Study of the stability and the physical property changes of amorphous inulin during moisture adsorption

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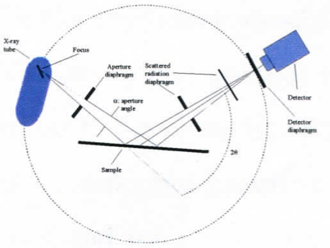
Introduction

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 solid is metastable. 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 this work 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 (T_g) 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.

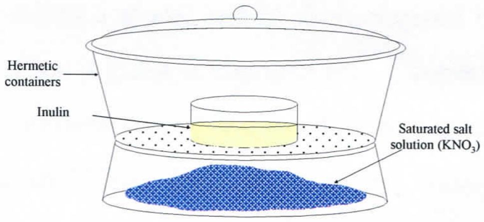
Experimentation and results

Wide Angle X-ray Diffraction



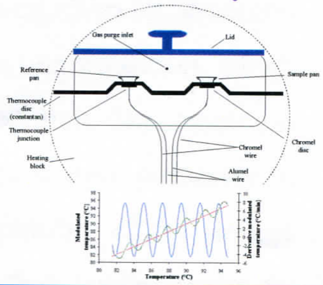
The powder X-ray diffractometer used was a PW3710 Philips Analytical X-ray B.V. with a Ni-filtered CuK$_\alpha$ radiation, generated by an anode device operating at 40kV and 30mA in conjunction with a proportionnal detector. The patterns were recorded with a fixed time of 0.4s per step of 0.02° in the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

Inulin conditioning



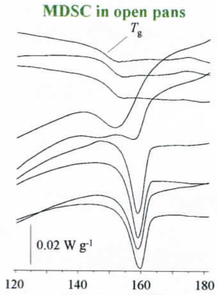
Inulin was stored over P_2O_5 for one week at 20°C to obtain a dehydrated product, then conditioned over KNO_3 for different times.

Modulated Differential Scanning Calorimetry

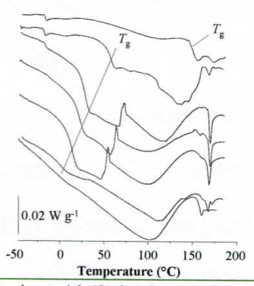


The MDSC measurements were realized by using a DSC 2920CE TA Instruments in hermetic and non hermetic aluminium pans. Heating rate was of 1.5°C min^{-1} and the DSC cell was purged with 70 cm^3 min^{-1} dry nitrogen.

MDSC in open pans

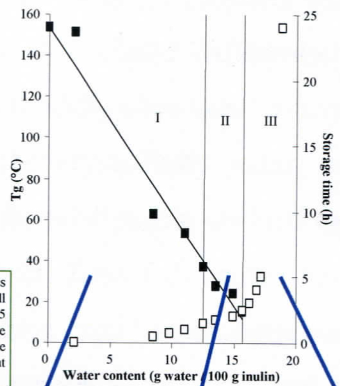


MDSC in hermetic pans



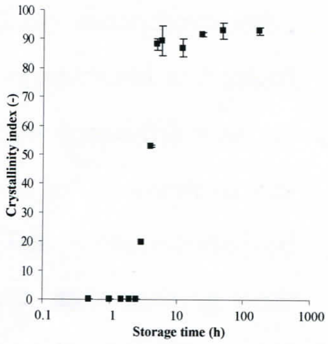
The starting material and the inulin stored up to 1 h 45 min only presented a glass transition at around 150°C. Although the samples stored at 2 h and 2h 30 min were still amorphous, their thermal properties were different from those conditioned up to 1 h 45 min. At 2 h – 2 h 30 min, the T_g of the amorphous 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.

T_g – water content state diagram



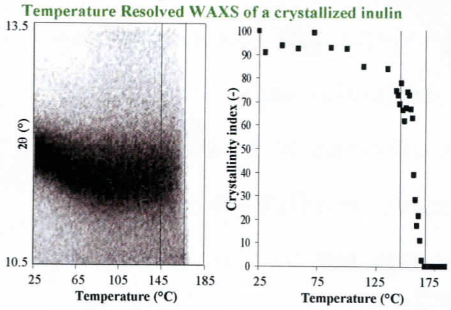
The relationship between water content, crystallization and thermal properties, permitted the determination of three zones in the state diagram. Zone I was the plasticization effect of water by depressing T_g, without physical property changes like heat capacity jump, crystallinity index or caking as the product was still in a powder form. Zone II characterized the product with a T_g 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 T_g 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.

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.

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.

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 T_g – water content state diagram allowed us to point out three zones. Zone I was the plasticization effect of water on T_g 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

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Reference: S. N. Ronkart, M. Paquot, C. Fougnies, C. Deroanne, C.S. Blecker. Effect of moisture uptake on amorphous inulin properties. Food Hydrocolloids. Article in press.

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Unlike crystalline structure, the amorphous state has a kinetically non-equilibrium structure. The 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. This transition is an important parameter for understanding the mechanisms of transformation processes in food and for controlling their shelf-life. Depending on the relative humidity of the storage temperature, the glass transition temperature of the product can be modified, leading to drastic property changes influencing the product stability.

For these reason, we investigated the physical property changes of amorphous spray-dried inulin during water uptake at 20°C. Modulated Differential Scanning Calorimetry (MDSC) and Wide Angle X-ray Scattering (WAXS) were used to investigate the evolution of the glass transition temperature (Tg) and the crystallinity index, respectively. The water content, crystallization and thermal properties relationship enabled the identification of three zones in the Tg – water content state diagram. Zone I delimited inulin in a glassy amorphous state, while zone II characterized inulin in a liquid amorphous state. Inulin crystallized and caked when Tg was below the storage temperature of 20°C, but crystallization (zone III) was not spontaneous and was delayed by the defined zone II. The crystallization led to thermograms similar to enthalpic relaxation, as an endotherm appeared close to Tg. Temperature-Resolved WAXS allowed to correctly ascertaining the MDSC endothermic peak as a melting peak because the crystallinity index was maximal at the onset temperature of the transition, and dropped to zero at the endset temperature. This working approach can be transposed to various amorphous food ingredients during storage.

Keywords: inulin, glass transition, thermal analysis, stability, x-ray diffraction.