QUANTIFICATION OF AMORPHOUS CONTENT IN MALTITOL BY StepScan DSC

Minna Lappalainen and Ilkka Pitkänen[*]

University of Jyväskylä, Department of Chemistry, P.O. Box 35, 40014 University of Jyväskylä, Finland

A method was developed for the quantification of low levels of amorphous content in maltitol with StepScan DSC. The method was based on the fact that the change of specific heat at the glass transition is linearly proportional to the amorphous content. The influence of different measurement parameters of StepScan DSC was evaluated and two different calibration heating rates were tested. Synthetic mixtures with various proportions of crystalline and amorphous maltitol were prepared. Two different measurement methods were compared and the linear regression between ΔC_p and amorphous content was obtained. The limit of detection (LOD) and the limit of quantification (LOQ) values were for the fictive temperature 0.24% (amorphous content) and 0.81% and for the half point temperature 0.27 and 0.92%, respectively, (method 1) and for the fictive temperature 0.18 (amorphous content) and 0.61% and for the half point temperature 0.16 and 0.52%, respectively (method 2). Very low determination limits for the quantification of amorphous content could be attained with the StepScan DSC method. However, the realistic limit of quantification was somewhat higher (about 3%) because of noise in the StepScan measurement. The main advantage of the StepScan DSC method for quantification of amorphous content was that the glass transition and relaxation peaks are separated into different curves and the interpretation becomes easier.

Keywords: *amorphous content, maltitol, StepScan DSC*

Introduction

For the past several years, there has been remarkable interest in modulating or dynamic temperature programs to better separate kinetic and thermodynamic effects and obtain both with greater accuracy [1–7]. Temperature modulated DSC (TMDSC) applies periodic temperature oscillations to the system and analyzes amplitude and phase of the corresponding periodic heat flow rate [1–7]. StepScan DSC is software (PerkinElmer Instruments) for the characterization of the thermal properties of materials [8–16]. For better interpretation the technique permits the separation of DSC results into thermodynamic (reversing) and kinetic (non-reversing) components. StepScan produces a temperature program that consists of a series of short temperature steps [11, 12, 14]. After each step the heat flow is equilibrated until a criterion is satisfied, and then the next step is started. The StepScan DSC approach is only possible with the design of the power compensation DSC, with its very low mass sample and reference furnaces and rapid response time [8, 10, 12]. An empty pan baseline should be run if an accurate C_p is needed [9].

A thermodynamic C_p data set reflects 'fast' or reversible phenomena, such as the sample's heat capacity or T_g. The kinetic or IsoK Baseline data set reflects 'slow' or irreversible processes taking place during the experiment, such as relaxation or crystallization.

The StepScan DSC separates glass transition and relaxation peaks onto two different curves, which simplifies the interpretation and makes the calculation of ΔC_p much easier [9, 10, 12]. The approach used with the StepScan DSC uses either a constant heating rate or an isothermal holding step. The reversing component is only observed in the heating part of the cycle and the non-reversing one only in the isothermal part [8, 13, 14]. The basic equation describing the heat flow response in a StepScan DSC experiment is given as: $dQ/dt=C_p(dT/dt)+K(T,t)$. In this equation, dQ/dt is the DSC heat flow, C_p is the sample's heat capacity, dT/dt is the applied heating rate and $K(T,t)$ is the kinetic component [8, 13].

There are many measurement parameters in the StepScan DSC method. The three most important parameters are the length of the isothermal segment, the temperature jump between two subsequent isothermal segments and the linear heating rate in dynamic segments [13, 14]. There is also a criterion parameter (=criterion to shorten the isotherm) which determines the length of the isotherms [9, 11]. A fine criterion yields accuracy in the measurements while a coarse criterion gives short analysis times. The sensitivity of the measurements can be improved by using a high heating rate or a large sample. The calibration heating rate is recommended to be 2 K min^{-1} because, in spite of a high partial heating rate, the overall heating rate

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[*]   Author for correspondence: ipitkane@cc.jyu.fi

is usually quite slow in StepScan measurements. The heat flow can be calibrated either using the melting enthalpy of calibration standards or the specific heat of sapphire. It has been noticed that it is better to use the same parameter in the calibration as is used in the measurements [17]. In other words, when the glass transition is studied it is better to choose specific heat also for the calibration.

The present study is a continuation of our investigations into the thermal analysis of sugars and sugar alcohols [17–22]. In our previous study we developed a method for quantification of a low amorphous content by HyperDSC based on the fact that the change of specific heat (ΔC_p) at the glass transition is linearly proportional to the amorphous content [17]. The StepScan DSC is said to provide the ability to better determine heat capacity data and improve the sensitivity of T_g measurements. In this study we first varied the StepScan measurement parameters and used different calibration heating rates. Finally, we studied the potential of the StepScan method in the quantification of low amorphous levels in maltitol.

Experimental

Crystalline maltitol with a purity of >98% was obtained from Sigma. It was fully crystalline according to the powder diffraction and DSC measurements. For synthetic mixtures, the amorphous maltitol was prepared from crystalline maltitol by melting it in an oven at 165°C (*m.p.* 150°C) and keeping it at that temperature for 15 min. The degradation temperature of maltitol was checked with TG before the preparation of amorphous maltitol. The bright and colourless liquid was poured onto a cooled metal plate and the plate was put in a desiccator. The desiccator was refrigerated at 5°C at least for 1 h. The final product (glass) was glassy 'pearls'. After cooling, amorphous maltitol was crushed in a porcelain mortar. The amorphous maltitol powder was stored in a desiccator over P_2O_5 at 5°C.

The DSC measurements were performed on a PerkinElmer DSC Diamond using 50 μL aluminium sample cups and 30 μL aluminium cups with capillary holes as covers and a dynamic nitrogen atmosphere with a flow rate of 50 mL min^{-1}. The temperature calibration was carried out by indium and benzoic acid standards, and the heat flow was calibrated by the specific heat of sapphire. The calibration was done with heating rates of 2 and 10 K min^{-1}. The calibration was checked before running samples by measuring the melting enthalpy of indium at the same heating rate as the actual measurements were done.

The influence of the sample analysis parameters was initially investigated to determine the parameter values that resulted in constant values of the ΔC_p. For these measurements, the amorphous maltitol was produced in DSC by heating the crystalline compound above the melting point to 165°C before the measurements. The temperature range was –10–100°C. The parameters used in the different measurements are shown in Table 1. Two parallel measurements were taken at each set conditions. The influence of annealing on ΔC_p was investigated in our earlier study [17] and the annealing temperature of 40°C and annealing time of 60 min were also used in this study as done by Bustin and Descamps [23]. The following temperature program was used to run the experiments: (a) heating from room temperature to the annealing temperature (from 25 to 40°C) at heating rate of 10 K min^{-1} and (b) annealing at 40°C for 60 min, then (c) cooling to the starting temperature (–10°C) at cooling rate of 10 K min^{-1} and finally (d) StepScan measurement over the glass transition region (from –10 to 100°C). Different StepScan programs were

Table 1 The conditions of measurements

Measurement	Temperature increment/°C	Heating rate/K min^{-1}	Isothermal period/min	Criterion/mW
		calibration heating rate 2 K min^{-1}		
1	2	5	1	0.01
2	2	10	1	0.01
3	2	2	1	0.01
4	1	5	1	0.01
5	3	5	1	0.01
6	2	5	1	0.005
7	2	5	0.8	0.01
8	2	5	0.6	0.01
		calibration heating rate 10 K min^{-1}		
9	2	2	1	0.01
10	2	5	1	0.01
11	2	10	1	0.01
12	1	10	1	0.01
13	2	10	1	0.001
14	2	10	1	0.0001

used and their parameters are given in Table 1. In the specific heat calculation from raw data, it was possible to choose either peak height or peak area for the calculations. In this study, the peak area was used.

Two different heating rates were used in the calibration and for that reason two measurement programs were used and compared in the following measurements. For calibrations done at a heating rate of 2 K min^{-1} the temperature program of measurement 3 (=method 1) was used; for calibrations done at a heating rate of 10 K min^{-1} the temperature program of measurement 14 (=method 2) was used.

Synthetic mixtures were prepared by weighing known quantities of amorphous and crystalline maltitol at chosen ratios (3, 5, 7.5, 10, 15, 20, 25, 38, 50, 62 and 80 mass/mass% amorphous content) and by mixing them thoroughly in a porcelain mortar. In addition, 100 and 0% amorphous samples were used. Crystalline and amorphous samples were dried and stored over P_2O_5 before and between preparing synthetic mixtures. The amorphicity was checked by DSC (no melting peak was noticed) before the preparation of each mixture was started. The mixtures were prepared one at a time and measured immediately. Three parallel measurements were taken at each test point. Synthetic mixtures were measured with the above mentioned temperature program using the two methods mentioned earlier and the StepScan parameters of measurements 3 and 14. The sample masses were in the range of 4–6 mg.

Powder diffraction measurements were carried out using a Huber Imaging Plate Guinier camera G670. The X-ray source was germanium crystal monochromatized $CuK_{\alpha1}$-radiation (λ=1.54056 Å) and the X-ray tube was operated at 45 kV and 25 mA. The samples were prepared on Mylar film. The exposure time was 30 min and the imaging plate was scanned six times. ZDS software was used to process the measurement data.

Results and discussion

Influence of the measurement parameters on the ΔC_p

In StepScan measurements, the reversing and non-reversing parts of the components are separated. At the glass transition, the thermodynamic C_p signals show the classic stepwise change in the heat capacity which is simple and straightforward to analyze and interpret. The enthalpic relaxation events, which can occur in physically annealed samples at the glass transition, show up in the IsoK baseline data set. This is illustrated in Fig. 1.

The influence of the measurement parameters of the StepScan DSC method on the shape of the glass
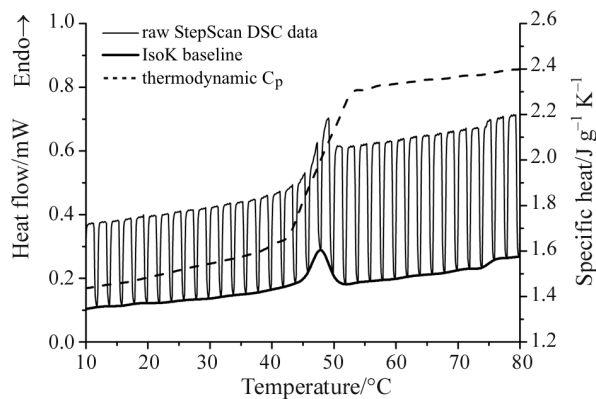

Fig. 1 StepScan DSC results. From the raw StepScan DSC data the IsoK baseline curve and thermodynamic C_p can be calculated. Step size 2°C, heating rate 2 K min^{-1}, isothermal time 1 min and equilibrium criterion 0.01 mW
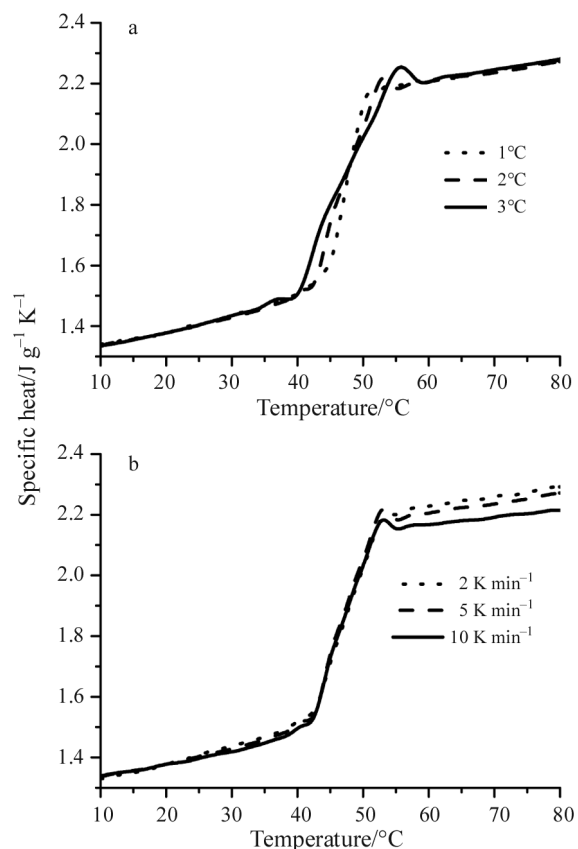

Fig. 2 Influence of the main StepScan parameters on the specific heat curve. a – different temperature jumps, heating rate 5 K min^{-1}, isothermal segment 1 min and criterion 0.01 mW; b – different heating rates, temperature jump 2°C, isothermal segment 1 min and criterion 0.01 mW

transition and the size of ΔC_p was evaluated. This was done by changing one parameter at a time while the others were kept constant. The results of changes of temperature jump and heating rate are shown in Fig. 2. The C_p curves have been normalized to the same value at 20°C to illustrate their different behaviour.

Table 2 The results of initial measurements. Two different calibration heating rates were used

	Fictive temperature		Half point temperature		Relaxation		
	T_g/°C	ΔC_p/J g^{-1} K^{-1}	T_g/°C	ΔC_p/J g^{-1} K^{-1}	Onset/°C	Peak/°C	ΔH/J g^{-1}
			calibration heating rate 2 K min^{-1}				
1	45.8±0.2	0.68±0.00	46.2±0.2	0.68±0.00	44.8±0.2	48.0±0.0	3.4±0.7
2	45.5±0.1	0.68±0.01	45.8±0.2	0.68±0.01	44.7±0.0	48.0±0.0	3.0±0.1
3	45.8±0.1	0.72±0.01	47.0±0.2	0.72±0.01	44.7±0.0	47.8±0.1	3.6±0.3
4	46.2±0.3	0.70±0.01	47.2±0.1	0.70±0.01	44.7±0.0	47.9±0.0	3.9±0.2
5	45.1±0.3	0.70±0.02	45.1±0.5	0.70±0.02	43.6±0.5	47.6±0.4	2.6±0.6
6	45.7±0.2	0.69±0.01	46.1±0.2	0.69±0.01	44.6±0.2	47.8±0.0	3.1±0.4
7	45.1±0.3	0.70±0.00	45.8±0.3	0.70±0.00	44.7±0.1	48.0±0.0	3.3±0.3
8	45.8±0.6	0.69±0.02	46.7±0.7	0.69±0.02	44.7±0.1	48.6±0.7	3.5±0.0
			calibration heating rate 10 K min^{-1}				
9	48.8±0.7	0.71±0.02	50.0±0.2	0.71±0.02	46.3±0.2	50.7±0.3	3.8±0.0
10	47.7±0.2	0.71±0.01	49.1±0.1	0.71±0.01	46.8±0.3	50.9±0.8	3.1±0.1
11	47.7±0.5	0.72±0.00	48.5±0.2	0.72±0.00	46.8±0.1	50.7±0.2	2.6±0.1
12	48.9±0.4	0.72±0.01	50.3±0.0	0.72±0.01	47.6±0.2	51.0±0.1	3.6±0.0
13	47.9±0.5	0.69±0.00	48.5±0.3	0.69±0.00	45.2±0.1	50 4±0.3	2.8±0.1
14	46.8±0.8	0.72±0.01	48.2±0.1	0.71±0.01	46.2±0.1	50.5±0.2	2.9±0.2

The temperature jump is one of the parameters that the user can change (Fig. 2a). As a coarse criterion it must amount to at least five data points in the region of the change. At slow heating rates in maltitol the glass transition occurred over a temperature range of about 10–15°C. As a temperature jump of 3°C was used, too few data points could be obtained in the glass transition region. However, if only the specific heat change at the glass transition is determined, the value obtained is correct, but the curve at the glass transition region is distorted.

The influence of the heating rate was investigated (Fig. 2b). It can be perceived that increasing the heating rate lowers the C_p values obtained particularly after the glass transition. In this case, the calibration was done at a heating rate of 2 K min^{-1} using the formula $C_{p(true)} = K_{C_p} C_{p(measured)}$. If the calibration constant (K_{C_p}) changes as the heating rate changes, it will affect the C_p curve also. This can be clearly seen in Fig. 2b. This means that the calibration should be performed at the same heating rate as the measurements.

The fictive temperature, the half point temperature, the specific heat change and the relaxation enthalpy were calculated from the curves of different measurements and the results are shown in Table 2. First the DSC was calibrated at a heating rate of 2 K min^{-1} and measurements 1–8 were done. In these measurements there were no large differences in the calculated glass transition temperatures. The fictive temperatures were quite similar for all measurements (about 45–46°C) and the half point temperatures differed only slightly from each other (about 45–47°C). The ΔC_p values from different measurements varied between 0.68–0.72 J g^{-1} K^{-1}. The onset and peak temperatures calculated from the relaxation peaks were

almost the same for all measurements while the enthalpy values of peaks differed more.

For these measurements the DSC was calibrated at a heating rate of 2 K min^{-1} as recommended in the manufacturer's manual. In these measurements, the best results were obtained at a heating rate of 2 K min^{-1} because of both the good shape of specific heat curve and the high value of ΔC_p. However, in most published StepScan studies a heating rate of 10 K min^{-1} has been used. In our measurements the shape of the T_g curve was not very good at this heating rate. For that reason, we decided to perform a new calibration at a higher heating rate (10 K min^{-1}) and repeat the measurements at different values of the parameters.

In earlier measurements it was noticed that the length of the isothermal period was limited because of too high criterion parameter. The criterion parameter
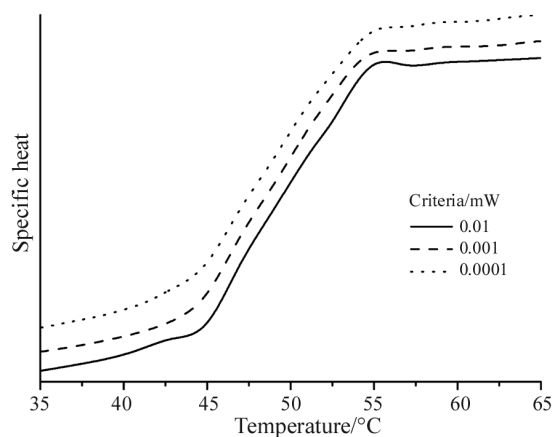

Fig. 3 Influence of the criteria parameter on the specific heat curve. Three different criteria values were tested. Other parameters were: heating rate 10 K min^{-1}, temperature jump 2°C, isothermal segment 1 min

determines the length of the isothermal period: when 10 consecutive data points (and a minimum of 6 s or 0.1 min) in the isothermal step fall within the criterion range selected, the isotherm step ends and the next scanning step starts. If the criterion parameter is set too high, the length of the isothermal period is not obtained in the measurements and this can cause a poor shape of the specific heat curve.

A series of measurements were performed with a calibration heating rate of 10 K min^{-1} (measurements 9–14). The heating rate was usually 10 K min^{-1}, but lower heating rates were also tested for comparison. Different criteria values were tested. The temperature increment was generally 2°C, but one measurement was performed with a temperature increment of 1°C to ensure that this was not the critical parameter. The calculated fictive temperature, the half point temperature, the specific heat change and the relaxation enthalpy results of the new measurements are included in Table 2. The fictive temperatures were between 47–49°C, the half point temperatures were between 48–50°C and the ΔC_p values were between 0.69–0.72 J g^{-1} K^{-1} in all measurements. The temperatures in these measurements were higher than in earlier measurements (where a slower calibration heating rate was used). The ΔC_p values agreed well with earlier measurements.

A notable difference was in the shape of the specific heat curves. Now, with the calibration done at a higher heating rate, the measurements where also the high heating rate was used resulted in a good shape of the specific heat curves. It was also noticed that the value of criterion was important: the lower was criterion, the better was the shape of the specific heat curve (Fig. 3). At the glass transition measurements big criterion values produce a short isothermal segment. This causes a problem that a sample does not reach a steady state, instead a part of a reversing process becomes non-reversing and a lower specific heat value is measured. Below the glass transition, the specific heat includes the effect of vibrations of the molecules and holes, which are fast phenomena. Above the glass transition, both the number of lattice holes and the translational motion of molecules (diffusion) that is slow in the viscous rubber state increase together with the reversible rotational motion of molecules. For these reasons the thermodynamic equilibrium is approached more slowly at glass transition and above and because of that, a longer isothermal segment is needed. This can be accomplished by decreasing the value of the criterion and increasing isothermal segment.

After these initial measurements, it was found that the heating rate used in the calibration had a significant effect on the shape of the specific heat curve at different StepScan parameters. Two heating rates were used in the calibration and for that reason two measurement programs (Table 1: measurement programs 3 and 14, methods 1 and 2, respectively) were carried out and compared during the following measurements.

Measurements on the 100% amorphous maltitol samples prepared in different ways

In order to study the precision of the measurements, six repeated measurements were made on 100% amorphous maltitol using both methods. The amorphous samples were prepared in DSC by heating the samples above the melting point (150°C) and thereafter cooling them to the glassy state in the same way for all samples. The measurements were done using the same methods that were used for the mixtures. The results are shown in Table 3. The mean of the ΔC_p for six parallel measurements was 0.711±0.009 J g^{-1} K^{-1} for the fictive and 0.709±0.009 J g^{-1} K^{-1} for the half point temperature in method 1 and 0.719±0.007 J g^{-1} K^{-1} for the fictive and 0.717±0.007 J g^{-1} K^{-1} for the half point temperature in method 2.

Because the amorphous sample for the synthetic mixtures was prepared in a different way (described in experimental part) than in earlier measurements, the precision was determined also for this sample and four repeated measurements were made using both methods. The measurement methods used were the same as earlier and the results are shown in Table 3. The mean of ΔC_p for four repeated measurements was 0.703±0.016 J g^{-1} K^{-1} for the fictive and 0.701±0.016 J g^{-1} K^{-1} for the half point temperature in method 1 and 0.713±0.011 J g^{-1} K^{-1} for the fictive and 0.713±0.012 J g^{-1} K^{-1} for the half point temperature in method 2.

As values for amorphous samples prepared in different ways are compared, no significant differences are seen in the results. The ΔC_p values for both samples are in a good agreement but the values for amorphous samples prepared inside DSC are slightly larger than those for amorphous sample prepared outside DSC. The differences for the glass transition temperatures are slightly larger: both the fictive and the half point temperatures are somewhat higher for samples prepared inside DSC than for those prepared outside DSC. The relaxation peaks are at almost the same temperature for both samples. However, there are differences in the relaxation enthalpy. In general, the standard deviations are smaller for the amorphous samples prepared in a carefully controlled way inside the DSC. Although the amorphous samples were prepared carefully also for synthetic mixtures, they were more exposed to moisture and room temperature before the measurements. These measurements established that the amorphous samples prepared for synthetic mixtures gave good results and were suitable for the preparation of mixtures.

Table 3 The results of repeated measurements of 100% amorphous samples measured with two different methods. Amorphous samples were produced either inside DSC sample holder by heating the crystalline compound above its melting point before measurements or outside DSC by heating the crystalline compound above its melting point in oven and thereafter refrigerating it at 5°C (crystalline malitol and amorphous samples were dried over P_2O_5 before measurements)

	Fictive temperature		Half point temperature		Relaxation		
	T_g/°C	ΔC_p/J g^{-1} K^{-1}	T_g/°C	ΔC_p/J g^{-1} K^{-1}	Onset/°C	Peak/°C	ΔH/J g^{-1}
amorphous sample produced inside the DSC equipment							
Method 1							
1	45.9	0.72	47.1	0.72	44.7	47.9	3.4
2	46.0	0.71	46.9	0.71	44.7	47.8	3.8
3	45.7	0.71	47.1	0.71	44.8	47.8	4.0
4	45.8	0.70	47.0	0.70	44.7	47.8	3.8
5	45.3	0.72	47.1	0.72	44.9	48.1	3.2
6	45.8	0.70	47.1	0.70	44.7	47.9	3.7
mean	45.7	0.71	47.0	0.71	44.7	47.9	3.6
S.D.	0.2	0.01	0.1	0.01	0.1	0.1	0.3
Method 2							
1	47.4	0.71	48.3	0.71	46.2	50.4	2.8
2	46.3	0.72	48.1	0.72	46.2	50.7	3.1
3	47.9	0.71	48.8	0.71	46.1	50.8	3.0
4	46.8	0.72	48.4	0.72	46.0	50.7	3.2
5	46.5	0.72	48.4	0.71	46.1	50.7	3.3
6	45.9	0.73	48.1	0.73	46.1	50.7	3.2
mean	46.8	0.72	48.4	0.72	46.1	50.7	3.1
S.D.	0.7	0.01	0.2	0.01	0.1	0.1	0.2
amorphous sample produced outside the DSC equipment							
Method 1							
1	38.9	0.70	40.6	0.70	43.9	47.6	1.6
2	39.6	0.71	41.4	0.71	44.9	48.7	0.9
3	41.6	0.68	43.1	0.68	44.1	47.6	2.0
4	44.7	0.72	45.9	0.72	42.8	47.4	3.6
mean	41.2	0.70	42.7	0.70	43.9	47.8	2.0
S.D.	2.6	0.02	2.4	0.02	0.9	0.6	1.2
Method 2							
1	45.9	0.72	47.5	0.72	46.0	49.9	2.5
2	45.9	0.71	47.2	0.71	45.7	49.8	2.0
3	45.4	0.73	46.9	0.73	45.4	49.7	2.6
4	44.3	0.70	45.5	0.70	41.9	48.6	2.8
mean	45.3	0.71	46.8	0.71	44.8	49.5	2.5
S.D.	0.8	0.01	0.9	0.01	2.0	0.6	0.3

S.D.: standard deviation

Table 4 Literature values of glass transition temperature (T_g) and the change of specific heat (ΔC_p)

Method	T_g/°C	ΔC_p/J g^{-1} K^{-1}	Reference
Hyper DSC			Hurtta et al. [17]
fictive	42.3	0.73	
half point	52.9	0.71	
Modulated DSC	49	0.61	Bustin et al. [23]
Adiabatic calorimeter	38	0.71	Lebrun et al. [24]
DSC	50	0.72	Claudy et al. [25]
DSC	44	0.56	Roos [26]

Literature values given in J mol^{-1} K^{-1} have been converted to J g^{-1} K^{-1} in this table

The values of T_g and ΔC_p reported in the literature for maltitol are given in Table 4. A comparison indicates that although the glass transition temperatures vary between different references, the values ob-

tained in this study are parallel to published values while the ΔC_p values differ slightly from each other, our values do not disagree from those reported in the literature. The differences of literature values are discussed more closely in our previous study [17].

The influence of the sample size on the ΔC_p

In DSC, the sensitivity can be improved by increasing the heating rate and by using a larger sample. In the StepScan method, it is possible to use partly high heating rate but average overall heating rate which leads to good resolution. In contrast to sinusoidal heating in TMDSC, there is an opportunity to use higher average heating rate and bigger sample because in StepScan DSC, the height or area of the response wave has meaning. In the sinusoidal heating, the shape of the response wave has to be taken into account.

Different sample sizes were tested and the ΔC_p was calculated. The results are in Table 5. According to Table 5 the largest ΔC_p value is obtained when the sample size is 6–8 mg; with larger samples the ΔC_p values became slightly lower. This may result from the fact that the heat conductivity of sapphire used in calibration is significantly higher than that of typical organic compounds. For that reason, when a large maltitol sample is used, large temperature gradients will be generated in the heating mode between different parts of sample and reaching steady state takes

more time than in the sapphire calibration. This can be improved by decreasing the criterion value with the resulting increase of the length of the isothermal segment. However, the noise of the curve limits the smallest value of the criterion. A better choice would be to find a calibration material with heat conductivity and specific heat close to those of the samples studied.

Synthetic mixtures

The ΔC_p values of synthetic mixtures were used to calculate the average and standard deviation values. The mean values of the specific heat change at the glass transition region were plotted *vs.* amorphous content and linear regression lines with R (correlation coefficient) values were calculated (Fig. 4). For comparison, the glass transition temperatures and specific heat changes were calculated for both fictive and glass transition temperatures. The equations are (x is amorphous content %):

Method 1

Fictive T	$\Delta C_p = 0.00547 + 0.00697x$	$R = 0.9987$
Half point T	$\Delta C_p = 0.00293 + 0.00699x$	$R = 0.9983$

Method 2

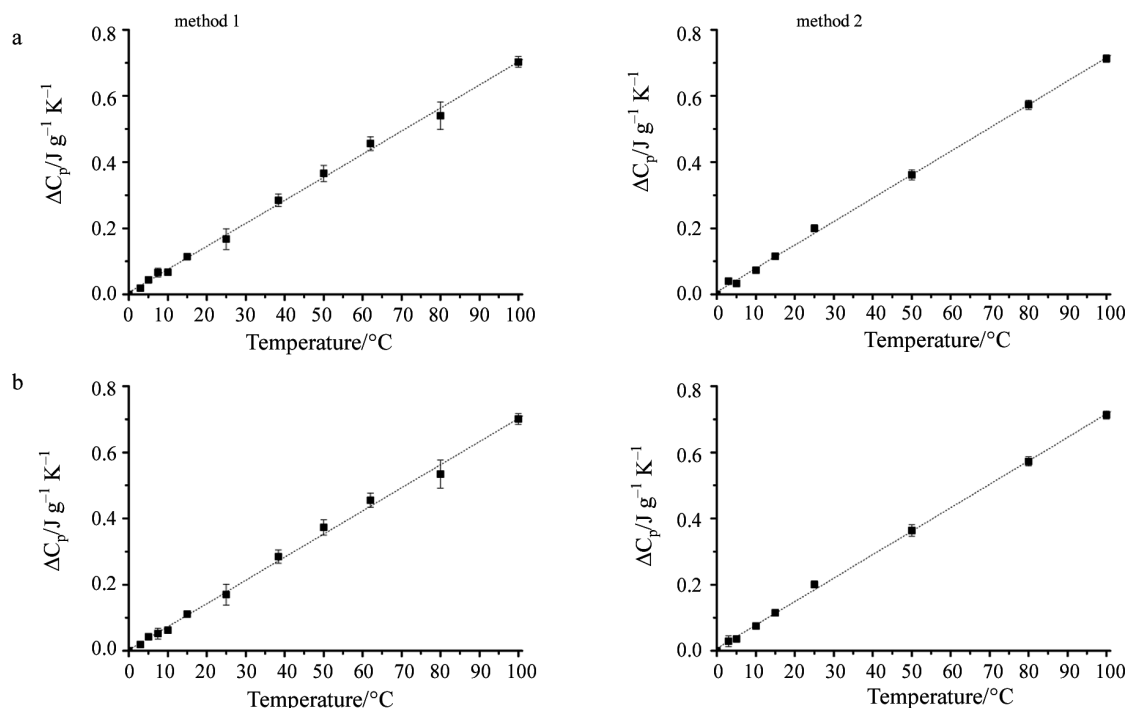|		
Fictive T	$\Delta C_p = 0.00789 + 0.00708x$	$R = 0.9995$
Half point T	$\Delta C_p = 0.00692 + 0.00709x$	$R = 0.9996$

Fig. 4 Average and standard deviation values for the change of specific heat at the glass transition temperature as a function of amorphicity. For comparison, the glass transition temperature and the specific heat change were calculated for both a – fictive and b – half point temperatures

Table 5 The effect of sample size on the ΔC_p. The amorphous phase was prepared from crystalline material inside the DSC cup

Sample mass/mg	Fictive temperature		Half point temperature	
	$T_g/°C$	$\Delta C_p/\text{J g}^{-1}\,\text{K}^{-1}$	$T_g/°C$	$\Delta C_p/\text{J g}^{-1}\,\text{K}^{-1}$
4.044	47.0	0.720	48.5	0.720
6.062	45.8	0.730	47.8	0.731
8.406	46.9	0.728	48.9	0.727
9.886	46.4	0.720	48.0	0.719
11.866	46.8	0.707	48.0	0.706
13.978	47.4	0.692	48.4	0.690

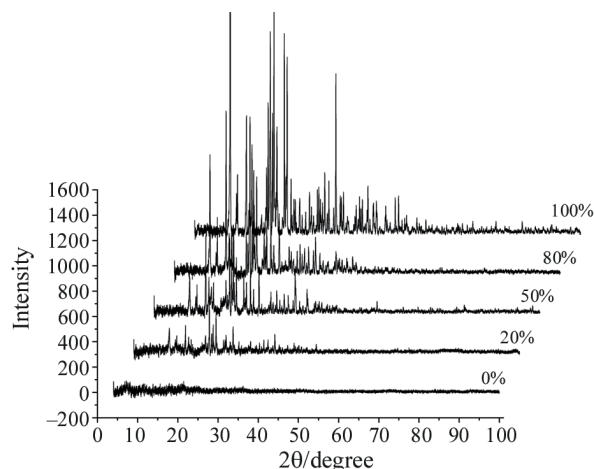

Fig. 5 Powder diffraction patterns for some synthetic mixtures of maltitol

Figure 4 demonstrates the clear correlation between the ΔC_p and the amorphous content in both methods. There were no significant differences in the results at fictive and half point temperatures. The results of the two methods were in good agreement.

The powder diffraction measurements were performed for mixtures and some of powder diffraction patterns are illustrated in Fig. 5. The baselines have been subtracted for better comparison. As can clearly be seen in the figure, the intensities of the reflections increased as crystallinity increased.

LOD (limit of detection) and LOQ (limit of quantification) values were calculated as described earlier [17]. The LOD and LOQ values were for the fictive temperature 0.24% (amorphous content) and 0.81% and for the half point temperature 0.27 and 0.92%, respectively, (method 1) and for the fictive temperature 0.18% (amorphous content) and 0.61% and for the half point temperature 0.16 and 0.52%, respectively (method 2). These values show that very low determination limits for the quantification of amorphous content can be attained with the StepScanDSC method. The lowest amorphous content of synthetic mixture used in the calculations was 3%. Although the calculated LOD and LOQ values are very low, realistic lim-

its of quantification are somewhat higher because of noise in the StepScan measurement.

In our previous study, the quantification of amorphous content in maltitol was studied with the hyperDSC method [17]. The ΔC_p values of 100% amorphous sample were 0.73 ± 0.03 J g^{-1} K^{-1} for fictive temperature and 0.71 ± 0.04 J g^{-1} K^{-1} for half point temperature. Good results were reached also for synthetic mixtures: LOD and LOQ values were 0.313 (amorphicity) and 1.04% for fictive temperature and 0.107 and 0.358% for half point temperature. The values agree well with the results of this study.

As the StepScan DSC and hyperDSC methods are compared for quantification of amorphous content, some differences can be noticed. In the HyperDSC the sensitivity is higher because high heating rates are used, so that lower limits of quantification can be reached. In StepScan DSC method, as well as in hyperDSC, the limit of quantification is determined by the noise of measurement. Because of the lower noise of hyperDSC, much lower LOD and LOQ values can be reached and also small glass transitions can be seen. The hyperDSC is clearly faster than StepScan DSC. However, the StepScan DSC separates glass transition and relaxation processes to different curves, which simplifies the interpretation and makes the calculation of ΔC_p much easier. Also recrystallization can disturb glass transition measurements in the HyperDSC.

Conclusions

The StepScan DSC and the specific heat change at the glass transition region provide a method for determining the amorphous content. However, the choice of suitable measurement parameters was important because they had a substantial effect on the results and the shape of the curves. Also the calibration method influenced the results. Two different measurement methods were tested and both gave satisfying results. However, the specific heat curves were improved when higher heating rates were used. There was the

clear linear correlation between ΔC_p and the amorphous content. The calculated LOD and LOQ values were very low, but the true limits of quantification were somewhat higher, about 3%. The main advantage of the StepScan DSC method for quantification of an amorphous content is that the glass transition and relaxation peaks are separated to different curves and the interpretation thus becomes easier.

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