Impact of crystallinity index on the stability and physical properties of inulin during moisture uptake

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

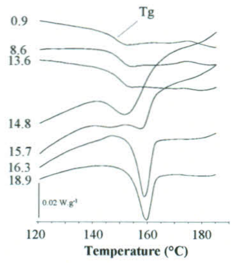
Introduction

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 the food technology domain, the study of the amorphous fraction by the mean of the glass transition temperature (T_g) is crucial for predicting powder stability during storage. Unlike crystalline structure, an amorphous is in a non-equilibrium state and will tend to crystallize depending on storage conditions (temperature, humidity). In this study, the impact of the crystallinity of spray-dried inulin on the powder stability was investigated during water uptake at 94% relative humidity (RH) storage at 20°C. Various spray-dried inulin powders with different crystallinity indexes but with identical chemical composition were used for this purpose. The resulting physical properties and powder stability of inulins were studied in detail at various water content. The plasticizing effect of water on glass transition temperature (T_g) and crystallinity was characterized by Modulated Differential Scanning Calorimetry (MDSC) and Wide Angle X-ray Diffraction (WAXS), respectively. Temperature-resolved WAXS was used to correlate the MDSC thermograms and the WAXS diffractograms when crystallization occurred in both amorphous and semi-crystalline inulins. In addition, the inter-particular properties which were related to the powder stability were visualized by Environmental Scanning Electron Microscopy (ESEM).

Experimentation and results

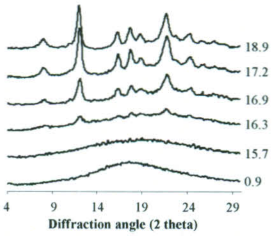
Amorphous inulin

MDSC in open pans



Up to 13.6 g water / 100 g dry inulin, amorphous inulin only presented a glass transition at around 150°C. Although the samples at 14.8 and 15.7 g water / 100 g dry inulin were still amorphous, their thermal properties were different from those containing up to 13.6 g water / 100 g dry inulin. Above 16.3 g water / 100 g dry inulin, an endothermic peak was present around the glass transition temperature.

Crystallinity development



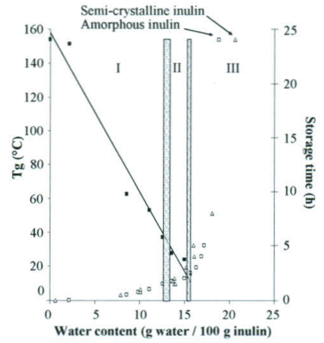
The samples were considered completely amorphous up to a water content of 15.7 g water / 100 g dry inulin (crystallinity index = 0%); while crystallization occurred between 15.7 and 16.3 g water / 100 g dry inulin. The crystallinity indexes increased up to 92-93% at 18.8 g water / 100 g dry inulin.

ESEM micrograph of amorphous inulin in Zone I

amorphous inulin in Zone III

Amorphous inulin in zone I was in a powder form; while amorphous inulin in zone III caked. The drop of the material's viscosity led to inter-particles fusion and thus the caking of the powder.

Tg – water content state diagrams of amorphous and semi-crystalline inulins



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.

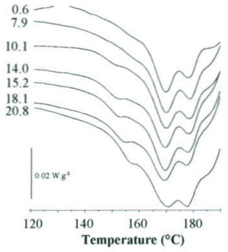
Zone II characterized the product with a T_g down to the storage temperature with some macroscopic and thermal property changes, but with a crystallinity index equal to zero as in zone I (for amorphous inulin). Moreover, in the fully amorphous samples, some parts of the amorphous phase were rubbery and others were in the powdered form. In zone II, some parts of the semi-crystalline of the sample were agglomerated but easily friable and others were in the powdered form.

Zone III characterized a free flowing loss for both amorphous and semi-crystalline inulin. Amorphous inulin caked (hard and brittle); while semi-crystalline inulin agglomerated (but easily friable).

Semi-crystalline inulin

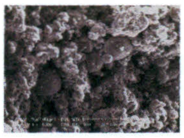
MDSC in open pans

Up to 7.9 g water / 100 g dry inulin, semi-crystalline inulin was characterized by a dual endothermic peak, which corresponded to the melting of a dual crystal population. Between 7.9 and 10.1 g water / 100 g dry inulin, and additional endothermic peak appeared at 157°C, which corresponded to the melting of crystals formed (see WAXS results).



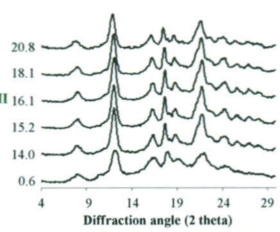
ESEM micrograph of semi-crystalline inulin in Zone I

semi-crystalline inulin in Zone III



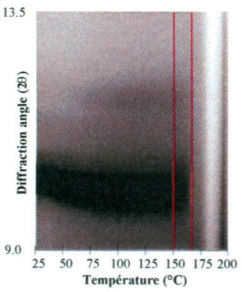
Semi-crystalline inulin in zone I was in a powder form; while semi-crystalline inulin in zone III was slightly agglomerated but the entire product was easily friable.

Crystallinity development

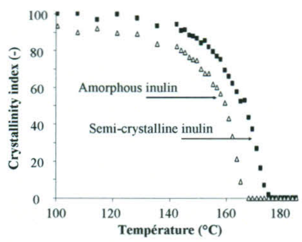


The semi-crystalline inulin recrystallized at a lower water content than the amorphous counterpart.

Temperature Resolved WAXS

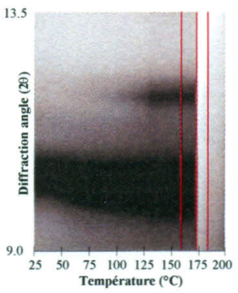


Temperature-Resolved WAXS of amorphous inulin stored one week at 94% RH (water content = 18.9 g water / 100 g dry inulin). Vertical lines correspond to the onset, midpoint and endset temperature of the MDSC endothermic peak.



Temperature-Resolved WAXS of semi-crystalline inulin stored one week at 94% RH (water content = 20.8 g water / 100 g dry inulin). Vertical lines correspond to the onset, and endset temperature of the MDSC endothermic peak centered at 170°C.

Temperature Resolved WAXS



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. Semi-crystalline inulin exhibited a total lost of crystallinity 12°C higher than its amorphous counterpart.

Conclusions

The effect of water content on amorphous and semi-crystalline inulin properties was investigated. Water content, crystallinity indexes, thermal properties and glass transition temperature evolution permitted the understanding of the physical and behavior changes of both powders. During water uptake, amorphous powders caked; while the semi-crystalline counterparts were agglomerated but friable. Both caking and agglomeration were observed when the T_g was below the 20°C storage temperature. This led to a higher mobility of the amorphous fraction of the powder and an increase of the crystallinity for both semi-crystalline and amorphous inulin. The experimentations have shown that the semi-crystalline inulins were stabler in the high humidity environment than the amorphous ones; which is of crucial importance for the stability of inulin during process, storage or incorporation in high moisture formulations. The T_g – water content state diagram of amorphous inulin 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

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-Christophe Lambrechts from the CERTECH (Seneffe, Belgium) for his help on ESEM.

Impact of crystallinity index on the state diagram of inulin during moisture uptake

Sébastien N. Ronkart[1,2], Michel Paquot[2],
Christian Fougnies[3], Claude Deroanne[1], Christophe Blecker[1],
[1,2] Gembloux Agricultural University, [1]Department of Food Technology; [2]Department of Industrial Biological Chemistry, Passage des Déportés, 2, B-5030 Gembloux, Belgium.
[3] Cosucra Groupe Warcoing SA, Rue de la sucrerie, 1, B-7740 Warcoing, Belgium.

In the food technology domain, the study of the amorphous fraction by the mean of the glass transition temperature (Tg) is crucial for predicting powder stability during storage. Unlike crystalline structure, an amorphous is in a non-equilibrium state and will tend to crystallize depending on storage conditions (temperature, humidity). In this study, the impact of the crystallinity of spray-dried inulin on the powder stability was investigated during moisture uptake at 94% relative humidity (RH) storage at 20°C. Various spray-dried inulin powders with different crystallinity indexes but with identical chemical composition were used for this purpose. The resulting physical properties and powder stability of inulins were studied in detail after various storage times at 94% RH. The plasticizing effect of water on glass transition temperature (Tg) and crystallinity was characterized by Modulated Differential Scanning Calorimetry (MDSC) and Wide Angle X-ray Diffraction (WAXS).

During moisture uptake, amorphous powders caked; while their partially crystalline counterparts were agglomerated but friable. Both caking and agglomeration were observed when the Tg was below the 20°C storage temperature. This led to a higher mobility of the amorphous fraction of the powder and an increase of the crystallinity for both partially crystalline and amorphous inulin. The experimentations have shown that the partially crystalline inulins were stabler in the high humidity environment than the amorphous ones; which is of crucial importance for the stability of inulin during process, storage or incorporation in high moisture formulations.

Keywords: inulin, caking, x-ray diffraction, glass transition