Impact of the physical properties of inulin on stability during moisture sorption

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Introduction

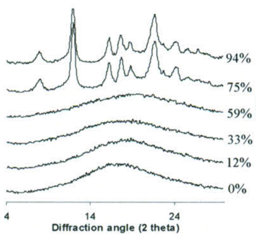
For now, commercial inulin is mainly extracted from chicory root and is available as a spray-dried powder product, which has the advantage of long shelf-life and low production costs, compared to other drying techniques (e.g. freeze-drying). Depending on the process conditions, inulin can be amorphous or semi-crystalline, meaning that crystals coexist with the amorphous phase. Amongst the physical properties, the study of the amorphous fraction of a powder is crucial for predicting its stability during storage. The moisture uptake of an amorphous powder can result in crystallization, depending on the amount of sorbed moisture, temperature and time. Usually this ordering of the molecules leads to caking of the powder. Although a relatively large amount of articles reported the crystallization and its impact on the caking of amorphous products, the influence of a residual crystallinity on the behavior of the powder is poorly described in literature.

Schaller-Povolny *et al.* (2000) pointed out the impact of the molecular weight on the stability of inulin; inulins with higher average degrees of polymerization were more stable than the lower ones. Crystallization and caking phenomena of the amorphous inulin powder occurred when the storage temperature was above the glass transition temperature. However, commercial inulins can be either amorphous or semi-crystalline, which must also have an impact on the flowability of the powder during storage. For this reason, the aim of this research was to investigate the influence of the powder's crystallinity on moisture sorption and the consequences to the physical and flowability properties of inulin powders with the same chemical composition. For this purpose, we needed to produce inulin powders with a broad range of crystallinity but with the same chemical features. In a previous study, we changed the crystallinity of a semi-crystalline commercial inulin by selecting appropriate feed temperatures and/or inlet air temperatures of the spray-drier. In this study, selected powders covering a broad range of crystallinity were conditioned at various levels of controlled relative humidity (RH). The resulting glass transition temperature (T_g) and crystallinity of inulins were determined by Modulated Differential Scanning Calorimetry (MDSC) and Wide Angle X-ray Scattering (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-particle properties which were related to the powder stability were visualized by Environmental Scanning Electron Microscopy (ESEM).

Experimentation and results

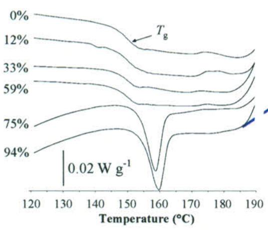
Amorphous inulin

Wide Angle X-ray Scattering



Inulins were amorphous up to 59% of relative humidity (RH), while at 75% RH and above, they crystallized in the mono-hydrated form.

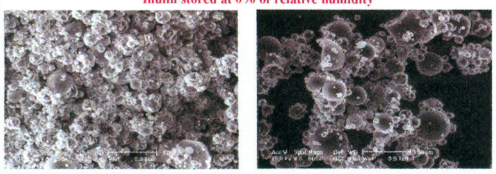
Modulated Differential Scanning Calorimetry



As long as the sample was in an amorphous state, the thermal profile (in open pans) was characterized by a jump at around 150°C, which corresponded to the glass transition temperature. When the inulin crystallized from the fully amorphous product (at 75% RH and above), a melting of the formed crystals at T_2 = 160°C.

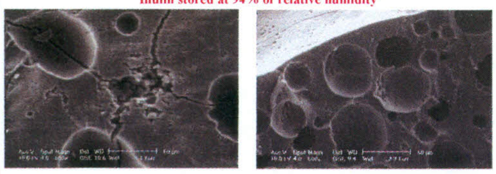
Environmental Scanning Electron Microscopy

Inulin stored at 0% of relative humidity



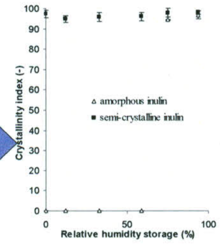
Inulin stored one week at 0% RH were in a powdered state.

Inulin stored at 94% of relative humidity

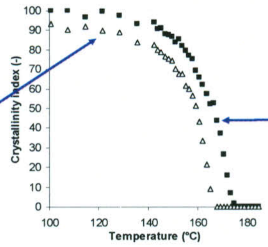


Inulin stored one week at 94% RH were in an advanced state of caking. A continuous hard and brittle mass was obtained. The initial particles appeared fused-agglomerated.

Experimentation and results (centre)

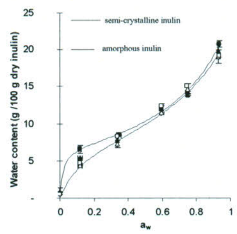


Temperature-Resolved Wide Angle X-ray Scattering



Up to 145°C, crystallized amorphous inulins showed diffraction peaks (open symbols); while above this value, the crystallinity index decreased. In comparison to the MDSC results, the beginning and the end of the endothermic peak corresponded to the melting of crystals observed in the TRWAXS experiments (145 and 165°C for onset and endset temperature, respectively).

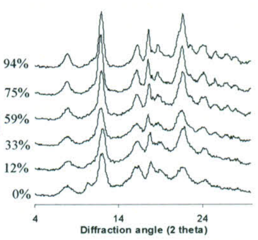
Concerning the semi-crystalline inulin, it showed a total loss of crystallinity 12°C higher than its amorphous counterpart.



In the low RH range (0-12%), the semi-crystalline inulins were more hygroscopic than their amorphous counterparts. This fact is unusual because it is recognized that amorphous saccharides are a lot more hygroscopic than crystal ones whatever their polymorph.

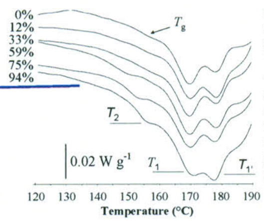
Semi-crystalline inulin

Wide Angle X-ray Scattering



In this RH range, we observed a pseudo-polymorphic transition from the hemi-hydrate to the mono-hydrate crystalline inulin form. The difference between these two crystalline forms is an increase in the number of water molecules in the unit cell lattice. So, we can suppose that the pseudo-polymorphic transition fills the crystal lattice with water molecules leading to higher water content than the amorphous sample in the low humidity range.

Modulated Differential Scanning Calorimetry

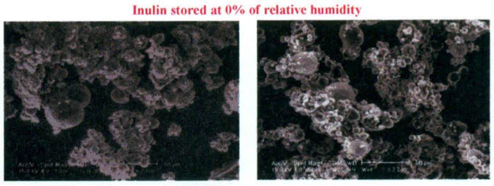


Stored at 0-59% RH, the semi-crystalline inulin was characterized by a dual endothermic peak at T_1 = 171-172°C and $T_{1'}$ = 178-179°C, which corresponded to the melting of a dual crystal population.

Crystallized inulin (at 75-94% RH) were characterized by an additional endothermic peak at T_2 = 157°C probably due to the formation of less perfect crystals.

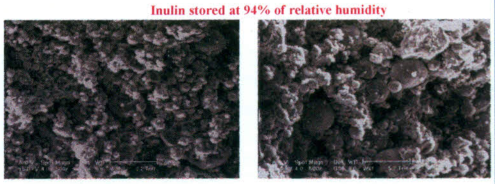
Environmental Scanning Electron Microscopy

Inulin stored at 0% of relative humidity



Inulins stored one week at 0% RH were in a powdered state.

Inulin stored at 94% of relative humidity



Inulin stored one week at 94% RH were slightly agglomerated but the entire product was easily friable.

Conclusions

This study pointed out the importance of inulin crystallinity in regards to its behavior during humidity storage. Amorphous inulin was in an advanced state of caking at RH > 75%; while their semi-crystalline counterparts were agglomerated but friable in the same humidity conditions. This caking occurred as the T_g dropped below storage temperature (20°C). This resulted in a crystallization of the amorphous fraction for both amorphous and semi-crystalline inulins, leading to a melting peak in the MDSC thermograms. In the low humidity range, the semi-crystalline inulin was more hygroscopic than its amorphous counterpart, which is in contradiction with the general thinking that amorphous materials are more hygroscopic than crystalline ones. This difference occurred in the hemi-hydrate / mono-hydrate pseudopolymorphic transition. The hemi-hydrate form found in the 0% RH was very unstable as less than 12% RH were enough for its conversion to the more stable mono-hydrate form. This difference in the stability between the semi-crystalline inulin and its amorphous counterpart is of crucial importance for the behavior of inulin during process, storage or incorporation in high moisture formulations. This study will help to predict the solid-state behavior of inulin powders in regards to humidity. It could also be extended to other molecules presenting similar properties, including the presence of an amorphous phase or polymorphic transitions.

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The impact of the physical properties of spray-dried inulin on the powder stability was investigated during moisture sorption at 20°C. Various spray-dried inulin powders with different crystallinity indexes but with identical chemical composition were used for the moisture sorption experiments. For this purpose, the physical properties and powder stability of inulins conditioned at different relative humidity levels were studied in detail. The effect of 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).
The amorphous powder caked at a relative humidity storage between 59 and 75%; while their partially crystalline counterparts were agglomerated but friable. Both caking and agglomeration were observed when the glass transition temperature (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.
An Environmental Scanning Electron Microscopy (ESEM) study showed a structural difference between amorphous and crystalline inulins stored at high relative humidities. The experimentations have shown that the partially crystalline inulins were more stable in the high humidity environment, 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.