

Determination of peak base line for semicrystalline polymers

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Abstract

To determine heats of fusion a base line is necessary. A DSC measures the heat flux into a sample, which is the sum of a part based on the excess enthalpy and another resulting from the heat capacity, which is the base line. The temperature dependences of these two parts describe the complex changes in morphology during the melting process.

A method for determination of the heat capacity part of the sample is proposed. It is based on an one dimensional three phase layer stack model. First results on different polyethylenes are represented.

1. INTRODUCTION

For several years Differential-Scanning-Calorimeter (DSC) has been available in physical chemical and industrial research. One of the main tasks of these calorimeters in the analysis of melting curves is the determination of heats of fusion. This is gotten from the area of the transition peak. To get a reliable value for this area it is necessary to determine an exact base line.

The DSC measures the heat flux Φ into the sample. This is the superposition of one part based on the heat capacity Φ_c and another resulting from the excess enthalpy Φ_H .

$$\Phi = \Phi_c + \Phi_H \quad \Phi_c = m \cdot c_p \cdot \frac{dT}{dt} \quad \Phi_H = m \cdot \frac{d\Delta H}{dt} \cdot \frac{dT}{dt} \quad (1)$$

Φ_c , the part arising from the heat capacity, characterises the unknown base line under the peak. That's why it is necessary for determination of the heat of fusion to calculate the heat capacity curve in the melting range to get the base line.

There are several methods in use to determine this base line. One of them is to carry out a linear interpolation of c_p between two points before and after the peak [1,2]. This method is also directly applicable to the heat flux curve. It is reliable for substances,

having negligible changes in $c_p(T)$ during the phase transition and a small temperature difference between peak-onset and peak-offset [3] temperature.

But there are also substances like polymers with broad transition peaks. In such substances there are lamellae with various thicknesses. The melting temperature of these lamellae depends on the thickness of them. Furthermore there is also a significant change in heat capacity during the broad phase transition. In this case it is impossible to get reliable results for heats of fusion with the above described method, because the obtained heat of fusion is dependent on the arbitrary chosen points of the linear interpolation.

BLUNDELL [4] suggested to use a linear extrapolation of the heat flux curve from the melt as the base line [Fig.1]. With this method we get a point of intersection at T^* between the measuring curve and the base line [Fig. 1]. This point occurs because the heat capacity curve extrapolated from the melt is that of the liquid state [5]. But the real heat capacity curve of a semicrystalline polymer lies between those of the solid $c_p^s(T)$ and the liquid $c_p^l(T)$ state [5,6] because the sample is a mixture of both states. This may be described by eq. (2) [7]

$$c_p(T) = \gamma(T) \cdot c_p^L(T) + (1 - \gamma(T)) \cdot c_p^S(T) \quad (2)$$

where γ is the liquid fraction.

So the heat capacity curve extrapolated from the melt is too high and the heat of fusion calculated above the point of intersection has a too low value. It may be corrected by adding an enthalpic part determined at temperatures below T^* [1,8]. This part is the area A_2 in Fig. 1. The results with this method are more analyst-independent as the results from the first one are [1]. But since the base line extrapolated from the melt lies too high, there are some facts against this method of base line determination: (i) a correction of the obtained heat of fusion is necessary [1,8, Fig.1]. But the amount of this correction depends on an arbitrary chosen starting temperature T_1 [Fig.1]. (ii) the extrapolated $c_p(T)$ curve at low temperatures lies above the measured curve [Fig.1]. This is not possible for endothermic processes, because the measured value is the sum of a c_p part and an excess enthalpic part for each temperature. (iii) the $c_p(T)$ function is not linear thus the linear extrapolation from the melt is.

That's why we recommend another method for base line determination which is based on an one dimensional three phase layer stack model, like it is common for the interpretation of Small-Angle-X-Ray-Scattering (SAXS) measurements on polymers. All information needed to determine the base line is available from this model. Furthermore the melting behaviour can be described with this method. At least first results on different polyethylenes will be presented.

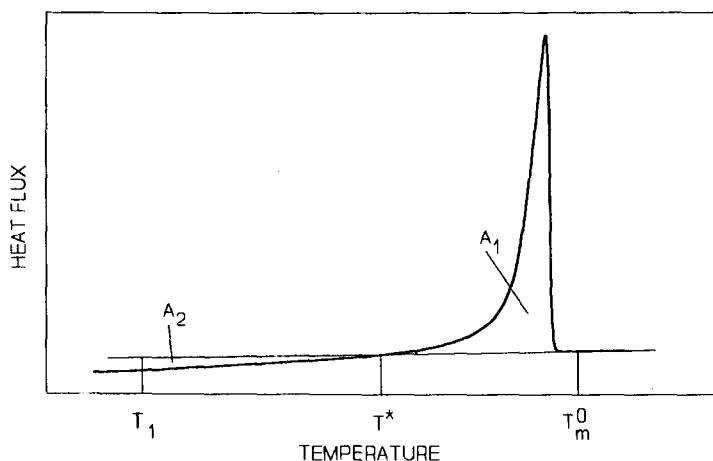


Figure 1. Heat flux curve and the base line extrapolated from the melt. A_1 is the peak area. A_2 is a correction term for heat of fusion

2. MODELL

A one dimensional three phase layer stack modell [9,10] is used as the structural modell. It is distinguished between the crystal lamella with the thickness d_c , the interfacial layer with the thickness d_i , and the melt like amorphous layer with the thickness d_a . In this modell the lateral dimension of a layer is much larger as its thickness is.

Then the thickness of the layers can be determined by $d_c=L\cdot\alpha$, $2\cdot d_i=L\cdot\beta$ and $d_a=L\cdot\gamma$ [10, Fig.2]. Thus the proportion of the fractions of lamella and interface equals the proportion of their thicknesses:

$$\frac{\beta(d_c)}{\alpha(d_c)} = \frac{2\cdot d_i}{d_c} \quad (3)$$

The material in the interfacial layers is in the rigid amorphous state. The interface of a lamella is formed together with the lamella during the crystallisation process. It contains e.g. refoldings, loops and branchings, which are not crystallisable. They are not part of the crystal lamella but coupled to it. This coupling is the reason for the

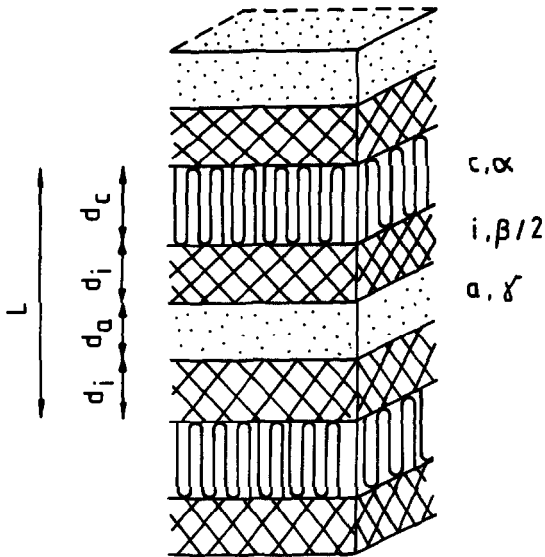


Figure 2. Stack of lamellae in semicrystalline polymers. c: crystalline layer; i: interfacial layer; a: amorphouse layer; α , β , γ : respective volume fractions; L: longperiod $L=d_c+2 \cdot d_i+d_a$;

hindering of molecular mobility. During the melting of the lamellae, this hindering of molecular mobility will disappear, Thus the interfaces of the lamellae will change from the glassy to the liquid state. This process may be considered as similar to a glass transition.

3. METHOD

Like mentioned above the $c_p(T)$ part of the curve yields the base line below the transition peak. It is the superposition of the heat capacity curves of the solid and liquid state [7, Eq. 2]. For every temperature T the solid fraction $1-\gamma(T)$ in eq.(2) is the sum of the lamellar part $\alpha(T)$ and the interfacial part $\beta(T)$. The specific heat capacity of the rigid amorphous interface and its temperature dependence is considered to be the same like that of the crystalline one.

The melting behavior of the sample can be described, if eq. (2) for the whole temperature range is known. The following options are used to calculate $c_p(T)$ from this equation:

- (i) All material is liquid ($\gamma=1, \alpha=0, \beta=0$) at temperatures up from maximum melting temperature T_m^0 .
- (ii) The temperature dependences $c_p^l(T)$ and $c_p^s(T)$ are known [5,6].
- (iii) The layer modell described above [Fig. 2] is applicable to the substance in question.
- (iv) The lamellae melt successively according to their thicknesses and no recrystallisation occurs during the melting process.
- (v) The exess enthalpie part Φ_H is considered to be zero at the starting temperature T_λ . That means $c_p(T_\lambda)$ can be measured directly.

Consider a small temperatur intervall T_1 to T_2 . The increase of liquid material within this intervall is equal to the decrease of the solid one:

$$\gamma(T_2) = \gamma(T_1) + \Delta\alpha_{1|2} + \Delta\beta_{1|2} \quad (4)$$

The decrease of the crystalline fraction $\Delta\alpha_{1|2}$ is determined from the exess enthalpie.

$$\Delta\alpha_{1|2} = \frac{\Delta h_m(T_{1|2})}{\Delta h_m^0(T_{1|2})} \quad (5)$$

In eq.(5) the temperature dependence of Δh_m^0 [5] has to be taken into account. The decrease of the interfacial fraction follows from the layer-stack modell [Eq.3, Fig. 2]. All interfacial layers of lamellae are assumed to have the same thickness independent of the thicknesses of the lamellae. Then eq. 3 reads

$$\Delta\beta_{1|2} = \frac{2 \cdot d_i}{d_c(T_{1|2})} \cdot \Delta\alpha_{1|2} \quad (6)$$

The thickness of the lamella $d_c(T_{1|2})$ melting at the temperature $T_{1|2}$ in eq. (6) may be described by the THOMSON-equation [11], if option (iv) is fulfilled.

$$T_m(d_c) = T_m^0 \cdot \left(1 - \frac{2 \cdot \sigma_e}{\Delta h_m \cdot d_c}\right) \quad (7)$$

The quotient $2\sigma_e/\Delta h_m$ is taken as constant [12].

From eqs. (5), (6) and (7) follows

$$\Delta\gamma_{1|2} = \gamma(T_2) - \gamma(T_1) = \left(1 + \frac{2 \cdot d_i}{d_c(T_{1|2})}\right) \cdot \frac{\Delta h_m(T_{1|2})}{\Delta h_m^0(T_{1|2})} \quad (8)$$

and thus

$$c_p(T_2) = (\gamma(T_1) + \Delta\gamma_{1|2}) \cdot c_p^L(T_2) + (1 - \gamma(T_1) - \Delta\gamma_{1|2}) \cdot c_p^S(T_2) \quad (9)$$

Eq. (9) gives the value of c_p at the upper temperature T_2 of the chosen interval and so the basis for calculations within the next one. Starting at a temperature T_A , where $c_p(T_A)$ is measured directly and $\gamma(T_A)$ is known from eq. 2, the temperature dependences of c_p and γ may be calculated successively. Since, at the beginning of iterative calculation, the interfacial thickness d_i is not known, it has to be chosen arbitrary. With this starting value, the calculated γ is usually not unity (option (i)). That's why the base line calculation has to be iterated with various interface layer thicknesses, until this option is fulfilled. Then $c_p(T)$, the liquid fraction $\gamma(T)$ and the interfacial thickness d_i are known. The curves for the crystalline fraction $\alpha(T)$ and the interfacial fraction $\beta(T)$ are calculable backward from the melt, (where $\gamma=1$, $\alpha=0$ and $\beta=0$) using eq. (6), the $\gamma(T)$ curve and the interfacial thickness. Thus the base line below the peak is determined and the melting behavior of the sample may be described.

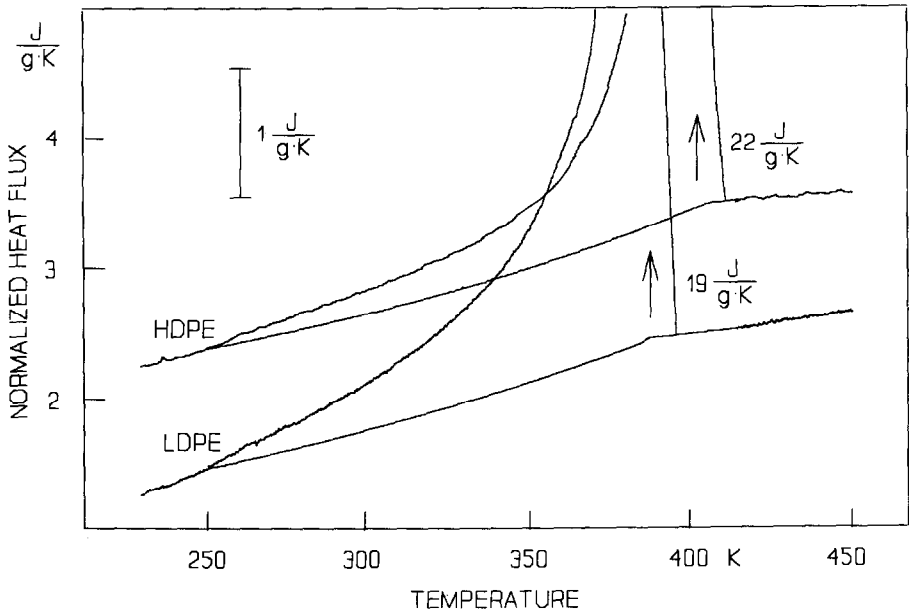


Figure 3. Normalized heat flux curves and calculated base lines of HDPE and LDPE. The curves of HDPE are shifted by $1 \text{ J}/(\text{g}\cdot\text{K})$. The arrows mark the peak maxima of the normalized heat flux curves.

4. RESULTS

The described method for base line calculation was tested on different polyethylenes. The values used for $c_p'(T)$ and $c_p^s(T)$ functions were taken from MATHOT [5]. The starting temperature for the base line calculation was $T_A=250$ K. This temperature is likely above the region of glass transition [13]. So it may be assumed, that the excess enthalpie part of the curve is zero at this temperature.

The measurements were carried out with a Perkin-Elmer-DSC-2. The calorimeter was controlled by an PC AT-286 [14]. The measurements were performed in the temperature range from 220 K to 450 K with a scanning rate of 10 K/min. The block was cooled with a mixture of ethanol and solid carbon dioxide.

Fig. 3 shows the normalized heat flux curves and the calculated base lines for a HDPE ($\rho=0.957$ g/cm³, 0,48 CH₂/100 C) and a LDPE ($\rho=0.929$ g/cm³, 1,88 CH₂/100 C). The iteration yields an interfacial thickness of 1.3 nm for HDPE and 1.6 nm for LDPE. This is in agreement with theoretical values [15] and such measured by SAXS [16]. The base lines are no linear functions of temperature. The more material melts the greater slope of the base line is obtained.

It is recognizable in Fig. 3, that melting occurs in both samples already below room temperature. This is also illustrated in Fig. 4, where the temperature dependence of the fractions of different molecular mobilities are shown.

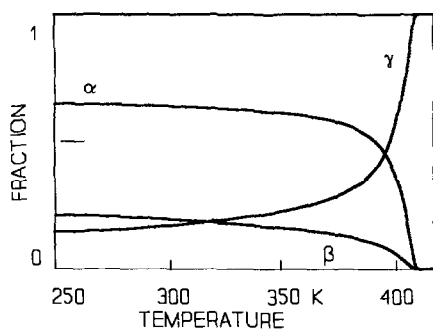


Figure 4a. Temperature dependence of the volume fractions of HDPE; α , β , γ see text.

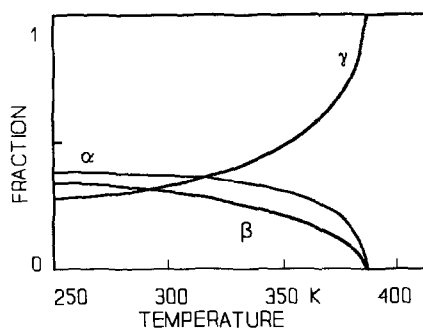


Figure 4b. Temperature dependence of the volume fractions of LDPE; α , β , γ see text.

In the temperature range of 250 K - 360 K the decrease of the crystalline fraction is about 0,05 for HDPE [Fig. 4a] and 0,10 for LDPE [Fig. 4b].

The crystalline fraction $\alpha=0,65$ at 250 K for HDPE is about 0,03 lower than those calculated with a base line linear extrapolated from the melt (method 2), and about 0,17 lower than those from the linear interpolation method. For LDPE the respective differences are about 0,02 and 0,23.

5. CONCLUSIONS

The presented method for base line calculation yields the temperature dependence of the fractions of different molecular mobility and the thickness of the interfacial layer as additional results. The calculated crystallinities are not very different from those gotten with the method of MATHOT. The main result from our method is the temperature dependence of the fractions of different molecular mobility. This may be useful for investigations of structure-property-relations of polymers. A more exact calculation of the lamellar thickness distribution is possible.

6. ACKNOWLEDGEMENT

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