
Characterization of Polymers with Differential Scanning Calorimetry

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1 Introduction

Polymers are in general large molecules composed of bounded monomers with covalent binding. Polymers have a wide range of physical properties, from very soft, rubbery to brittle, depending on the structure or the choice of monomers. Due to this property, they are widely used in every corner of the world, from toys for children to equipment on a spaceship. Considering the structure, most of the polymers are in solid state and can be grouped into three categories, thermoplastic, elastomer and thermoset.

2 Theory

2.1 Thermoplastic polymers

Thermoplastic has a linear or branched shape. Due to lack of crosslinks among the chains, thermoplastic soften and melts on heating, which weakens the inter-molecular force, Van der Waals force.

2.2 Thermal analysis by differential scanning calorimetry

Thermoplastics can be further categorized into two types according to its structure, amorphous or semi-crystalline, due to the incompleteness of crystallization. Semi-crystalline features a fair amount of spatial regularity or strong inter-molecular forces, with the rest of its structure being amorphous domain. These two different domains react differently under heating. This leads to three processes, glass transition, melting and crystallization.

2.2.1 Glass transition

Amorphous domains do not undergo change of phases under heat, therefore the process known as glass transition can't be described with a thermodynamic potential as the other two processes. However, the correlated temperature T_g is used to designate the process, after which an increase in heat capacity can be observed. This is due to the increase of degree of freedom regarding translation caused by weakening of the inter-molecular force. Overall, the glass transition is characterized by rise of the heat capacity.

2.2.2 Melting and Crystallization

Melting and crystallization can only occur to semi-crystalline. Melting can be observed after reaching certain temperature, that the semi-crystalline domain disappears and the polymer becomes liquid. Being a change of phases in first order. Melting can be described with Enthalpy ΔH . Crystallization is the reverse process of melting. These two processes can be easily recognized on the DSC data, being two distinctive peaks. The amount of heat absorbed for melting the crystalline fraction of the polymer can be used to calculate the Crystallinity

$$\chi_c = \frac{\Delta H}{\Delta H_{crystal}} \quad (1)$$

$\Delta H_{crystal}$ is the heat needed to melt the crystal per unit mass.

2.3 Differential Scanning Calorimetry

The DSC furnace contains two positions for samples (1). One serve as reference, which is stable under the pre-programmed measuring process and doesn't under go any thermal changes and the other is the sample to be measured. The DSC measures the amount of heat that is absorbed or emitted by the sample. Processes

such as melting and glass transition are endothermic and crystallization is for example exothermic. The difference between the heat absorbed or emitted by the sample and the references is designated as total heat flow $\Phi = \Phi_s - \Phi_r = -K(T_s - T_r)$, K is a constant which can be determined by calibration. To be specific, DSC measures the temperature difference of two samples by a thermopile sensor, giving the differential thermocoupled voltage. It is then converted into Watt per unit time by the instrument.

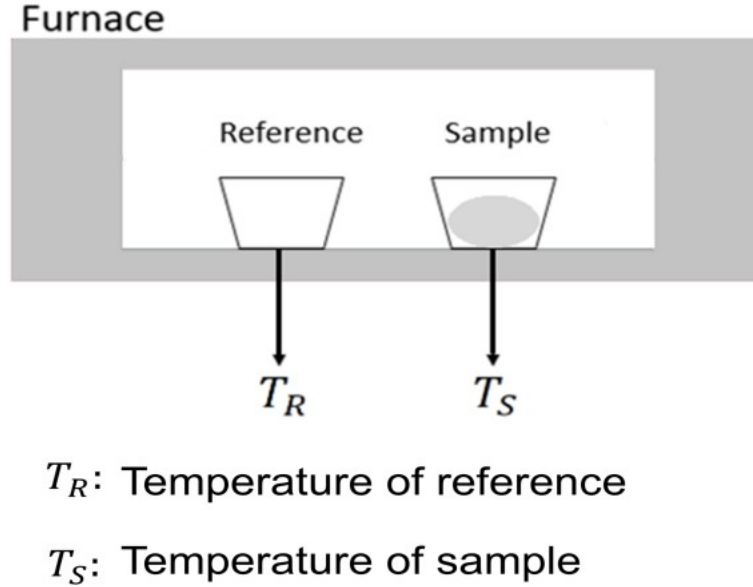
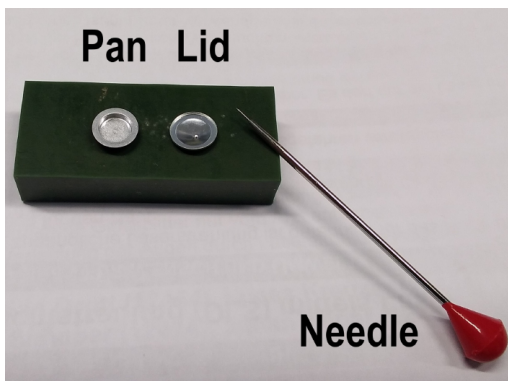


Figure 1: Scheme of a DSC apparatus

3 Experimental procedure

The DSC experiment is done on three different samples—polypropylene (PP), poly methyl methacrylate (PMMA) and polyvinyl chloride(PVC)—under different temperature ranges. The relevant measurement parameters are given in table 1.

First, the samples have to be weight using a micro balance, where sample masses around 5 mg around employed. The sample will be put on a 40 μ L aluminium pan (figure 2a) , which doesn't undergo any physical transition in our temperature range of interest. The lid of the aluminium crucible has to be pierced with a needle to ensure direct contact between the furnace atmosphere and the sample; the hole also counteracts pressure build up in the crucible when heating up the sample. At last, the crucible is sealed using a press and then put into the DSC chamber (figure 2b).



(a) 10 μL aluminium crucible with hole in the lid.



(b) Press to seal the crucible with the sample.

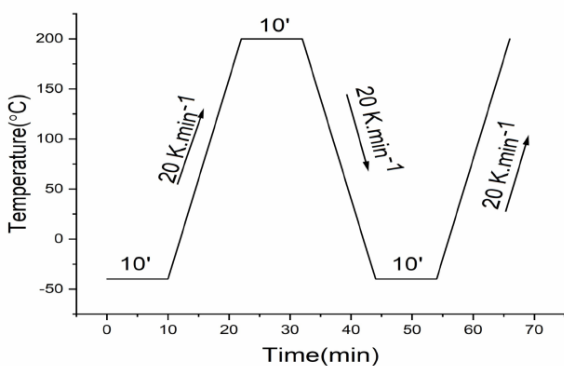
Figure 2: These figure are taken from the instruction manual of the experiment.

To prevent unwanted reaction between the sample and the atmosphere, we create a dynamic inert atmosphere in the DSC chamber with N_2 gas with a flow of $50 \frac{\text{ml}}{\text{min}}$.

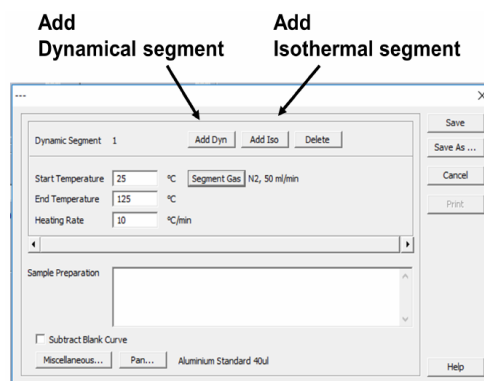
Next step is to set the temperature program at predetermined temperature ranges and scan rates (figure 3a) in the software program "METTLER TOLEDO" (figure 3b). In case of the DSC, three dynamic segments—two heating runs and one cooling—are programmed, each separated by an isothermal segment of 10 minutes.

Note, that the first heating run only erases the thermal history prompted by the processing of the polymer. The thermal history can possibly lead to changes of the glass transition temperature and the crystallinity of the polymer and will not be considered for data treatment.

Only the second heating run and the cooling run is be considered for data treatment, since these reveal the characteristic properties of the polymer.



(a) Temperature program in the DSC experiment.



(b) User interface of the METTLER TOLEDO software.

Figure 3: These figure are taken from the instruction manual of the experiment.

Table 1: Measurements and relevant experimental data of for the studied polymers.

Polymer	m_{Sample} [mg]	T_{range} [°C]	Scan rate [$\frac{K}{min}$]	N ₂ flow [$\frac{ml}{min}$]
Polypropylene (PP)	4.4	[-40, 200]	20	50
Polymethyl methacrylate (PMMA)	5.0	[70, 170]	20	50
Polyvinyl chloride (PVC)	5.3	[40, 130]	20	50

4 Analysis & Results

4.1 Structure of the polymers

The structure of the polymer can be deduced from the characteristic Φ - T curve. Semi-crystalline have additional crystalline regions in between amorphous regions, which means there is additional bonding energy (because of Van-der-Waals forces) between the ordered polymer chains that the increase the overall internal energy (Enthalpy), H , of the polymer. Since $H \propto \int \Phi dt$, we can assume, that heat flow Φ increases sharply at the temperature, where the crystalline regions are broken and the inner energy is released. This means, semi-crystalline polymers have a melting and crystallization peak, and amorphous polymers do not.

From this explanation, we can deduce that PP is a semi-crystalline polymer, and that PMMA and PVC is an amorphous polymer.

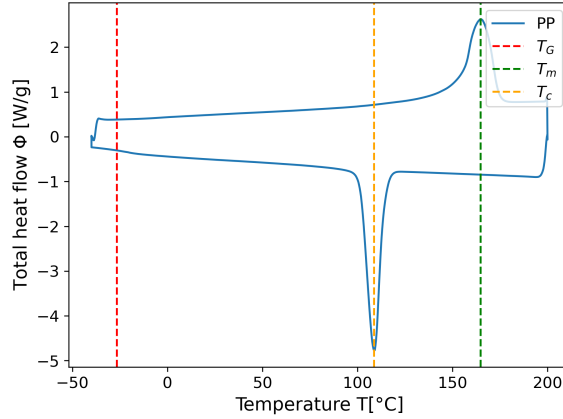
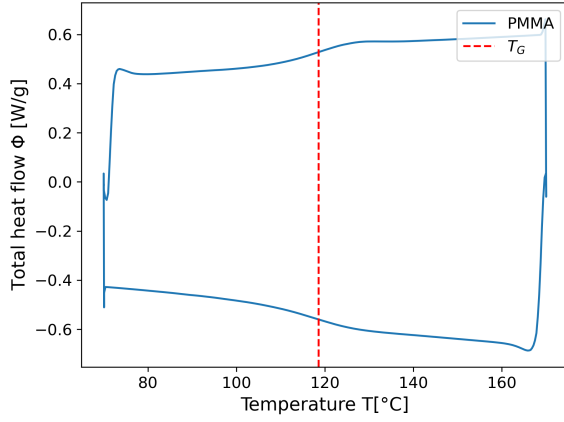
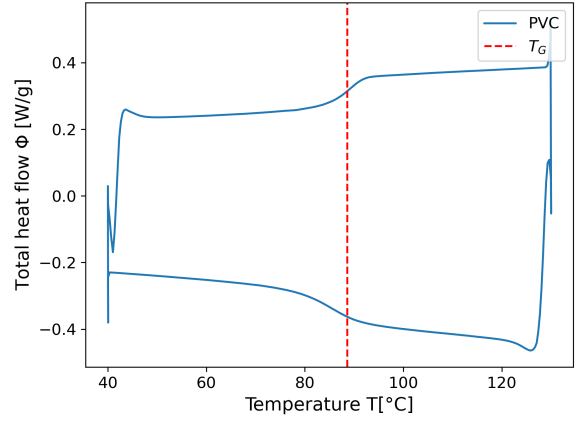


Figure 4: Characteristic Φ - T curve of PP. Because there are significant peaks in this plot, PP is a semi-crystalline polymer.



(a) Characteristic Φ - T curve of PMMA.



(b) Characteristic Φ - T curve of PVC.

Figure 5: These plots show no significant peaks, therefore PMMA and PVC are amorphous polymers.

4.1.1 Characterization of the amorphous polymers

Amorphous polymers can only undergo glass transition phase change, which means there is a sudden, endothermic step-like increase in the heat flow. We can determine the glass transition temperature, T_G , with the midpoint method. First, we look at a subset of the data, which includes the endothermic step-like increase of the heat flow. If we take in the first and last heat flow data point and their corresponding temperatures, T_1 , T_2 , we can find the midpoint temperature with

$$T_m = \frac{T_1 + T_2}{2}. \quad (2)$$

This results in the following glass transition temperatures for PMMA and PVC:

$$\begin{aligned} T_G^{PMMA} &= 118.56^\circ\text{C} \\ T_G^{PVC} &= 88.61^\circ\text{C} \end{aligned}$$

4.1.2 Characterization of the semi-crystalline polymer

Different from PMMA and PVC, as one can already tell from figure (4), PP belongs to semi-crystalline with two distinct peaks, corresponding to melting and crystallization. The correlated temperature read

$$\begin{aligned} T_m &= 164.815^\circ\text{C} \\ T_c &= 108.786^\circ\text{C} \end{aligned}$$

Following the same method as for PMMA and PVC, the glass transition temperature of PP yields

$$T_G^{PP} = -26.64^\circ\text{C}$$

As for the peaks, we first set the onset and offset points for the peaks and do a curve fit with a polynomial function in third order(2), which serves as baseline (6a) and (6b). Then the raw data of heat flow is subtracted with the baseline, which provides corrected signal without background. The melting/crystallization Enthalpy

ΔH can be obtained with an integral over the time. In this case simply a numeric sum of the heat flow between on-/offset points.

$$\Delta H = \int_{t_i}^{t_f} \Phi dt \quad (3)$$

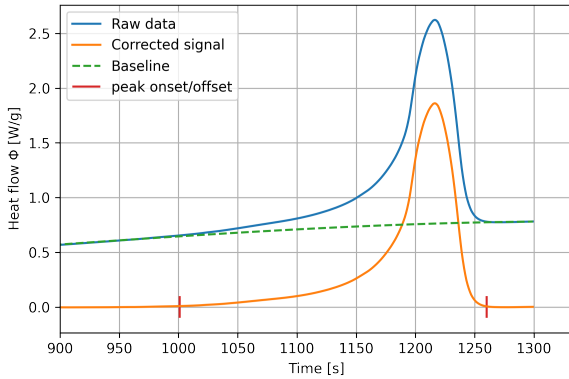
As final results we have

$$\Delta H_{melting} = 102.468 \frac{\text{J}}{\text{g}}$$

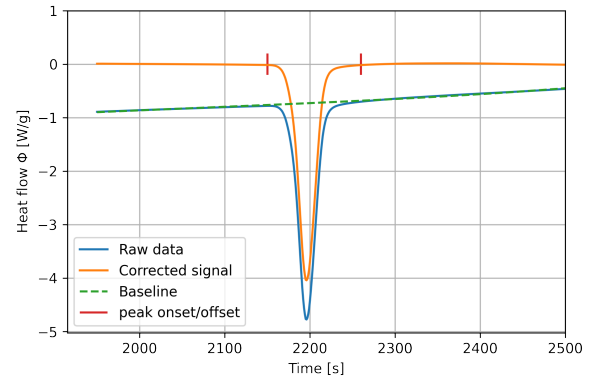
$$\Delta H_{crystallization} = -101.117 \frac{\text{J}}{\text{g}}$$

the negative pre-factor stays for emitting heat. Just as expected, both value don't differ much from each other. To evaluate the crystallinity ω_c of the substance, we have to compare the melting Enthalpy of the sample with the Enthalpy of an ideal crystalline[1], which gives

$$\omega_c = \frac{\Delta H_m}{\Delta H_{m,o}} = \frac{102.468}{207} = 49.502\% \quad (4)$$



(a) Melting



(b) Crystallization

Figure 6: Baseline subtraction from raw data of PP

Fit parameters	a	b	c	d
Melting	$-1.142 \cdot 10^{-9}$	$2.937 \cdot 10^{-6}$	$-1.746 \cdot 10^{-3}$	$5.962 \cdot 10^{-1}$
Crystallization	$9.901 \cdot 10^{-10}$	$-6.133 \cdot 10^{-6}$	$1.332 \cdot 10^{-2}$	-10.907

Table 2: Fit parameters for baseline fit with $ax^3 + bx^2 + cx + d$

5 Short Questions

1. In the plots of the DSC results, what does “exo” and “endo” mean? Is it relative to the polymer sample or relative to the DSC instrument?

⇒ Exothermic and endothermic processes correspond to positive and negative heat flow, respectively. It is relative to the polymer sample.

2. Compare the DSC plots from the first heating run with the second heating run of the three polymer samples. Do they provide the same glass transition temperature and melting temperature? Try to give some possible reasons for the difference.

⇒ The first heating run only erases the thermal history prompted by the processing of the polymer. The thermal history can possibly lead to changes of the glass transition temperature and the crystallinity of the polymer.

3. Why does the melting peak (for crystalline polymers) span over a certain temperature range rather than being a sharp peak?

⇒ The breaking of bond between the polymer chains happens continuously piece-wise per monomer by rotating the bond angle between each monomer in the chain away from neighboring chains. Since the intramolecular force between the chains is dependant on the distance, this increases the released energy continuously monomer by monomer. If the heat flow were to peak like a delta function at the melting temperature, all the bonds between the polymer chains had to have been broken in an instant, which would break the speed of light barrier.

4. Provide the definition of heat capacity.

⇒

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{V,N} = \left(\frac{\partial E}{\partial T} \right)_{V,N} \quad \text{heat capacity with constant volume}$$

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_{p,N} = \left(\frac{\partial H}{\partial T} \right)_{p,N} \quad \text{heat capacity with constant pressure}$$

5. Looking at the heat flow rate curves of the second heating run, does the heat capacity increase or decrease, after the temperature is increased from below to above T_g ? What is the reason for this decrease/increase?

⇒ The heat capacity increases for all of the three samples. Since the glass transition temperature T_g of three samples are mostly in high temperature region ($T > 300K$), even for amorphous polymer, the tunnel effect plays a non-distinctive role. Thus consider the high temperature limit case of Debye model for specific heat capacity, to be specific Dulong-Petit-law $C_v = 3pN_A k_B$, after glass transition, the mobility of polymer chains increases, which corresponds to a higher degree of freedom. This leads to a higher heat capacity.

6. Try to find the heat capacity of polymers, wood, glass and metals, and sort the values. Which one is the largest and which one the smallest? How can the difference of heat capacity be felt, when we hold the materials in our hands?

⇒ As listed in the following table, wood has the highest specific heat capacity, whereas stainless steel the smallest. This reflects in daily experience, that metal changes its surface temperature more rapidly than wood when exposed to environment with temperature difference. So to speak, If we take a piece of metal and wood outdoor in winter, metal would feel much colder than wood in the hand.

material	polymer (polystyrene)	wood	glass	metal (stainless steel)
specific heat capacity [$\frac{J}{kg \cdot K}$]	1130	2301	840	502

Table 3: Specific heat capacity of different materials [2]

7. Based on the experimental results, which polymers among the three are glassy, and which ones are more fluid-like at room temperature? Try to explain how T_g affects the applications of these polymers. \Rightarrow PP has the lowest T_g , which means it is most elastic under room temperature, whereas PMMA has the highest T_g makes it more brittle. PP can be used for manufacturing textile. PMMA on the other hand, is often used as substitute to glass, for it is well-known as plexiglass. PVC in between is often used for pipelines.

6 Literature

References

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