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The use of modulated temperature differential scanning calorimetry for the characterisation of food systems

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Abstract

Modulated temperature Differential Scanning Calorimetry (MTDSC) is used to characterise food systems. It is shown that by splitting the total heat flow into reversing (related to heat capacity) and non-reversing contributions, overlapping thermal events can be separated. The combination of excellent sensitivity and high resolution provides more accurate results for weak and/or broad transitions. The thermal transitions of maltotriose, maltohexaose and thermoplastic starch are treated as examples. It is also shown that MTDSC is very useful to follow in situ slow crystallisation processes. These structural changes are detected by measuring the heat capacity in the quasi-isothermal mode. The (quasi-)isothermal crystallisation of pregelatinised waxy corn starch is given as an example. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Modulated DSC; Polysaccharides; Oligosaccharides; Starch; Glass transition; Crystallisation

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1. Introduction

Thermal analysis has been used for many years to characterise synthetic polymers. More recently, a growing interest has been shown from both the academic and industrial world to use thermal analysis techniques to characterise model food systems and real food products. A broad variety of food systems have already been studied using these techniques (Slade and Levine, 1995).

Not only the fundamental structure–property relationships of the separate ingredients are studied, but also the complex behaviour of complete food products. Examples are the detection of water loss, uptake or migration (Roos et al., 1996), the denaturation of proteins (Kitabatake et al., 1990; Sessa, 1993) and the crystallisation of starch (Jouppila and Roos, 1997; De Meuter et al., 1999). Thermal analysis techniques are also useful to simulate and design new processes, like spray-drying (Busin et al., 1996), freeze-drying (To and Flink, 1978), extrusion (Anker, 1996; Bent et al., 1997), and hydro-thermal treatment. They also allow prediction and improvement of product quality, safety and storage stability.

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One of the most popular thermal analysis techniques is differential scanning calorimetry (DSC). Interpretation of heat flow curves of DSC thermograms, however, is often difficult due to the complex nature of real food products. The purity of the ingredients is often low, the polydispersity and the heterogeneity high. Another problem is the presence of water in most foods. Special attention has to be paid to avoid water evaporation during the measurement. Other difficulties are weak, broad and overlapping transitions, degradation at relatively low temperatures and slow crystallisation of some products.

With modulated temperature DSC (MTDSC), a recent extension of conventional DSC using a modulated temperature input signal, information on the ‘amplitude of the complex heat capacity’ (termed ‘heat capacity’ in this paper) is obtained, both in (quasi)isothermal and non-isothermal conditions. This complementary information, giving rise to a deconvolution of the (total) heat flow signal into ‘reversing’ and ‘non-reversing’ contributions, enables a more detailed study of complicated material systems. More details on terminology, theory, instrumentation and applications of MTDSC are given in two recent Special Issues of *Thermochimica Acta* (Schick and Hôhne, 1997) and *Journal of Thermal Analysis and Calorimetry* (Menczel and Judovits, 1998).

While MTDSC has proven to be beneficial for the thermal characterisation of synthetic polymers in general, this relatively new technique has not yet been extensively applied to food systems. Glass transitions of gelatin, polydextrose, sucrose, corn flakes, pasta and aqueous glucose/glycine solutions have been studied (Dollimore, 1994; Bell and Touma, 1996; Schmidt, 1996; Urbani et al., 1997). Results on frozen sugar solutions (Izzard et al., 1996; Aubuchon et al., 1998; Knopp et al., 1998; Wang and Haymet, 1998) and freeze-concentrated aqueous solutions of ascorbic acid (Andersen and Skibsted, 1998) have also been reported. Work on (poly)carbohydrates, including the measurement of slow crystallisation processes, is in progress (De Meuter et al., 1999).

In this paper, the intrinsic benefits of MTDSC are highlighted with three typical examples of food systems, enabling a better characterisation and understanding of their thermal behaviour. In the first experiments, MTDSC results are shown on products with overlapping thermal events, such as a glass transition region in combination with an enthalpy relaxation effect or with the melting of water. Secondly, a material with very weak and broad thermal transitions is discussed. In the third part, a new procedure is presented for the in situ measurement of a slow crystallisation process.

2. Materials and methods

2.1. Materials

Maltotriose was obtained from Sigma. The water content was 6% w/w, as determined by thermogravimetric analysis (see Section 2.2.2). Maltohexaose was also obtained from Sigma. The water content of the product was adjusted to 30% w/w by adding water with a micro-syringe in the DSC sample pan. After closing the pan, the sample was equilibrated overnight at room temperature to obtain a uniform distribution of water in the sample. Pregelatinised waxy corn starch was supplied by Cerestar. About 0.5 g starch was compressed to a pellet. In order to facilitate the filling of the sample pan and to enable the use of larger sample masses, pieces of approximately 25 mg of compressed material were used for analysis. As explained for maltohexaose, water was added to the sample pan to a final dry substance of 76% w/w (24% w/w water). Thermoplastic starch products were supplied by Cerestar. These extruded products are mainly composed of starch, water and glycerol.

2.2. Methods

2.2.1. (Modulated temperature) DSC

The measurements were performed on a DSC 2920 (TA Instruments) equipped with modulated DSC software. Two types of cooling accessories were used, depending on the temperature of analysis and the duration of the experiment. If the sample had to be cooled to below −60°C, a Liquid Nitrogen Cooling Accessory (LNCA) was used. For experiments of more than 24 h, with a minimum temperature of −60°C, a Refrigerated Cooling System (RCS) was used. The purge gas was helium at a flow rate of 25 ml min^{-1}.

For water-containing samples that had to be heated above 120°C, reusable high-pressure stainless steel pans (HPS) from Perkin-Elmer were chosen. In all other cases, hermetically sealed aluminium pans from TA Instruments were used. The sample weight varied between 6 and 8 mg for low molecular weight samples and between 20 and 30 mg for starch samples.

The choice of heating rate and modulation conditions are important to obtain reliable results and should be adapted to the type of pan used. The TA Instruments hermetic pans were heated and cooled at 2.5°C min^{-1}. The period was 60 s and the amplitude was 0.5°C. For the Perkin-Elmer HPS pans, the heating and cooling rate was decreased to 1°C min^{-1}, with a period of 100 s and an amplitude of 0.5°C. For the DSC experiments without modulation (conventional), the heating rate was increased to 10°C min^{-1} for the Al hermetic pans and to 5°C min^{-1} for the HPS pans.

Temperature calibration was performed with indium and cyclohexane. The enthalpy was calibrated with indium. For the calibration of heat capacity (C_p), water at 35°C was used. The modulation parameters for the calibration were the same as for the experiments.

2.2.2. Thermogravimetric analysis

The dry substance of the samples was determined by thermogravimetric analysis (TGA 7 from Perkin-Elmer). The purge gas was helium. The samples were dried at 125°C for at least 3 h, until the weight stabilised.

2.2.3. Dynamic mechanical analysis

DMA 7 from Perkin-Elmer was used, equipped with a 1-mm quartz probe. The purge gas was helium. A special set-up was developed to avoid evaporation of water out of the sample during the analysis. The heating rate was 2°C min^{-1}. A frequency of 1 Hz was applied.

3. Results and discussion

3.1. Overlapping thermal events

3.1.1. Maltotriose

After storage at room temperature, the DSC thermogram of maltotriose (94% w/w) shows an endothermic signal around 40°C. From this signal, it is difficult to conclude whether this thermal event is a melting endotherm or a glass transition with a superimposed enthalpy relaxation. This endothermic signal is also observed in the total heat flow curve of the corresponding MDSC thermogram, which is similar to the heat flow measured by conventional DSC (Fig. 1a). By splitting the total heat flow into the heat capacity (related to reversing heat flow) and the non-reversing heat flow (Fig. 1b), it becomes possible to differentiate between the thermal events occurring simultaneously.

A glass transition (T_g) at ca. 43°C is observed as an increase in the heat capacity signal. The ΔC_p value at T_g (0.58 J g^{-1} K^{-1}) is in agreement with data reported in literature (Orford et al., 1989). The non-reversing heat flow shows only the endothermic signal, related to the enthalpy relaxation.

MTDSC enables the enthalpy relaxation to be separated from the stepwise change in heat capacity at the glass transition. This allows measuring the glass transition during the first heating of the sample, which can be very beneficial for some applications. In the case of physical ageing of a food system in storage conditions, this procedure to determine T_g is important. The maltotriose sample in Fig. 1, measured in the first heating after storage at room temperature, is an illustration. The enthalpy relaxation peak observed in the non-reversing heat flow is the result of a preceding ageing step at a temperature close to T_g.

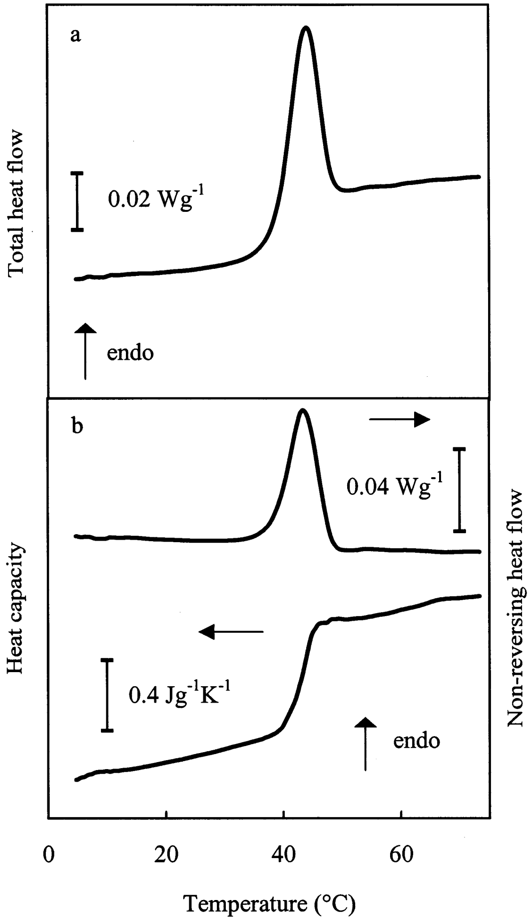

Fig. 1. MTDSC thermogram of maltotriose (94% w/w): (a) total heat flow; (b) heat capacity and non-reversing heat flow (first heating).

3.1.2. Maltohexaose

After a controlled cooling of maltohexaose (70% w/w) from 90 to -60°C at 2.5°C min^{-1}, the MTDSC thermogram of the subsequent heating shows a complex total heat flow signal between -40 and 0°C (Fig. 2a). The MTDSC heat capacity and non-reversing heat flow signals (Fig. 2b) provide a better understanding of the thermal transitions taking place.

The heat capacity (reversing heat flow) signal shows a glass transition with a calculated value of T_g of 32°C. In the non-reversing heat flow curve, a small endothermic enthalpy relaxation peak in the temperature region of T_g is observed, overlapping with the exothermic cold crystallisation peak of a water-rich phase. This exothermic signal is immediately followed by the melting endotherm of this phase. The observed melting point depression of water is caused by dissolved maltohexaose. Note that the melting process is partially retrieved in the heat capacity (reversing heat flow) as well as in the non-reversing heat flow signal. The high

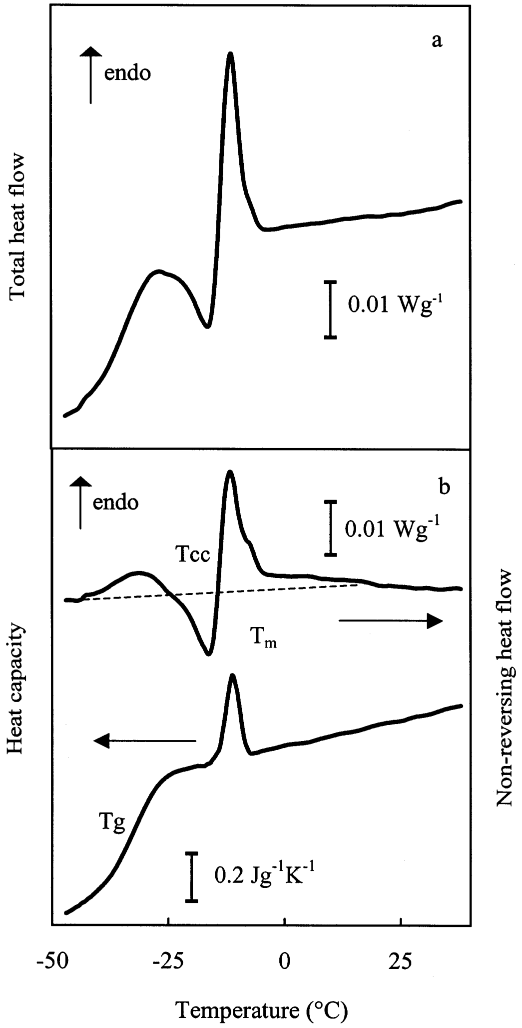

Fig. 2. MTDSC thermogram of maltohexaose (70% w/w): (a) total heat flow; (b) heat capacity and non-reversing heat flow (heating after cooling at 2.5°C min^{-1}). Glass transition (T_g), cold crystallisation (T_{cc}) and melting (T_m) regions are indicated.

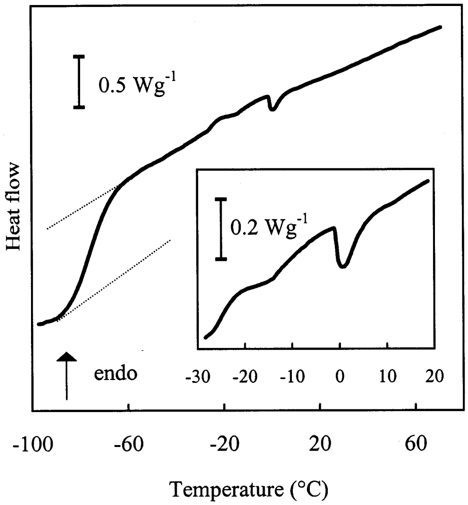

Fig. 3. DSC (conventional) heat flow measured at 5°C min^{-1} of thermoplastic starch, containing water and glycerol as plasticizers. A detail of the heat flow signal between −40 and 20°C is shown.

concentration of maltohexaose in the binary mixture with water prevents crystallisation during cooling at 2.5°C min^{-1} and an amorphous vitrified phase is formed. MTDSC is very suited to study the influence of experimental conditions on vitrification, (cold) crystallisation and melting of such systems.

3.2. Weak and broad thermal transitions

By extrusion of starch in the presence of plasticizers, such as water and glycerol, a thermoplastic starch material (TPS) can be obtained (De Bock and Van Den Broecke, 1994). Fig. 3 shows a typical (conventional) DSC thermogram of a thermoplastic starch material. At −75°C a glass transition is clearly observed. It is know from literature that this T_g is related to the presence of a glycerol-rich phase (T_g of glycerol is −81°C) and is influenced by the presence of a β-relaxation of starch (Lourdin et al., 1997). The inset of Fig. 3 also shows that the glass transition temperature of the starch-rich phase, located around 0°C (see discussion below), cannot be detected with conventional DSC (Poutanen and Forssell, 1996).

The glass transition of the glycerol-rich phase of TPS can also be measured with Dynamic mechanical analysis (DMA) (Fig. 4). At about −70°C, the storage modulus (E') decreases, while a maximum in the loss modulus (E'') at −69°C and in the tangent of the phase angle (tan δ) at −61°C are observed.

Moreover, this DMA experiment shows an even more marked transition at about 0°C, providing additional information on the starch-rich phase of TPS. A much larger drop in E', with a factor of about 10^3, is detected. Maxima in E''

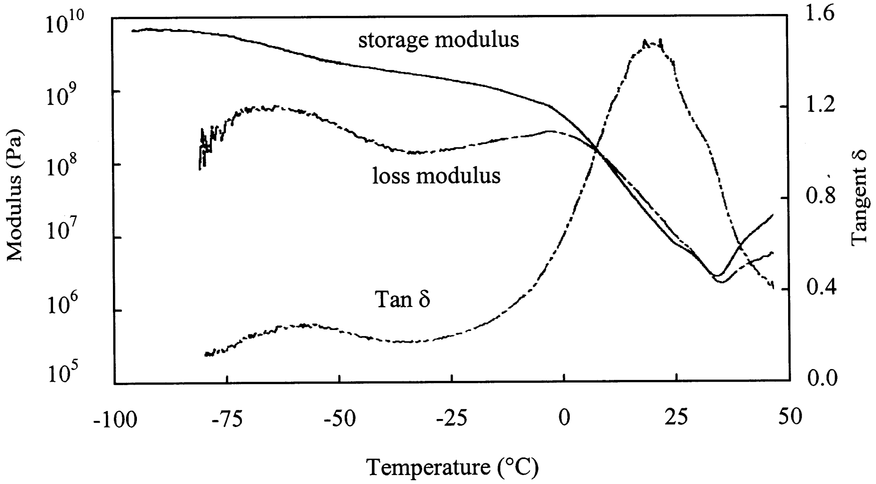

Fig. 4. DMA data for the same thermoplastic starch as in Fig. 3: storage modulus (E'), loss modulus (E'') and tan δ.

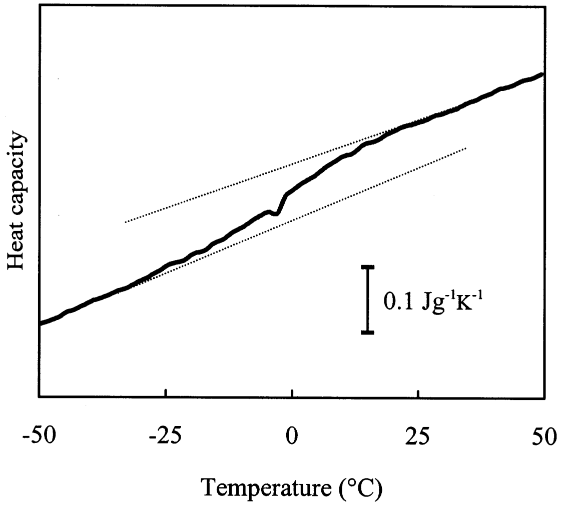

Fig. 5. MTDSC heat capacity signal of the same thermoplastic starch as in Fig. 3, measured in HPS pans.

and tan δ, at −2 and 23°C, respectively, are observed. This result shows that the influence of the glass transition of the starch-rich phase on the mechanical properties of TPS is large and clearly seen with DMA. The disadvantage of DMA, however, is the technique's sensitivity for the loss of plasticizer in experimental conditions. Even with a specially designed experimental set-up (De Meuter et al., 1999), measurements at high temperatures cannot be performed since the evaporation of the plasticizer cannot be avoided completely.

Fig. 5 shows that the glass transition of the starch-rich phase of TPS can also be determined using MTDSC. The heat capacity evolution shows a distinct increase centered around 0°C, indicating a broad glass transition region of about 50°C. By splitting the total heat flow signal into a reversing (related to heat capacity) and a non-reversing component, the noise and baseline curvature are retrieved in the non-reversing signal. Therefore the detection limit of a glass transition, measured via the heat capacity (reversing) signal, is increased substantially. The increased sensitivity arises because of the high instantaneous heating rate, while the increased resolution occurs because of the low average (underlying) heating rate. These are major benefits associated with MTDSC for the determination of weak and broad thermal transitions, such as the glass transition of the starch-rich phase of TPS.

The advantage of MTDSC, in comparison with DMA, is the easier sample preparation and the better control of the sample's water content. During a MTDSC experiment, even up to high temperatures, water evaporation is avoided by the use of HPS pans (see Section 2.2.1).

3.3. Slow crystallisation processes

The crystallisation of starch has been extensively described in literature (Keetels et al., 1996; Fisher and Thompson, 1997; Kim et al., 1997). Using conventional DSC, however, the crystallisation of starch could never be measured in situ. The problem is that the exothermicity of the crystallisation process cannot be detected, because the crystallisation rate of starch is too low. This results in too small a heat flow signal, compared to the baseline drift and noise. Therefore, attempts were made to measure the crystallisation rate of starch by determining the enthalpy of fusion after different isothermal crystallisation times. This approach, however, is very time consuming.

MTDSC enables measurement of the kinetics of starch crystallisation in situ, by following the change in heat capacity under quasi-isothermal conditions (De Meuter et al., 1999). During isothermal crystallisation, the heat capacity of the system drops. As an example, the isothermal MDSC heat capacity change during crystallisation at 52°C of pregelatinised waxy corn starch (24% w/w water) is shown in Fig. 6.

The change in heat capacity describing the structural conversion from a totally amorphous to a semi-crystalline sample with maximum crystallinity is 0.14 J g^{-1} K^{-1}, and half of this ΔC_p (or the time to half conversion) is reached after

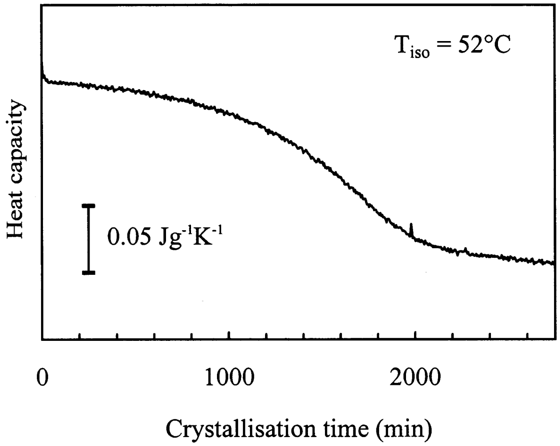

Fig. 6. MTDSC heat capacity evolution of the crystallisation at 52°C of pregelatinised waxy corn starch (76% w/w).

1600 min in these conditions. The heat capacity evolution is reproducible, illustrating that the slow crystallisation process of starch can be followed in situ qualitatively and quantitatively. These results are important for the study of ageing of food products. The crystallisation process is influencing the thermal and environmental behaviour of these products.

The starch crystals formed during isothermal crystallisation at 52°C show a broad melting endotherm with a bimodal distribution (De Meuter et al., 1999). This bimodal distribution is also described in literature (Fredriksson et al., 1998).

The glass transition temperature of the amorphous starch system shown in Fig. 6 decreases from an initial value of 13 to -6°C after isothermal crystallisation at 52°C. During crystallisation water is expelled from the crystals and is acting as a plasticizer for the remaining amorphous starch phase, giving rise to the observed decrease of T_g. The maximum amount of water that can act as a plasticizer for starch is 27% w/w. If more water is present in the amorphous phase (due to crystallisation), it behaves as freezable water (Silverio et al., 1996). In this case, the melting endotherm of ice is overlapping with the glass transition of starch. Using MTDSC, the major part of the melting of ice is seen in the non-reversing heat flow, while T_g is observed in the heat capacity. This again enables a more accurate determination of T_g of the semi-crystalline starch.

In conclusion, the examples discussed show that MTDSC can be applied to characterise food systems, for which conventional DSC provides less accurate results or even fails. MTDSC is an excellent characterisation tool for food science by the ability to separate thermal events in heat capacity and non-reversing heat flow contributions, the stability and reproducibility of the signals, and the ability to measure at low heating and cooling rates, including the measurement of heat capacity in quasi-isothermal conditions. MTDSC will enable a better understanding of thermal events in food systems to be established and contribute to a more systematic knowledge in topics such as glass formation, vitrification and devitrification processes, the influence of water content, phase diagrams, structural changes as a function of time, temperature and composition, (slow) crystallisation processes, and ageing during storage.

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References

Andersen, A.B., Skibsted, L.H., 1998. Glass transition of freeze-concentrated aqueous solution of ascorbic acid as studied by Alternating Differential Scanning Calorimetry. Lebensm.-Wiss. u.-Technol. 31, 69–73.

Anker, M., 1996. Edible and biodegradable films and coating for food packaging—a literature review. SIK rapport 623, 112.

Aubuchon, S.R., Thomas, L.C., Theuerl, W., Renner, H., 1998. Investigations of the sub-ambient transitions in frozen sucrose by modulated differential scanning calorimetry (MDSC). J. Therm. Anal. 52, 53–64.

Bell, L.N., Touma, D.E., 1996. Glass transition temperatures determined using a temperature-cycling differential scanning calorimeter. J. Food Sci. 61 (4), 807–828.

Bent, J.L. Jr, Mulvaney, S.J., Cohen, C., Bartsch, J.A., 1997. Viscoelastic properties of extruded cereal melts. J. Cereal Sci. 26 (3), 313–328.

Busin, L., Buisson, P., Bimbenet, J.J., 1996. Notion of glass transition applied to the spray-drying of carbohydrate solutions. Science des Aliments 16 (5), 443–459.

De Bock, I., Van Den Broecke, P., 1994. Starch based material, EP 0599535, Cerestar holding B.V.

De Meuter, P., Amelrijckx, J., Rahier, H., Van Mele, B., 1999. Isothermal crystallisation of concentrated amorphous starch systems measured by Modulated Differential Scanning Calorimetry. J. Polym. Sci. Part B Polym. Phys., (in press).

Dollimore, D., 1994. Thermal analysis. Anal. Chem. 66 (12), 17–25.

Fisher, D.K., Thompson, D.B., 1997. Retrogradation of maize starch after thermal treatment within and above the gelatinisation temperature range. Cereal Chem. 74 (3), 344–351.

Fredriksson, H., Silverio, J., Andersson, R., Eliasson, A.-C., Aman, P., 1998. The influence of amylose and amylopectin characteristics on gelatinisation and retrogradation properties of different starches. Carbohydr. Polym. 35, 119–134.

Izzard, M.J., Ablett, S., Lillford, P.J., Hill, V.L., Groves, I.F., 1996. A modulated differential scanning calorimetric study. Glass transitions occurring in sucrose solutions. J. Therm. Anal. 47, 1407–1418.

Jouppila, K., Roos, Y.H., 1997. The physical state of amorphous corn starch and its impact on crystallisation. Carbohydr. Polym. 32, 95–104.

Keetels, C.J.A.M., Oostergetel, G.T., Van Vliet, T., 1996. Recrystallization of amylopectin in concentrated starch gels. Carbohydr. Polym. 30, 61–64.

Kim, J.O., Kim, W.S., Shin, M.S., 1997. A comparative study on retrogradation of rice starch gels by DSC, X-ray and α-amylase methods. Starch 49 (2), 71–75.

Kitabatake, N., Tahara, M., Doi, E., 1990. Thermal denaturation of soybean protein at low water contents. Agric. Biol. Chem. 54 (9), 2205–2212.

Knopp, S.A., Chongprasert, S., Nail, S.L., 1998. The relationship between the TMDSC curve of frozen sucrose solutions and collapse during freeze-drying. J. Therm. Anal. 54, 659–672.

Lourdin, D., Bizot, H., Colonna, P., 1997. 'Antiplastization' in starch-glycerol films? J. Appl. Polym. Sci. 63, 1047–1053.

Menczel, J.D., Judovits, L. (Eds.), 1998. Special Publication of Temperature-Modulated Differential Scanning Calorimetry. J. Therm. Anal. 54.

Orford, P.D., Parker, R., Ring, S.G., Smith, A.C., 1989. Effect of water as a diluent on the glass transition behaviour of maltooligosaccharides, amylose and amylopectin. Int. J. Biol. Macromol. 11, 91–96.

Poutanen, K., Forssell, P., 1996. Modification of starch properties with plasticizers. TRIP 4 (4), 128–132.

Roos, Y.H., Karel, M., Kokini, J.L., 1996. Glass transitions in low moisture and frozen foods: effect on shelf life and quality. Food Technol. 50, 95–108.

Schick, C., Hôhne, G.W.H. (Eds.), 1997. Special Issue on Temperature Modulated Differential Scanning Calorimetry. Thermochim. Acta, 304–305.

Schmidt, S.J., 1996. Probing molecular level changes in carbohydrate based food systems using NMR and DSC, United States of America, Institute of Food Technologists (1996 Annual Meeting).

Sessa, D.J., 1993. Thermal denaturation of glycinin as a function of hydration. JAOCS 70 (12), 1279–1284.

Silverio, J., Svensson, E., Eliasson, A.-C., Olofsson, G., 1996. Isothermal microcalorimetric studies on starch retrogradation. J. Therm. Anal. 47, 1179–1200.

Slade, L., Levine, H., 1995. Glass transition and water–food structure interactions. Adv. Food Nutr. Res. 38, 103–234.

To, E.C., Flink, J.M., 1978. 'Collapse' a structural transition in freeze-dried carbohydrates. III Prerequisite of recrystallisation. J. Food Technol. 13 (6), 583–594.

Urbani, R., Sussich, F., Prejac, S., Cestro, A., 1997. Enthalpy relaxation and glass transition behaviour of sucrose by static and dynamic DSC. Thermochim. Acta 304/305, 359–367.

Wang, G.M., Haymet, A.D., 1998. Trehalose and other sugar solutions at low temperature: Modulated Differential Scanning Calorimetry (MDSC). J. Phys. Chem. B 102, 5341–5347.