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PRECISE DETERMINATION OF LOW LEVEL SUCROSE AMORPHISM BY MICROCALORIMETRY

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The DSC curve of freeze-dried amorphous sucrose shows the glass transition, the crystallization and the melting (just before decomposition) of the sample. Sucrose crystallization occurs below 100°C: this phenomenon can therefore be observed with the microcalorimeter Setaram Micro-DSC used in the scanning mode. Mixtures of amorphous and crystalline sucrose in known proportions were used to calibrate the instrument. Low level amorphism (down to about 0.5%) could be detected and quantitatively evaluated on the basis of the crystallization enthalpies determined. The calibration curve obtained can be applied to determine the degree of amorphism in milled sucrose. A simple gravimetric method, based on the desorption of water induced by recrystallization of the amorphous layer can be used to obtain similar data more rapidly. This simple method is particularly useful for controlling the amorphism on line during a process, and is also briefly described.

Keywords: sucrose, carbohydrate, amorphism, crystallinity

Introduction

In a food research environment, amorphous sucrose is generally obtained by freeze-drying or by spray-drying of sucrose solutions. Partially amorphous sucrose can however also be formed by other means or in other operations such as grinding (milling) of crystalline sucrose. Due to important mechanical friction and to quick cooling, a thin amorphous layer may effectively be formed at the surface of the sucrose particles.

The calorimetric method presented here quantitatively evaluates low level amorphism of solid sucrose. It is based on the crystallization peaks shown in the calorimetric curves of solid sucrose by the amorphous part of the sample.

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In addition, a simple gravimetric method is also presented, which measures the degree of amorphism of sucrose by following water sorption and desorption by the sample.

Instrument and method

The calorimetric method gives high performance due to the high sensitivity of the Setaram Micro-DSC microcalorimeter. This instrument is used in the scanning mode between 20° and 100°C, its upper temperature limit. Calorimetric curves are usually obtained at a heating rate of 1 deg·min^{-1}. The reference material is Al_2O_3.

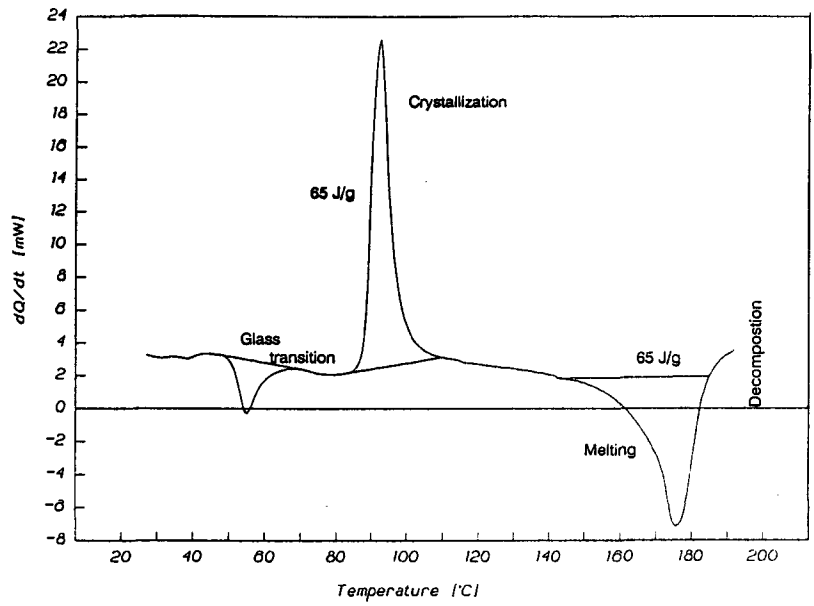

Fig. 1 Typical calorimetric curve of (freeze-dried) amorphous sucrose

Commercial sucrose (Sucrerie et Raffinerie Aarberg S. A., Switzerland) was used for these tests. As shown in the literature and in Fig. 1, the calorimetric curve of amorphous sucrose (obtained here with a standard DSC apparatus, the Setaram DSC 111, at a heating rate of 5 deg·min^{-1}) shows the glass transition, the crystallization and the melting (just before decomposition) of the sample [1–4].

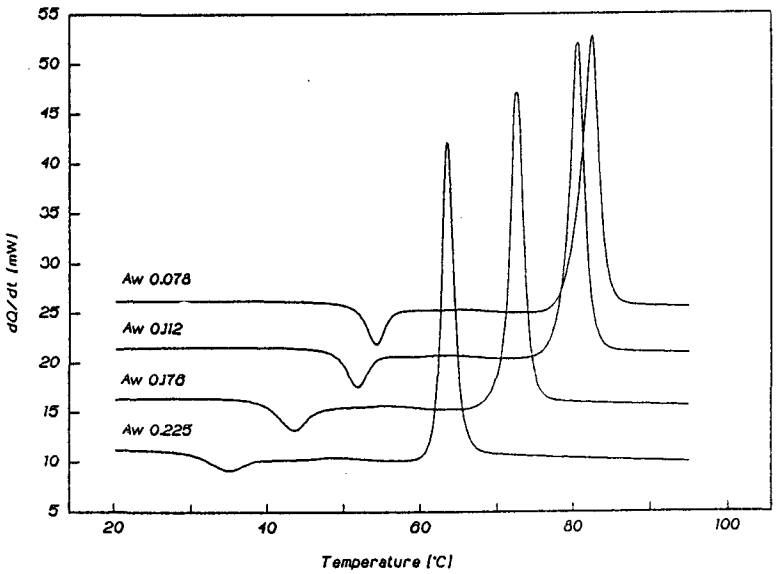

Fig. 2 Calorimetric curves of amorphous sucrose at different water activities

As demonstrated by the calorimetric curves presented in Fig. 2, obtained with the Micro-DSC at 1 deg·min^{-1}, glass transition as well as crystallization depends on water activity in the sample.

Experiments and results

Mixtures of amorphous and crystalline sucrose in known proportions were prepared in the range of low level amorphism, which was the main area of interest. These standard mixtures were analysed with the Micro-DSC and the observed crystallization peaks recorded (Figs 3 and 4).

The crystallization enthalpies were determined by peak integration to calibrate the instrument. The calibration curve obtained this way (Fig. 5) shows perfect linearity and a remarkable correlation coefficient. Low level amorphism (down to about 0.5%) could thus be detected without difficulty.

The regression equation of the data presented in Fig. 5 and giving the degree of amorphism, da(%), of a ground sucrose sample is:

$$da(\%) = 1.69 \text{ Enthalpy (J/gDM)}.$$

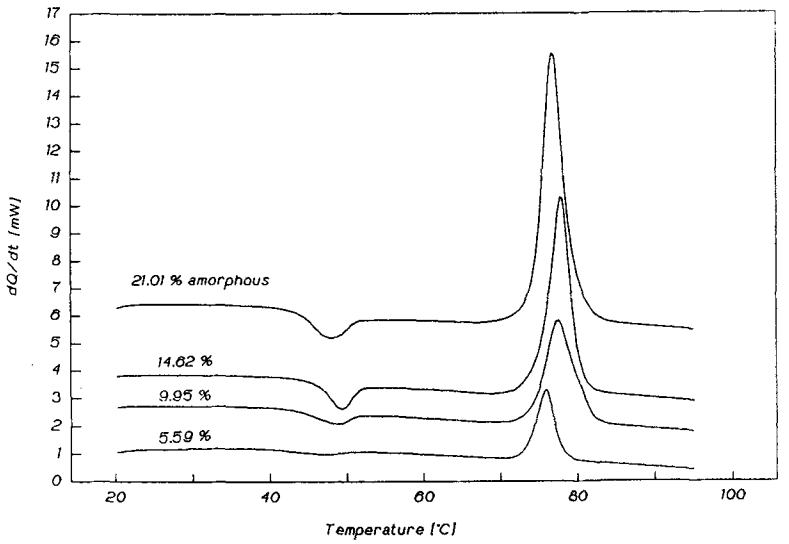

Fig. 3 Calorimetric curves of partially amorphous sucrose

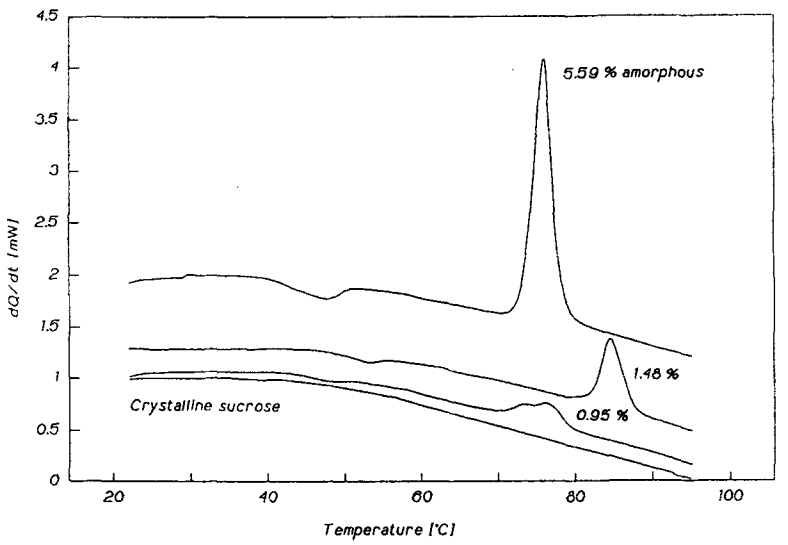

Fig. 4 Calorimetric curves of crystalline and partially amorphous sucrose

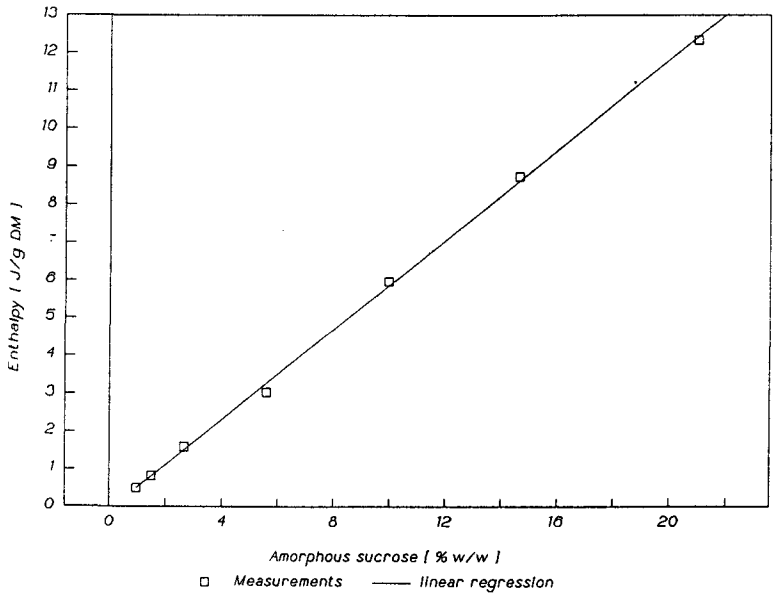

Fig. 5 Calibration curve: crystallization enthalpy as a function of the percentage amorphous sucrose

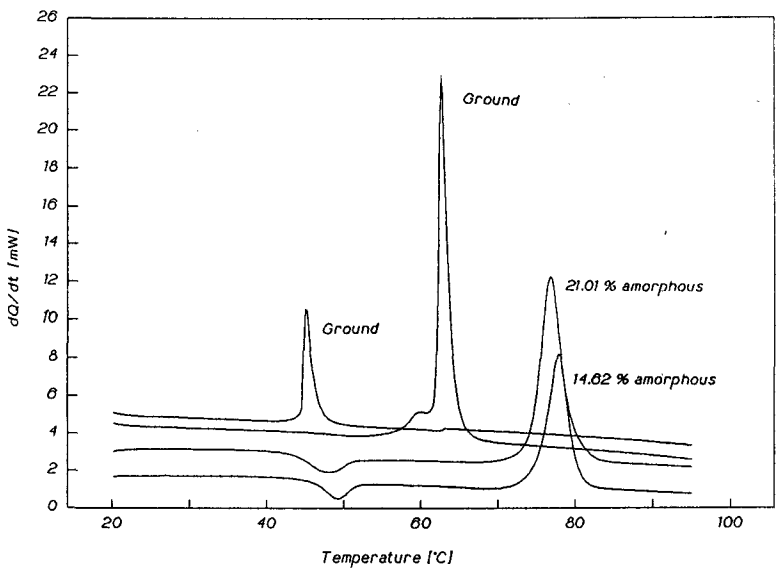

Fig. 6 Comparison of the calorimetric curves obtained with ground sucrose to those of standard mixtures

The calorimetric curves of partially amorphous sucrose obtained by milling for instance could then be compared to those of the standard mixtures (Fig. 6), and the degree of amorphism determined.

Thus, for both ground samples shown in Fig. 6, enthalpies of 2.85 J/gDM and 10.58 J/gDM were determined. These values correspond to amorphism degrees of about 5% and 18%, using the DSC calibration equation.

Alternative methods

Other more sophisticated techniques (X-ray diffraction, near infrared reflectance,...) may also give valuable information on crystallinity and amorphism of carbohydrates. However, in an industrial environment, a simple gravimetric method may be used for rapidly controlling the degree of amorphism during a process. It is based on the sorption of water by amorphous sucrose and on the con-

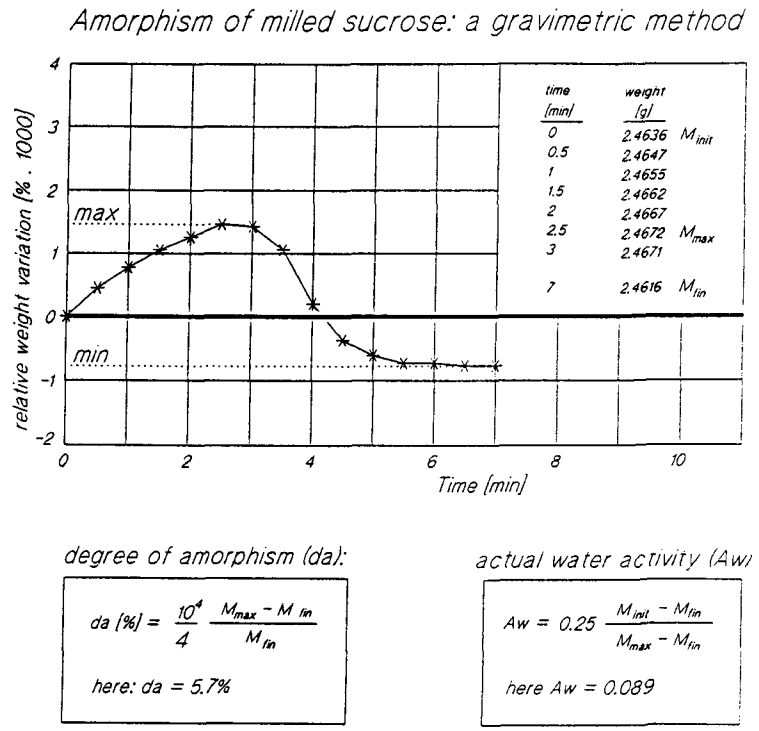

Fig. 7 Amorphism of ground sucrose as determined by the gravimetric method

secutive desorption of the water, induced by recrystallization of the amorphous part of the sample [5–8].

It must be understood that, at normal room temperature and relative humidity, amorphous sucrose is not stable: it is in the glassy state. By water uptake and/or temperature increase, it even changes into a more labile (rubbery) state at the glass transition temperature T_g. Crystallization then may occur, after a time, depending on the difference $(T-T_g)$ between the actual temperature T and T_g. At ambient, the amorphous part of a sucrose sample (an amorphous layer in the case of milling) may remain stable for hours if the relative humidity (water activity) is lower than 25% ($Aw<0.25$).

Thus, to determine the degree of amorphism of milled sucrose, some grams of sample have to be exposed, on a microbalance, to a mean relative humidity (40% to 60%). As shown in Fig. 7, the powder will adsorb water up to about 4% of the amorphous mass of the sample. Once this maximum humidity is reached, the amorphous sucrose layer will crystallize and the total amount of adsorbed water will be released in the atmosphere. Assuming that the maximum water content of 100% amorphous sucrose is 4%, the unknown degree of amorphism will be calculated according to the formula presented in Fig. 7. It depends on the maximum and on the final sample masses but neither on the initial sample mass nor on the surrounding relative humidity.

Assuming that the maximum of Aw for short time stability is 0.25, the actual Aw value of a ground sample may be calculated according to the second formula indicated in Fig. 7 (linear interpolation).

It must still be noted that the higher the relative humidity, and the thinner the amorphous layer, the more rapid the sorption/desorption kinetics.

Conclusion

As shown in the literature, this method can be of use in the pharmaceutical industry [8] as well as in the food industry [9, 10].

The impressive sensitivity of the available microcalorimeters allows, in specific cases, to develop analytical methods based on microcalorimetry. The simple procedure presented here is thus a selected example of the use of microcalorimetry as an analytical tool.

This work also fits well in the present trend to develop measuring techniques in relation to amorphism, crystallinity and glass transition of polymers and biopolymers.

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Zusammenfassung — Die DSC-Kurve von gefriergetrockneter amorpher Saccharose zeigt den Glasumwandlungspunkt, die Kristallisation und (kurz vor der Zersetzung) das Schmelzen der Probe. Die Kristallisation von Saccharose erfolgt unterhalb 100°C: diese Erscheinung kann deshalb mit einem Setaram Micro-DSC Mikrokalorimeter in der Betriebsart Scanning erfaßt werden. Zur Kalibrierung des Gerätes wurden Gemische aus amorpher und kristalliner Saccharose bekannter Zusammensetzung verwendet. Auf der Grundlage der bestimmten Kristallisationsenthalpien konnte eine low-level-Amorphie (herab bis etwa 0,5 %) erfaßt und quantitativ ermittelt werden. Die Kalibrationskurve kann zur Bestimmung des Amorphiegrades von gemahlener Saccharose verwendet werden. Auf der Basis von durch Rekristallisation der amorphen Schicht induzierter Wasserdesorption kann eine einfache gravimetrische Methode eingesetzt werden, um ähnliche Angaben noch schneller zu erhalten. Diese einfache Methode ist besonders nützlich für eine on-line-Kontrolle der Amorphie während eines Verfahrensprozesses und wird ebenfalls kurz beschrieben.