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Determination of physical changes of inulin related to sorption isotherms: An X-ray diffraction, modulated differential scanning calorimetry and environmental scanning electron microscopy study

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Abstract

This paper gives a relationship between powdered inulin behaviour and physical parameters determination. Glass transition temperature (T_g) and development of crystallinity were measured in relation to the water moisture of the polymer. These parameters were obtained by Modulated Differential Scanning Calorimetry (MDSC) and powder X-ray diffraction, respectively. In order to change the water content of the powder, adsorption and desorption isotherms (using different relative humidity storage conditions) were done and successfully fitted to the Guggenheim–Anderson–de Boer (GAB) model. Dependent on the relative humidity storage, a caking phenomenon occurred when glass transition temperature was under storage temperature. An Environmental Scanning Electron Microscopy (ESEM) study showed a structural change when water activity increased above 0.56 at 20 °C. A correlation between the increase of the crystallinity and the hardening of the powder was determined. ESEM permitted an observation of the development of some crystal structures among the amorphous system, confirmed by an increase of the diffraction peaks obtained by powder X-ray diffraction. These observations lead to an understanding of the physical characteristics of inulin related to the water moisture.

Keywords: Inulin; Polymer; Crystallinity; Glass transition; Plasticization

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1. Introduction

Inulin, depicted in Fig. 1, is a natural storage carbohydrate found in chicory roots, Jerusalem artichoke and dahlia tubers. It is a mixture of polysaccharides composed of fructose unit chains (linked by β-(2→1) D-fructosyl-fructose bonds) of various length, terminated generally by a single glucose unit (linked by an α-D-glucopyranosoyl bond). Only a small fraction depending essentially of hydrolysis rate does not contain any glucose units at all (Blecker et al., 2002). Its composition depends on the plant source, harvesting date but also on extraction and post extraction process. During the last decade, a lot of attention has been paid to inulin because it is classified as a prebiotic dietary fibre and as a ‘fat or sugar substitute’ (O’Brien, Mueller, Scannell & Arendt, 2003). These aspects and other nutritional interests are broadly discussed in the literature. Consequently, its use in the food industry is in constant increase. More information on structure, conformation, solubility and the numerous texturing properties offered by this functional food are reported in a recent review (Blecker et al., 2001).

The most stable form for the commercialisation of inulin is the powdered form, which has the advantage of facilitating manipulation, transport, storage and consumption. However, when a food product is exposed to a certain relative humidity, it loses or gains water to adjust its moisture to equilibrium with the environment conditions. For these reasons, water activity and moisture content have long been considered relevant parameters to describe food stability. The relationship between the equilibrium moisture content and the water activity at a given temperature and pressure, yields a moisture sorption isotherm when expressed graphically. This isotherm curve can be obtained in one of two ways: adsorption or desorption.

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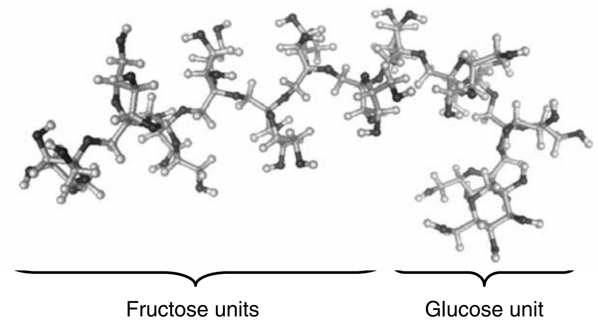

Fig. 1. Chemical structure of inulin. Image obtained by the Qmol version 3.0 software (Gans J.D. from the Cornell University) with a Ball and stick rendering. Courtesy to PhD Nicolas Delsaux from the 'Centre de Biophysique Moléculaire Numérique', Agricultural University of Gembloux.

The adsorption and desorption processes are not fully reversible, therefore a distinction can be made between them by determining whether the moisture levels within the product are increasing or decreasing (Al-Muhtaseb, McMinn & Magee, 2004).

When the moisture content of inulin powder varies, some physical changes like agglomeration or caking can occur (Schaller-Povolny, Smith & Labuza, 2000). In order to determine and understand the physico-chemical property changes of the powder in relation with sorption isotherms, some physical parameters can be determined.

The most important change in the amorphous state occurs over the glass transition temperature (T_g) range, which is the temperature at which polymeric materials change from an amorphous solid (glass) to an amorphous rubber. T_g, which can be investigated by Modulated Differential Scanning Calorimetry (MDSC), is specific to each amorphous material and can be correlated to some caking or agglomeration of polysaccharide powders, like inulin (Schaller-Povolny et al., 2000) or maltodextrin (Roos and Karel, 1991). This concept appeared to be a powerful tool for understanding the mechanisms of processes in food products and for controlling their shelf-life (Champion, Le Meste & Simatos, 2000). It is well known that water is the major component responsible for depressing the T_g of food material. For this reason, water is considered as a strong plasticizer in a food system (Kalichevsky & Blanshard, 1993). This consideration is important since, it was established that for storage temperature below T_g, the food was expected to be stable; while above T_g, the storage temperature was assumed to control the rate of physical changes.

Slade and Levine (1991), reported the strong influence of water on crystallization of amorphous biopolymers. Powder X-ray diffraction has been used to understand the crystallization behaviour of the amorphous fraction of polysaccharides relating it to the physical state and glass transition of the powder (Jouppila & Roos, 1997; Jouppila et al., 1998; Zimeri & Kokini, 2002).

Cleaver et al. (2004), used the Scanning Electron Microscopy (SEM) technique in order to visualize the formation of solid bridges between adjoining particles in boric acid powder. This technique seems to be a powerful tool for determining and observing the caking phenomenon on a polysaccharide surface. However, literature about the utilization of such a technique applied to biopolymer behaviour is very poor. The introduction of the Environmental Scanning Electron Microscopy (ESEM) technique has revolutionized the observation of biological samples by Scanning Electron Microscopy by enabling direct examination of biological specimens in an aqueous environment (Cohen et al., 2003).

For these reasons, the aim of the present study was to determine and understand the behaviour of inulin powder, related to adsorption and desorption isotherms. In relation with sorption isotherms, glass transition temperature (T_g), development of crystallinity and structural changes were investigated by MDSC, powder X-ray diffraction and ESEM. Understanding these parameters will lead to an explanation of the powder properties.

2. Materials and methods

2.1. Sample preparation

The inulin used was an industrial spray dried product kindly supplied by Warcoing (Belgium), characterized by an average degree of polymerization in number (DPn) of 10. Inulin was initially stored over P_2O_5 or KNO_3 in Petri dishes. This step was done to obtain a dehydrated or humidified product. The inulin samples were left to equilibrium for three weeks, then conditioned at least six weeks at 20 °C at different a_w values by storing them in desiccators containing different saturated salts solutions (P_2O_5, LiCl, $MgCl_2$, NaBr, NaCl and KNO_3). These salts covered a large relative humidity range (<0.06–0.93 at 25 °C). Before and after conditioning, inulin samples were analysed by MDSC, powder X-ray diffraction, moisture content, water activity and ESEM.

2.2. Modulated differential scanning calorimetry

The apparatus used was an 2920 TA Instrument (New Castle, Delaware, USA) with a refrigerated cooling assessory (RSC) and modulated capability. The MDSC cell was purged with 70 ml min^{-1} dry nitrogen and calibrated for baseline on an empty oven and for temperature using two temperature and enthalpy standards (indium, T_{onset}: 156.6 °C, ΔH: 28.7 J g^{-1}; eicosane, T_{onset}: 36.8 °C, ΔH: 247.4 J g^{-1}). Specific heat capacity (C_p) was calibrated using a sapphire. The empty sample and reference pans were of equal mass to within ± 0.10 mg. All measurements were made at least in triplicate over a temperature range from −50 to 180 °C, with a heating rate of 1.5 °C min^{-1}. After equilibration, inulin samples were analysed in hermetically sealed aluminium pans. Hermetic pans were used in order to avoid water evaporation. T_g was determined as the mid-point of the observed change in the heat capacity. The amplitude and the period of the MDSC were 1.5 °C and 90 s, respectively.

2.3. Powder X-ray diffraction

Development of crystallinity during storage of inulin was analysed by powder X-ray diffractometry, following a procedure previously described by Blecker, Chevalier, Fougnies, Van Herck, Deroanne and Paquot (2003). The apparatus used was a PW3710 Philips Analytical X-ray B.V. with a Ni-filtered Cu Kα radiation, generated by an anode device operating at 40 kV and 30 mA in conjunction with a proportional detector. The patterns were recorded with a fixed time of 0.4 s per step of 0.02° in the $4<2\theta<30°$ range, at 20 °C.

Hardened inulin was milled just before the analysis. This step was done in order to avoid the preferential reflection of the caked sample.

2.4. Environmental scanning electron microscopy

The samples were examined in the Environmental Scanning Electron Microscope (ESEM), XL30 type ESEM-FEG (Philips/FEI) at 20 kV, using wet mode at 3.4–5.4 Torr at 10.0 mm working distance. The detection system used was a Gaseous Secondary Electron Detector (GSED).

2.5. Sorption isotherm

The moisture sorption isotherms consisted of a plot of moisture content versus a_w at a fixed temperature. After equilibration at different a_w values, moisture content was determined by weight lost by oven drying at 105 °C for 24 h The a_w was measured at 20 °C with an Aqualab hygrometer. Samples were analysed at least in triplicate and the average value was reported on the adsorption and desorption isotherms.

In the last years, the Guggenheim, Anderson and de Boer (GAB) model has been widely utilized to describe the sorption behaviour of foods, and was characterized by Figueira, Park, Reis Brod, and Honorio (2004), as the best mathematical sorption isotherm model at constant temperature. For these reasons, this model was used in order to fit the different experimental points of the sorption and the desorption isotherms. The GAB equation is normally written in the following Eq. (1) form:

$$m=\frac{CKMa_w}{(1-Ka_w)(1-Ka_w+CKa_w)} \tag{1}$$

where m is the moisture content of the material on a dry basis (g water/g dry solids), C is the Guggenheim constant related to heat of sorption, a_w is the water activity, K is the constant related to multilayer molecules properties and M is the moisture content of monolayer in BET theory (g water/g dry solids). In order to determine these parameters, Eq. (1) was transformed into a second order polynomial function form, as follows Eq. (2):

$$\frac{a_w}{m}=\alpha a_w^2+\beta a_w+\gamma \tag{2}$$

where α, β and γ are constants that were obtained by plotting a_w against a_w/m. The constants C, K and the monolayer value M were calculated from Eq. (3–5).

$$M^2=\frac{1}{\beta^2-4\alpha\gamma} \tag{3}$$

$$K=\frac{(1/M)-\beta}{2\gamma} \tag{4}$$

$$D=\frac{1}{MK\gamma} \tag{5}$$

This GAB equation has been found to adequately represent the experimental data in the range of water activity of most practical interest in food (0.10–0.90). As an indication of the fit of the GAB model, the relative percentage Root Mean Square (RMS) was calculated according to Lievonen and Roos (2002), as Eq. (6).

$$\%\mathrm{RMS}=\sqrt{\frac{\sum_i^N\left[\frac{m_i-m_i^*}{m_i}\right]^2}{N}}100 \tag{6}$$

where m_i is the experimental water content, m_i^* is the predicted water content and N is the number of experimental data.

3. Results and discussion

Before physical analysis, the integrity of the chemical composition of inulin was checked in order to determine if the long storage at high relative humidities induced or not a variation in the chemical composition of the sample. This precaution was important because in some conditions (pH and temperature), inulin can be hydrolysed, with production of smaller DP inulin, sucrose and fructose (Blecker, Chevalier, Van Herck, Fougnies, Deroanne and Paquot, 2002). This lower DP production can lead to false conclusions. Indeed, it is well known that sucrose or fructose have very different sorption isotherm shapes, in comparison with inulin. As reported by Grosso et al. (2000), sucrose and fructose have a sorption isotherm with a high increase of water moisture when $a_w>0.8$, while inulin has a sigmoid shape sorption isotherm (Schaller-Povolny et al., 2000; Zimeri & Kokini, 2002). Moreover, the presence of low molecular weight substances in a given polymer, can modify the T_g values related to a_w storage (Roos and Karel, 1991). Analysis by High Performance Anion Exchange Chromatography coupled with Pulse Amperometric Detection (HPAEC-PAD) of inulin in extreme a_w storages (P_2O_5 and KNO_3) are compared in Fig. 2. Results showed no degradation during the storage. So, in this study, the behaviour of inulin during storage resulted of physical changing and not from chemical composition modification.

3.1. Sorption isotherms

Adsorption and desorption experimental points were drawn by curve-fitting to the GAB mathematical model as presented

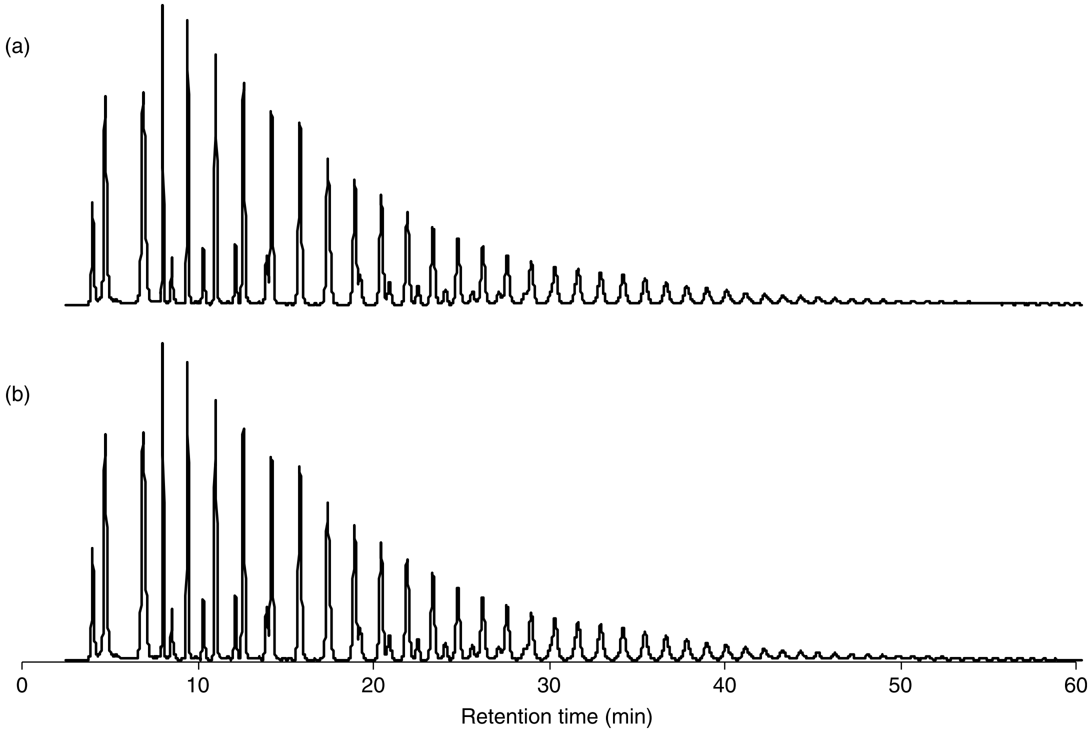

Fig. 2. Chromatographic profiles of inulin obtained by HPAEC-PAD on a Dionex DX500 chromatrography system operating at 1 ml min^{-1}. Aliquots of 25 µl of a 0.8 g l^{-1} solution were injected. Separation of the various chain lengths (DP) was achieved on a Dionex PA100 column. Sodium hydroxide (150 mM) was used as eluent. Sodium acetate gradient was applied and amperometric detection was used (Dionex Corp, 1999). (a) storage in P_2O_5 and (b) storage in KNO_3.

in Fig. 3. The shape of the lines indicated that as moisture content increased, free water expressed by a_w increased accordingly. The calculated GAB model constants and the RMS values are given in Table 1. The RMS values correspond to 3.44 and 4.37% for adsorption and desorption isotherms, respectively. From these values, we conclude that the GAB model is well adapted to fit experimental points for inulin adsorption and desorption isotherms, in agreement with Lomauro et al. (1985), who estimated the fitting as adapted for practical purpose when the RMS modulus value was below 10%. The sigmoidal shape curve obtained for both adsorption and desorption isotherm, reflect a Type II isotherm, according to Bruauer's classification (Brunauer et al., 1940). Depending on the DP of inulin, Schaller-Povolny et al. (2000), found some differences in the sorption isotherms. As the effective molecular weight of the inulin decreased, the *K* values of the GAB model increased, indicating a shift from a Type II to a Type III isotherm curve. This may be due to the fact that inulin was enriched by fructose and sucrose, which have more hydroxyl groups available to bind water, moving the sigmoidal shape of the Type II isotherm curve to the flat shape Type III isotherm curve typical of amorphous sugars. *K* value of this study (0.73) is in good agreement with those published by Schaller-Povolny et al. (2000), (0.64 and 0.76 for an average DP of 11 and 9, respectively). Furthermore, sorption isotherms clearly showed that the equilibrium moisture content for

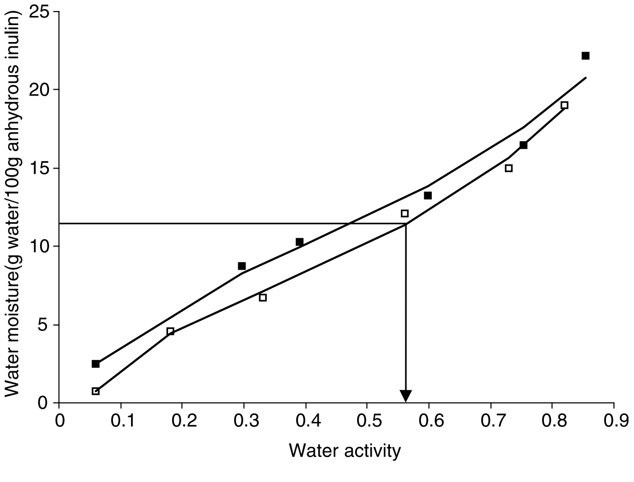

Fig. 3. Experimental adsorption (□) and desorption (■) isotherm points of inulin (20 °C), fitted using the GAB mathematical model. The arrow on the figure represents the critical a_w at which the product caked, determined for a critical water moisture value at which storage temperature (20 °C) was above T_g.

Table 1
Estimated values of intermediate parameters, GAB parameters and RMS values obtained for adsorption and desorption isotherms

	Adsorption	Desorption
Intermediate parameters		
α	−0.0717	−0.0568
β	0.0768	0.0745
γ	0.0288	0.0189
GAB parameters		
M	8.40	10.08
K	0.73	0.65
D	5.64	8.03
RMS (%)	3.44	4.37

desorption is higher than for adsorption at low water activity. This observed hysteresis in the low a_w range may be due to a reduction in the total number of active sites for water binding as a result of physical changes in the product. Moreover, a caking phenomenon of the powder was observed for desorption isotherm, while in adsorption isotherm up to 0.33, inulin samples were still in a powder form. At a_w of 0.56 and above, native inulin shrank, caked and then changed to a shiny white mass. This behaviour has been reported by Schaller-Povolny et al. (2000), for the native inulin Frutafit® (DP = 11), which caked at a_w 0.54 and above.

3.2. Modulated differential scanning calorimetry

MDSC allowed an accurate determination of T_g by using the derivative in time of the reversing component signal. It revealed a glass transition at temperatures comprised between −10 and 110 °C, depending on the moisture content. The heat capacity jump corresponded to the glass transition and was related to the amorphous phase content. Fig. 4 represents MDSC thermograms for adsorption and desorption isotherms at the a_w range investigated (<0.06–0.93). For a completely amorphous sample, the heat capacity jump was maximum while a semi-crystalline sample exhibited a reduce heat capacity jump. Fig. 5 shows the relationship between T_g of inulin and moisture content for both adsorption and desorption isotherms. By its plasticising effect on inulin, water decreased the T_g of the samples as the moisture content increased. This observation is important as it is well established that agglomeration and/or caking can occur when storage temperature is above the glass transition temperature (Mathlouthi and Rogé, 2003). Usually, the evolution of experimental T_g versus moisture content can be fitted to the Gordon–Taylor equation (Gordon & Taylor, 1952). According to Matveev et al. (2000), this Gordon–Taylor equation predicted the glass transition temperature of binary copolymers from the T_g values of the pure anhydrous polymers and those obtained for pure water (T_g water = −139 °C) (Kalichevsky & Blanshard, 1993). The application of the Gordon–Taylor equation is well established for fitting experimental T_g values of different low-molecular weight sugars and food biopolymers like polydextrose (Ribeiro, Zimeri, Yildiz & Kokini, 2003), inulin (Zimeri & Kokini, 2002) and maltodextrins (Roos and Karel, 1991). As glass transition was nearly abolished for the NaCl and KNO_3 storage ($a_w > 0.75$) on adsorption isotherm, the Gordon–Taylor fitting was not used in this study, and a linear relationship was made in the <0.06–0.75 a_w range.

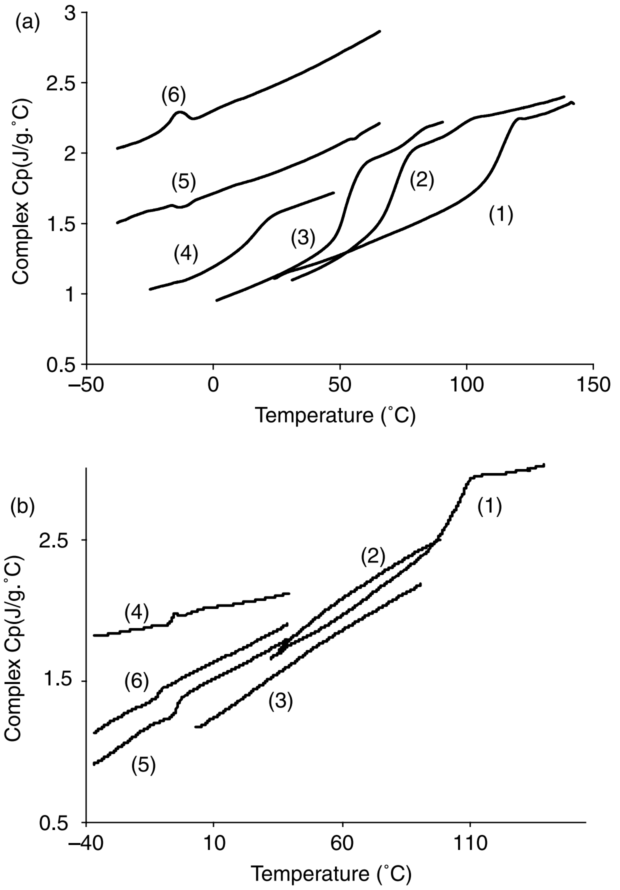

Fig. 4. MDSC thermograms of inulin obtained on (a) adsorption and (b) desorption isotherm in the water activity range investigated (<0.06–0.93). The different saturated salts used were P_2O_5 (1), LiCl (2), $MgCl_2$ (3), NaBr (4), NaCl (5), and KNO_3 (6).

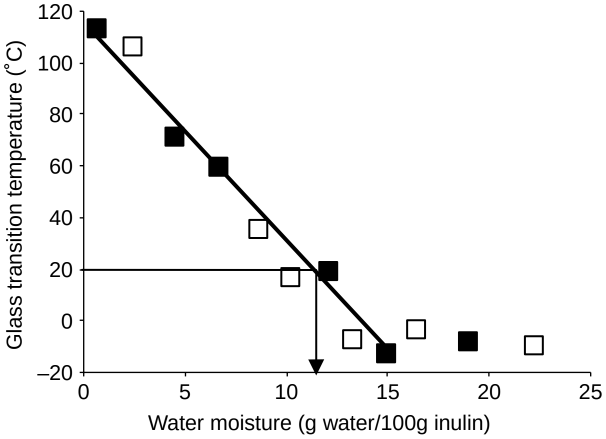

Fig. 5. Evolution of T_g of inulin according to their water moisture, at the adsorption (☐) and desorption (■) isotherms. Experimental T_g points were fitted using the Gordon–Taylor equation. The arrow represents the critical water moisture at which storage temperature (20 °C) was above T_g.

Critical moisture content can be defined as the moisture content at which caking begins under normal storage conditions, in this case (20 °C) as represented at Fig. 5. The critical moisture content at 20 °C (11.4 g water/100 g inulin) can be translated into critical a_w by using the GAB model established at the Fig. 3, and was ≈0.57. This value can be a good indicator of textural stability of the powder. So, this critical a_w could be a good indicator of the moisture content able to depress T_g under the storage temperature (20 °C), resulting in caking of the sample.

3.3. Powder X-ray diffraction

Fig. 6 shows the crystallinity changes of inulin during storage at different relative humidities at 20 °C. Powder X-ray

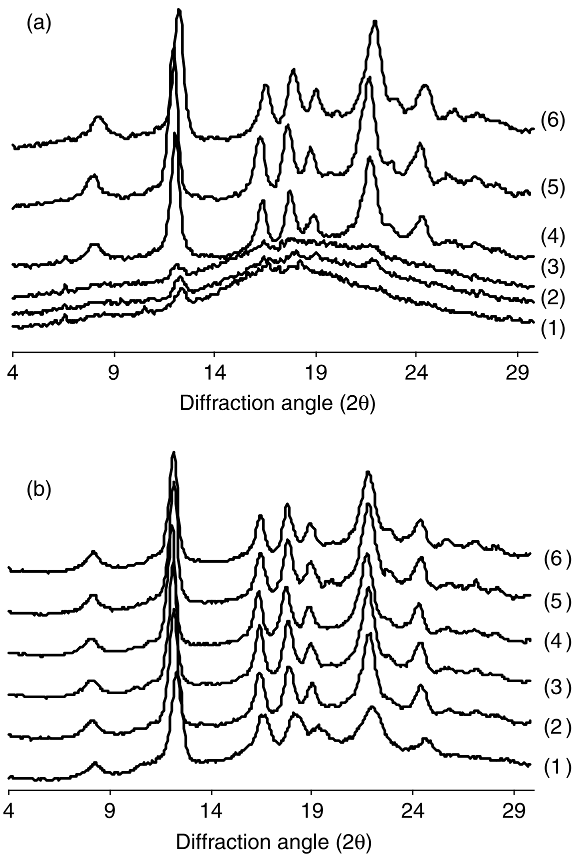

Fig. 6. Powder X-ray diffractograms of inulin obtained on (a) adsorption and (b) desorption isotherm in the water activity range investigated (<0.06–0.93). The different saturated salts used were P_2O_5 (1) LiCl, (2) $MgCl_2$, (3) NaBr, (4), NaCl, (5) and KNO_3 (6).

diffraction study showed two different behaviours depending on the sorption type.

3.3.1. Adsorption isotherm

Initially and at low relative humidity, only one weak diffraction peak was present, which indicated the amorphous structure of the native inulin. This observation was mainly due to the insufficient time for crystallization to occur in industrial spray drying conditions. Up to 0.56 a_w conditioning, the inulin powder stayed in an amorphous form. With the a_w increase, the diffractograms showed some diffraction peaks. The increasing intensities and peak areas showed development of crystallinity. These results confirmed a crystallization, resulting from an increase in the system's mobility (facilitated by water), which favoured reordering into a more stable crystalline structure. The crystallinity of the sample reached a maximum value at NaBr conditioning ($a_w=0.56$) and remained unchanged, regardless of a_w. Crystallization occurred when T_g was below storage temperature. In this case, T_g dropped from 48 to 15 °C falling below the storage temperature of 20 °C.

3.3.2. Desorption isotherm

For desorption isotherm, conditioning in KNO_3 resulted in an increase of crystallinity, accompanied by a hardened inulin form. Storage in containers with saturated salts of lower a_w, maintained the crystallinity of inulin, except for the P_2O_5 storage, which may have induced a change of crystal structure due to the drying conditions, as reported in Fig. 6. This phenomenon may be explained by the experimentations of André, Putaux, Chanzy, Taravel, Timmermans and de Wit (1996), and Marchessault, Bleha, Deslandes, and Revol (1980). Marchessault et al. (1980), showed some X-ray diffractograms of inulin powder recorded at various times after removal from a vacuum oven at 90 °C. These results can be interpreted as the effect of inulin hydration on the diffractograms obtained. However, they did not observe any increase in crystallinity as the 'moisture content' of the sample increased. We interpret their experimentations by the initial crystallinity of the material used by these authors. In addition, André et al. (1996), reported two crystalline inulin allomorphs, depending on the hydration conditions: a hydrated form and a semi-hydrated form. The difference between these unit cells did not seem to correspond to any change in the conformation of inulin, but rather to a variation in water content. However, André et al. (1996), claimed that the drying of these crystals with concomitant partial departure of water and unit cell shrinkage will invariably lead to crystalline defects and, therefore, to a loss of crystalline perfection. This fact may explain the lower intensity and the broad peak of the powder X-ray diffractogram obtained for the P_2O_5-desorption analysis.

A difference in crystallinity on adsorption and desorption isotherm were observed in the low a_w range, leading to an additional explanation of the hysteresis phenomenon. Indeed, hysteresis is not fully understood, although there is general agreement that some thermodynamically irreversible processes must occur during desorption or adsorption or both. According to Al-Muhtaseb et al. (2004), this thermodynamical oddity may be due to the fact that in wet conditions, polar sites in the molecular structure of the material are almost entirely satisfied by adsorbed water. Upon drying and shrinkage, the molecules and their water-holding sites were drawn closely enough together to satisfy each other. This reduces the water-holding capacity of the material upon subsequent adsorption. Furthermore, the crystalline regions typically exhibit resistance to solvent penetration. This hypothesis is in agreement with the work of Van den Berg (1981), who reported the hysteresis phenomenon as a changing amorphous structure between adsorption and desorption isotherm on starch.

3.4. Environmental scanning electron microscopy

Fig. 7 illustrates ESEM pictures of inulin in the powdered or caked form. When inulin was in the powder state (Fig. 7(a) and (b)), microscopy showed amorphous spherical shapes with an average size of about 50–100 μm. At $a_w>0.56$ for adsorption isotherm and for all experiments on desorption isotherm, a continuous mass was observed, showing some crystal development between amorphous particles as illustrated in Fig. 7(c) and (d).

Bhandari and Howes (1999), assumed that if a local portion of the product in a packaging picks up moisture, the glass transition temperature is locally depressed for that particular

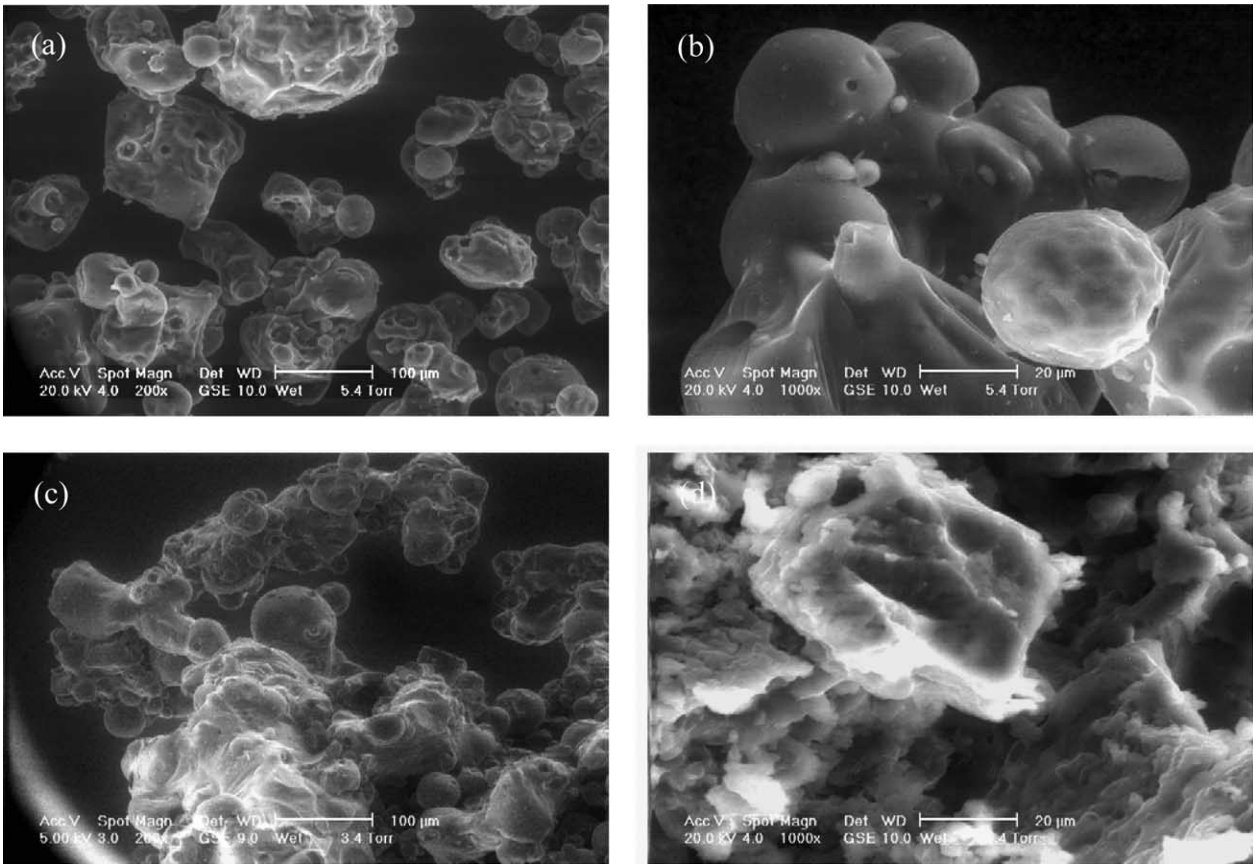

Fig. 7. Visualization of inulin using the Environmental Scanning Electron Microscopy (ESEM). (a) and (b) inulin in a powder form; (c) and (d) inulin in a caked form.

portion and crystallization rate will be accelerated. Tight and orderly molecular packing during crystallization cannot generally accommodate excess moisture which results in the loss of adsorbed water and absorption of this ejected moisture at the surface of neighbouring particles creating interparticulate liquid bridges resulting in caking (Bhandari & Howes, 1999). Peleg (1993), assumed that if a dried product with relatively higher moisture content was warmed to above its glass transition, the powder surface became viscous and formed a bridge between adjacent particles which resulted in agglomeration and caking. Moreover, Levine and Slade (1986), claimed that the faster amorphous sugars in the rubbery state can nucleate, form crystals and give up their water of hydration to the surrounding matrix resulting in caking of the matrix. These hypotheses were confirmed by our ESEM experiments, showing the agglomeration and caking phenomena. So, the hardening of inulin when crystallization occurred can be explained by the interactions induced at the amorphous-crystalline interface which acts as physical cross-links, and adds rigidity to the amorphous regions.

4. Conclusion

This paper has shown that the a_w storage of inulin influenced the evolution of several physical parameters, like glass transition temperature or development of crystallinity, having an effect on the stability of the powder. Modulated Differential Scanning Calorimetry, Powder X-ray Diffraction and Environmental Scanning Electron Microscopy experiments, permitted the visualization and the estimation of these parameters, related to adsorption and desorption isotherms.

The increase of the water moisture (above a_w: 0.56) decreased the T_g under the storage temperature (20 °C), leading to a development of crystallinity between the amorphous particles, resulting in a caking of the powder. These results were confirmed by powder X-ray diffraction and ESEM experimentations. In addition, the T_g–a_w relationship coupled to the sorption isotherms fitted to the GAB model, allowed the estimation of the hardening of inulin using a quite simple a_w determination. In this study, the caking phenomenon occurred at a_w:0.56 and above.

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