Effect of moisture uptake on amorphous inulin properties

Sébastien N. Ronkart[1,2], Michel Paquot[1], Christian Fougnies[3], Claude Deroanne[2] and Christophe Blecker[2]

1 Gembloux Agricultural University, Department of Food Technology (Head: Prof. C. Deroanne), URL: http://www.fsagx.ac.be/ta
2 Gembloux Agricultural University, Department of Industrial Biological Chemistry (Head: Prof. M. Paquot),
Passage des Déportés, 2, B-5030 Gembloux, Belgium,
3 Cosucra Groupe Warcoing SA, Rue de la sucrerie, 1, B-7740 Warcoing, Belgium

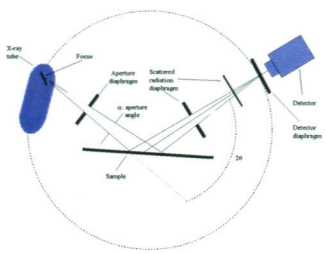
Introduction

Inulin is a natural storage carbohydrate composed of a chain of fructose units with generally a terminal glucose unit, industrially extracted from chicory root and commercially available in the powdered form. In a previous study, we engineered physical properties and controlled the amorphous/crystallinity content of inulin by selecting appropriate feed temperature and/or inlet air temperature of the spray-drier.

Unlike a crystalline structure, the amorphous state has a kinetically non-equilibrium structure. Amorphous solids are commonly formed through rapid cooling of a liquid melt to a certain temperature so that the molecules in the melt do not have enough time to rearrange and are frozen in their original position. An amorphous solid is also called a glass, and is characterized by a glass transition, which refers to the phase transition when a glass is changed into a supercooled melt. The glass transition is an important parameter for understanding the mechanisms of transformation processes in foods and for controlling their shelf-life. Depending on the moisture and/or the storage temperature, the amorphous product can physically change in order to attain a more thermo-dynamical stable state. For this reason, the aim of the present paper was to determine the kinetic of the physical changes of amorphous inulin powder stored at high relative humidity. The physical parameters investigated were the glass transition temperature (Tg) and the crystallinity index, determined by Modulated Differential Scanning Calorimetry (MDSC) and Wide Angle X-ray Scattering (WAXS), respectively. Temperature-resolved WAXS was used to understand the MDSC thermograms when crystallization occurred. In addition, surface analysis was used to correlate the measured parameters to the observed macroscopic property changes of the amorphous powder.

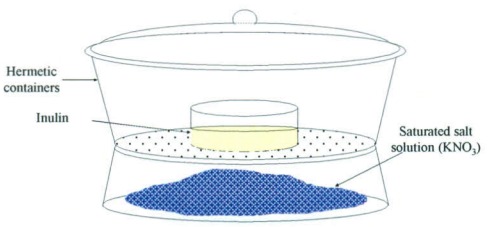
Experimentation and results

Wide Angle X-Ray Scattering (WAXS)



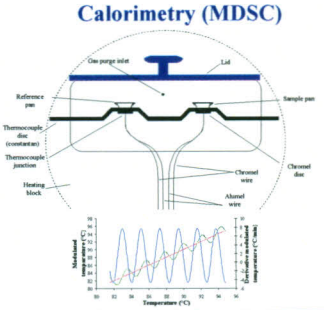
The powder X-ray diffractometer used was a PW3710 Philips Analytical X-ray B.V. with a Ni-filtered CuK_α radiation, generated by an anode device operating at 40kV and 30mA in conjunction with a proportionnal detector. The patterns were recorded with a fixed time of 0.4s per step of 0.02° in the 4<2θ<30° range.

Inulin conditioning



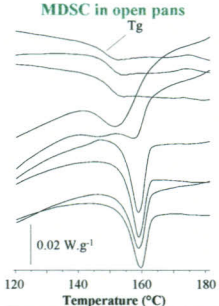
Inulin was stored over P_2O_5 for one week at 20°C to obtain a dehydrated product, then conditioned over KNO_3 for different times.

Modulated Differential Scanning Calorimetry (MDSC)

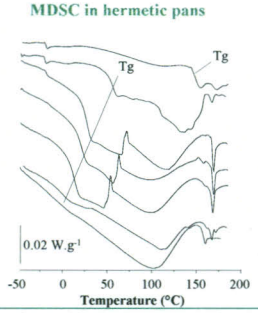


The MDSC measurements were realized by using a DSC 2920CE TA Instruments in hermetic and non hermetic aluminium pans. Heating rate was of 1.5°C.min^{-1} and the DSC cell was purged with 70 cm^3.min^{-1} dry nitrogen.

MDSC in open pans

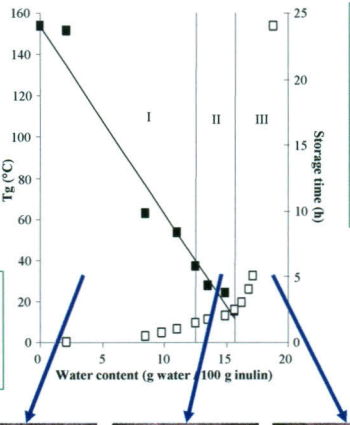


MDSC in hermetic pans



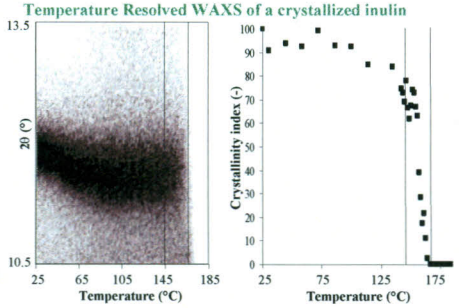
The starting material and the inulin stored up to 1 h 45 min only presented a glass transition at around 150°C. Although the samples stored at 2 h and 2h 30 min were still amorphous, their thermal properties were different from those conditioned up to 1 h 45 min. At 2 h – 2 h 30 min, the Tg of the amorphous product was below the storage temperature (20°C), due to the plasticizing effect of water, as determined by the reversing heat flow using hermetic pans. After 3h, an endothermic peak was present above the glass transition temperature observed for the amorphous samples.

Tg – water content state diagram

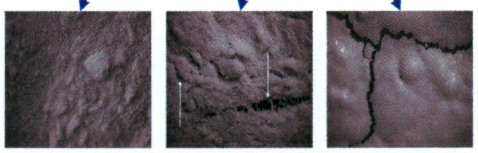


The relationship between water content, crystallization and thermal properties, permitted the determination of three zones in the state diagram. Zone I was the plasticization effect of water by depressing Tg, without physical property changes like heat capacity jump, crystallinity index or caking as the product was still in a powder form. Zone II characterized the product with a Tg down to the storage temperature with some macroscopic and thermal property changes, but with a crystallinity index equal to zero as in zone I. Stereomicroscopy analysis showed some cracking, probably due to the specific volume decrease above Tg and thus the retraction of the powder. Moreover, in these fully amorphous samples, some parts of the amorphous phase were rubbery and others were in the powdered form. During storage in the zone II, the glassy / rubbery amorphous inulin ratio decreased, allowing an increase in the molecular mobility and thus the crystallization of inulin in the defined zone III.

Temperature Resolved WAXS of a crystallized inulin

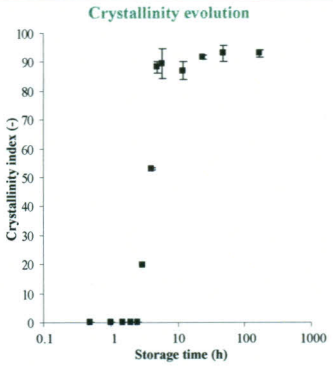


Stability of the powder in the 3 zones



In comparison to the MDSC results, the beginning and the end of the endothermic peak corresponded to the transition observed in the Temperature-Resolved Wide Angle X-ray Scattering experiment (145 and 165°C for onset and endset temperature, respectively). Indeed, up to 145°C, crystallized amorphous inulin showed diffraction peaks; while above this value, the crystallinity decreased drastically, as showed by the drop of the crystallinity index. A completely amorphous sample was observed at 166°C.

Crystallinity evolution



The samples were considered completely amorphous up to a storage time of 2 h 30 min (crystallinity index = 0%), while the crystallinity indexes increased up to a plateau limit of 92-93% after 24 h of storage, and can be considered as reaching an equilibrium state.

Conclusions

The effect of moisture uptake during storage on amorphous inulin properties has been investigated. Water content, crystallinity indexes, thermal properties and glass transition temperature evolution permitted the understanding of the physical and behaviour changes of the amorphous material. The Tg – water content state diagram allowed us to point out three zones. Zone I was the plasticization effect of water on Tg with inulin in a powdered amorphous state. The defined zone II was an intermediate state between glassy amorphous and crystallized inulin, with some macroscopic and thermal property changes. In zone III, the product crystallized, caked and no glass transition was observed. An endothermic peak appeared at the initial glass transition, which was attributed to the melting of inulin crystals, as confirmed by Temperature-Resolved Wide Angle X-ray Scattering.

Acknowledgments

Financial support was provided for this study by the Walloon Region of Belgium (DGTRE) and Cosucra Groupe Warcoing SA. The authors are grateful to Mrs Lynn Doran for technical assistance, Mrs. Bernadette Norberg and Prof. Johan Wouters from the 'Department of Structural Biological Chemistry' of the 'Facultés universitaires Notre Dame de la Paix' (Namur, Belgium) for the use of the WAXS and the Temperature-Resolved WAXS, and Jean Detry for his help on the stereomicroscope.