass transition temperature of the different polymers?
7. Addition of plasticizer

10 wt% of diethyl bis(hydroxymethyl) malonate (DBM) has been extruded with polylactic acid (PLA). How does the addition of DBM affect the glass transition temperature? Why is it affected in this way?

8. The effect of cooling rate on glass transition temperature

Samples of PMMA have been annealed and then cooled at different rates (3 °C/min or 30 °C/min). How does the cooling rate affect the glass transition temperature? Why is it affected in this way?

9. Investigate how the glass transition temperature of a polymer blend can be calculated with Fox Equation;

\[
\frac{1}{T_g} = \phi_1 \frac{1}{T_{g1}} + \phi_2 \frac{1}{T_{g2}}
\]

\[\phi_1 + \phi_2 = 1\]

\(T_g\) is the glass transition temperature for the blend, \(T_{g1}\) the glass transition temperature and \(\phi_1\) the weight fraction of material 1, and \(T_{g2}\) the glass transition temperature and \(\phi_2\) the weight fraction of material 2.

DSC measurements have been performed on two 50/50 blends of poly(styrene-maleic anhydride) (SMA) and poly(styrene-acrylonitrile) (SAN). According to the theory, SMA and SAN will be miscible if the content of maleic anhydride (MA) and acrylonitrile is about the same in the respective polymers. The content of MA has been varied in the SMA polymer and is 14 or 24 weight% in the blends. The concentration of AN in the SAN polymer is 25 weight% in both blends.

Evaluate the DSC curves for pure SAN 25 and the blends, SMA14/SAN25, SMA24/SAN 25. Which blends are miscible? Explain! Compare the measured \(T_g\)s for the blends with the calculated values according to the Fox equation.

\(T_g[SMA14]=130°C\)

\(T_g[SMA24]=153°C\)