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TEMPERATURE DISTRIBUTION IN POLYMER SAMPLES DURING DSC-SCANS

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Abstract

Differential Scanning Calorimetry is frequently used for measurements of thermal properties on all kinds of substances. The temperature lag in the samples depend on the thermal properties and the thermal contact between sample and sample holder. In the paper, we discuss the temperature distribution in samples of comparatively low thermal conductivity, such as polymers. The purpose of this study is to pinpoint the substantial temperature differences that may occur in such bad conducting samples under different conditions. The calculations of the temperature gradients have been carried out by using a finite element software package.

Keywords: DSC, finite element method, temperature gradients, polymer

Introduction

A differential scanning calorimeter (DSC) is usually operated with the sample in an aluminium capsule. The sample capsule is then placed in the DSC sample holder. The temperature at the bottom of the sample holder changes linearly during the scan, however, how the temperature in the sample follows this change and the amount of lag is generally not asked. The temperature distribution in a sample during the DSC scan depends on the inherent sample properties, such as specific heat capacity, thermal conductivity and possible sample reactions. The scanning rate, sample thickness and the contact areas between the sample and the bottom of the capsule holder are also important. Samples with high thermal conductivity, such as metals, have usually uniform temperature distributions, while for organic substances large temperature differences may arise in the sample. The effect of the temperature lag on the calculation of thermodynamic functions, such as specific heat capacity, is discussed by Höhne [1], Schawe and Schick [2] and also in a review by Sarge with co-workers [3]. A theoretical treatment of a power compensated DSC is done by Hoff [4], who gives analytical solutions of the heat conduction equation for some different conditions. In this paper we show and discuss the temperature distribution in polymer samples for some different realistic DSC cases, which include crystallization and thermal resistances between sample and sample holder.

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Results and discussion

The circular design of the DSC sample holder and sample capsule reduces the three dimensional problem to a two dimensional with axial symmetry. Using this approach, we write the partial differential equation, that governs the heat conduction, in cylindrical coordinates (r, z) [5, 6] as follows:

$$\rho c_p \frac{\partial T}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}\left(-kr\frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial z}\left(-k\frac{\partial T}{\partial z}\right) = 0 \qquad (1)$$

Here ρ is the density, c_p the specific heat capacity, k the thermal conductivity, T the temperature and t finally the time. The calculations of the temperature profiles are done, according to the above equation with boundary conditions, by using the software PDEase® version 2.5 [7] based on finite element analysis and described by Bäckström [6]. The applied boundary conditions consist of a linear temperature change at the bottom of the sample holder combined with no heat flow across the other sides of the sample holder. Further, the start temperature, (at time zero) is 300 K in the entire region. The thermal properties of the sample holder made of an alloy of platinum-iridium are set equal to platinum's. All properties of the polymer sample encapsulated in aluminium are set equal to those of polyethylene. Nitrogen atmosphere surrounds sample and sample capsule. All material properties are assumed to be constant within the narrow temperature range used here. Further, the small contributions from convection and radiation to the heat transfer are neglected. Unless otherwise is mentioned, the scanning rate, i.e. the linear temperature change at the bottom of the sample holder, is 40 K min^{-1}.

In a previous paper [8], we compared the behaviour of metallic and polymeric samples during DSC scans. We found, for a cylindrical shaped polyethylene sample in perfect thermal contact with the surrounding aluminium capsule both from the top and bottom, that the sample temperature is almost identical at the top and the bottom, due to the good thermal conductivity of aluminium. Further, in this case where the sample capsule is in ideal contact with the sample holder, the sample surface has almost the same temperature as the bottom of the sample holder. Steady state temperature gradients were found within 10 s for a scanning rate of 40 K min^{-1} and a sample thickness of 1 mm. The maximum sample temperature difference was about 0.6 K and observed between surface and the centre of the sample. A change in the contact surface, by inserting a space of nitrogen gas of 0.35 mm between the top of the sample and the aluminium capsule, raised the temperature difference close to 1.9 K. This maximum temperature difference was now appearing between the top and the bottom of the sample. In this paper, we have extended the study of temperature gradients in polymer samples. In Fig. 1 we show a symmetry part of the sample holder with sample capsule and sample. The isotherms show the temperature profiles, 10 s after the onset of cooling, in a sample with both top and bottom contact with the capsule. The sample thickness has been reduced by 50% to 0.5 mm (≈5 mg) compared to the sample in our previous paper [8]. This decreases

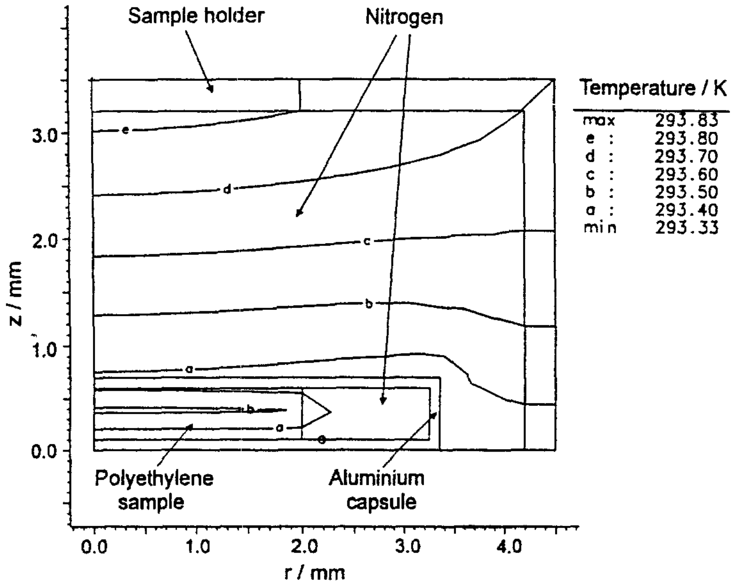

Fig. 1 Cross-section of a symmetry part of the calorimeter sample holder with an aluminium capsule enclosing a polyethylene sample. The sample is in contact with the bottom and top of the aluminium capsule. The isotherms show the temperature distribution 10 s after the onset of a linear cooling rate of 40 K min^{-1} at the bottom of the holder

the maximum steady state temperature difference to about 0.15 K. A nitrogen gas filled space of 0.35 mm between the top of the sample and the aluminium sample capsule increases this temperature difference to 0.55 K, as seen in Fig. 2. Thus, for this thinner, 0.5 mm thick sample, the contact surface between sample and sample capsule is of less importance for the temperature differences than for the 1 mm thick sample. The strong dependence of the sample thickness is readily explained by Eq. (2) below. The equation is valid at the one dimensional heat flow case, for a rod shaped sample heated or cooled from below and adiabatically insulated at the top, and shows the steady state temperature difference between the sample bottom and the sample at a distance z from the bottom [4].

$$\Delta T = \frac{c_p\rho}{k}\dot{T}zd\left(1-\frac{z}{2d}\right) \qquad (2)$$

Here $\dot{T}$ is the scanning rate and d is the sample thickness. Thus, after derivation we find a maximum in ΔT at $z=d$, giving $\Delta T_{\max}=c_p\rho\dot{T}d^2/2k$. We note that the maximum in ΔT depends on the square of the sample thickness. Due to the high conductivity of the aluminium capsule, in a sample having both top and bottom contact, the thermal symmetry halves the thermal sample thickness, and a fourfold decrease is found in the maximum temperature difference. Further, this equation gives maximum temperature differences of approximately 0.6 K and 2.5 K for sample thicknesses of 0.5 and 1 mm respectively. The $\Delta T_{\max}$ values are compared with the maxi-

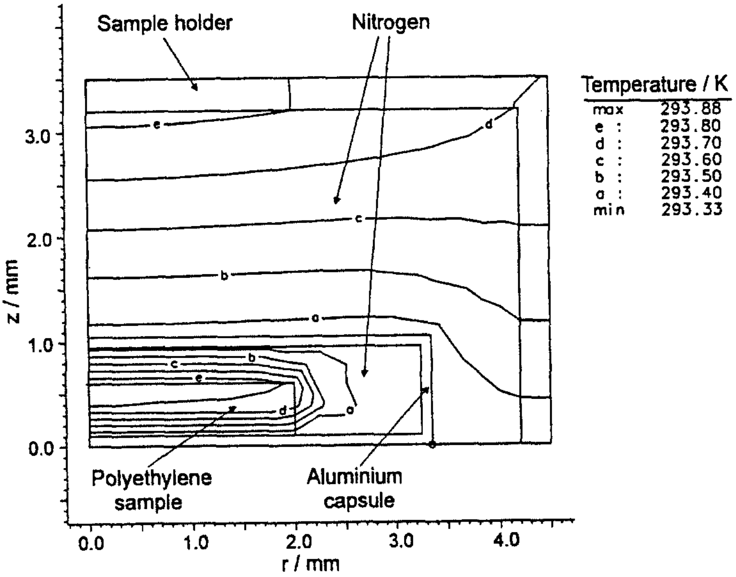

Fig. 2 Cross-section of a symmetry part of the calorimeter sample holder with an aluminium capsule enclosing a polyethylene sample. The sample is only in contact with the bottom of the aluminium capsule. The isotherms show the temperature distribution 10 s after the onset of a linear cooling rate of 40 K min^{-1} at the bottom of the holder

mum differences of about 0.55 and 1.9 K found from finite element analyses. The differences are mainly due to the non adiabatic condition at the top end of the sample, and the results agree if the boundary conditions at the sample top are changed to almost adiabatic. This is easily done by increasing the space between the sample top and sample capsule or decreasing the thermal conductivity of the medium between sample top and sample capsule.

So far, we have assumed ideal thermal contact between sample bottom, sample capsule and sample holder. Good thermal contact between sample and sample capsule can often be achieved by melting and/or pressing the sample into the sample capsule. It is, however more complicated to ensure good contact surface between the sample holder and the sample capsule. According to Janeschitz-Kriegl with coworkers [9] the heat transfer coefficient between sample capsule and sample holder can be deduced from the exponential decay of the heat flow curve on the high temperature side of a melting peak of metal standards. They estimate the heat transfer coefficient to about 0.038 W K^{-1} for a Perkin Elmer DSC-7. Using their value, the heat transfer coefficient is simulated by an extra thermal resistance, introduced as a 0.1 mm thick plate placed between sample holder and sample capsule with appropriate thermal conductivity. This gives an increased maximum temperature lag from 0.15 to about 0.75 K for the case of Fig. 1, and an increase from 0.55 to 1.15 K in Fig. 2. Thus, for polymer samples, the temperature lag within the sample can be of the same order as the one between sample capsule and sample holder.

If a sample exhibits an exothermal reaction, such as a crystallization, the released heat will increase the temperature differences within the sample. In an effort to estimate the effect of a such extra heat flow, on the temperature distribution in the sample during the crystallization, we have added a crystallization term to Eq. (1). Experiments on a 0.5 mm thick sample of polycaprolactone, a semicrystalline linear polyester with similar diffusivity as polyethylene, showed that the measured exothermal crystallization power per unit volume, is described with a Gaussian temperature function. This function is inserted as an extra heat source term into Eq. (1) to describe the progress of the heat released during the crystallization. However, if the nucleation and growth rates of the spherulites are known, a kinetic model for the crystallization could of course be used instead. For this rather fast crystallizing polymer, the functions fitted with and without contact between sample top and sample capsule, are rather similar and we receive the following results. For the case where the sample is in contact with the sample capsule from top and bottom and the capsule is in ideal thermal contact with the sample holder, we get a maximum temperature difference close to 0.5 K. Without this crystallization term, the difference was 0.15 K. For the case where the sample is in contact with the sample capsule from the bottom only we find 2.0 K, to be compared with 0.55 K without the crystallization term. Using the earlier discussed extra thermal resistance, simulating the non ideal contact between sample capsule and

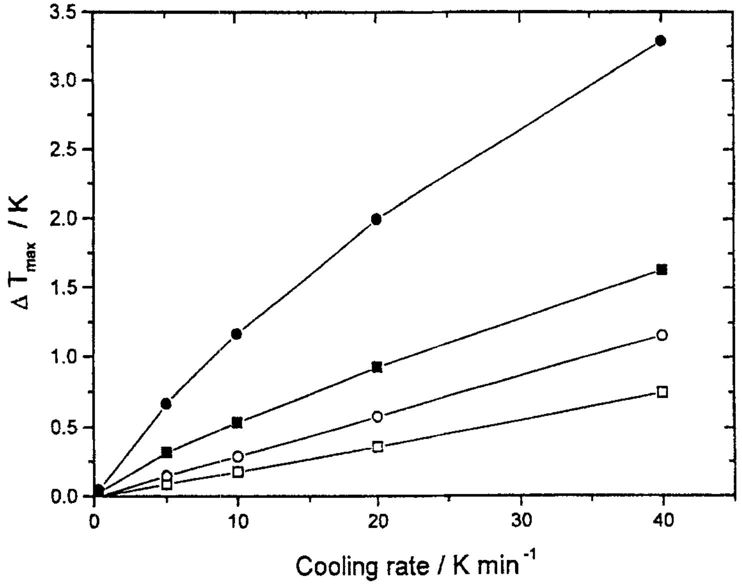

Fig. 3 Maximum temperature difference between the polycaprolactone sample of thickness 0.5 mm, and the bottom of the sample holder *vs*. cooling rate. Included is the thermal lag between sample holder and sample capsule. Labels: Unfilled squares, sample in contact with sample capsule from bottom and top. Unfilled circles, sample in contact with sample capsule from bottom. Filled squares, crystallizing sample in contact with sample capsule from bottom and top. Filled circles, crystallizing sample in contact with sample capsule from bottom. The curves are just a guide to the eye

sample holder, the temperature differences for the two cases discussed increases further to 1.6 K and 3.3 K respectively. It must be emphazised that the used model is empirical, but it does give an estimate of how large the temperature gradients may be during the crystallization. By using a kinetic model for polymer crystallization, with rate equations for the nucleation and growth rates of spherulites, Wu *et al.* [10] have carried out computations of DSC curves for some different heat transfer conditions. For the case where the surfaces of the sample are assumed to follow the temperature of the sample holder, they found, with crystallization parameters for polypropylene and with a sample thickness of 0.3 mm, a maximum temperature difference within the sample of about 0.8 K. In this area valuable work is also carried out by Chan and Isayev [11].

For all cases discussed the scanning rate is very important. In Fig. 3, we show how the maximum temperature difference between sample and sample holder changes with scanning rate for the cases of Figs 1 and 2, with and without the crystallization term. Note that in Fig. 3 is also the effect of the term that takes the non ideal contact between sample holder and sample capsule included. For the cases without crystallization, the temperature difference increases basically linearly with scanning rate as expected from Eq. (2). As mentioned earlier, if the sample capsule is in ideal contact with the holder, the maximum temperature difference within the sample increases with a factor of four, if the sample is in contact with the capsule from bottom only compared to the case with both top and bottom contact. Although, this effect is not explicitly seen in Fig. 3, where we have chosen to show the total maximum temperature lag between holder and sample. However, it is of course found for all scanning rates and, as discussed earlier, due to the high conductivity of the aluminium capsule. Having both top and bottom contact is almost equal to having a sample of half the thickness, but with capsule contact only from the bottom. Since, it is found from Eq. (2), that the maximum temperature difference is proportional to the square of the thickness, this gives a fourfold increase if the sample thickness is doubled. Concerning the cases with crystallization, we find, a similar strong dependence of the contact surface on the maximum temperature differences.

Conclusions

Since, the temperature lag within polymer samples may be of the same order as the temperature lag between sample holder and sample capsule, both should be taken into account. The need for separate temperature calibration scales for each scanning rate is clear, although the thermal resistance between sample capsule and sample holder may vary from capsule to capsule. The contact surface between sample and sample capsule is very important. For samples in thermal contact from both top and bottom, with the highly conductive aluminium capsule, the temperature gradients are substantially smaller than for samples with only bottom contact. This strong dependency is also clear from calculations using Eq. (2), where the temperature difference between sample bottom and the maximum sample temperature depends on the square of the sample thickness. The results show a possibility to improve the temperature calibration during crystallization.

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