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# Effects of moisture content, molecular weight, and crystallinity on the glass transition temperature of inulin

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ABSTRACT

Effects of moisture content, molecular weight (MW), and crystallinity on the glass transition temperature ($T_g$) and freeze-concentrated glass-like transition temperature ($T'_g$) of a fructan (inulin) were investigated using differential scanning calorimetry. The $T_g$ of inulin samples decreased with increasing moisture content. The $T_g$ of semi-crystal inulin was higher than that of amorphous inulin. These results were fitted to the Gordon–Taylor equation, and $k$ values, reflecting the sensitivity to the water plasticizing effect, were obtained. The $k$ value was plotted against anhydrous $T_g$, and the relationship of amorphous inulin was described with a linear function. $T_g$ of anhydrous inulin samples and $T'_g$ of inulin–water mixtures increased with increasing MW, and the results were described empirically by a stretched exponential equation. These results will help to predict $T_g$ and $T'_g$ of inulin, depending on the moisture content, MW, and crystallinity.



## 1. Introduction

Inulin is a fructan that is linked by β(2–1) glycosidic bonds and contains either a terminal β-D-fructose or an α-D-glucose. The degree of polymerization (DP) of inulin is usually 2–60 units with an average DP = 12. Inulin has attracted much attention in the food and pharmaceutical industries for its multiple benefits, such as dietary fiber (Carabin & Flamm, 1999; Causey, Feirtag, Gallaher, Tungland, & Slavin, 2000; Davidson, Maki, Synecki, Toni, & Drennan, 1998; Kim, 2002) and prebiotic nature (Buriti, Cardarelli, Filisetti, & Saad, 2007; Corradinia et al., 2004; Fooks & Gibson, 2002; López-Molina et al., 2005; Rao, 2001). In addition, inulin–water mixtures show fat-mimetic properties. In order to produce fat-free foods, extensive efforts have been undertaken to investigate the rheological properties of inulin mixtures (Akalm, Karagözlü, & Ünal, 2008; Fagan, O'Donnell, Cullen, & Brennan, 2006; Gonzalez-Tomás, Coll-Marqués, & Costell, 2008; Hennelly, Dunne, O'Sullivan, & O'Riordan, 2006; Kim, Faqih, & Wang, 2001; Tárrega & Costell, 2006; Tseng & Xiong, 2009; Villegas & Costell, 2007; Zimeri & Kokini, 2003a).

Inulin exists, at least partially, in an amorphous state and thus glass transition occurs during dehydration/rehydration and/or freeze/thaw processing. Since various physical properties (*e.g.*, viscoelasticity) are changed drastically by the glass transition (Levine & Slade, 1988; Roos, 1995; Le Meste, Champion, Roudaut, Blond, & Simatos, 2002), it is important, from a practicality viewpoint, to understand the glass transition temperature ($T_g$) and freeze-concentrated glass-like transition temperature ($T'_g$). There have been many studies on the glass transition properties of inulin (Chiavaro, Vittadini, & Corradini, 2007; Hinrichs, Prinsen, & Frijlink, 2001; Ronkart et al., 2006; Ronkart, Deroanne, Paquot, Fougnies, & Blecker, 2010; Ronkart, Deroanne, et al., 2007; Ronkart, Paquot, Fougnies, Deroanne, & Blecker, 2009; Zimeri & Kokini, 2002, 2003b). For example, Hinrichs et al. (2001) investigated the glass transition properties of various types of inulin of varying DP, and reported the $T_g$ of anhydrous inulin and $T'_g$ of an inulin–water mixture; however, the effect of moisture content on the $T_g$ of inulin sample was not investigated. Zimeri and Kokini (2002) investigated the $T_g$ of inulin–water mixtures, and the dependence of $T_g$ on moisture content was characterized using a $T_g$-curve, by plotting $T_g$ versus moisture content, although the DP or molecular weight (MW) of inulin sample was unclear. More recently, Ronkart et al. investigated the glass transition properties of inulin samples having a DP = approx. 10 (2006) and a DP = approx. 30 (2009), and reported the $T_g$-curve of the inulin–water mixture. Although there have been many efforts to understand the glass transition properties of inulin, the published data were limited for prediction of glass transition properties, because both $T_g$-curve and $T'_g$ depend on DP or MW and

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its crystallinity. Therefore, further systematic study in addition to application of the obtained results is required.

In this study, the $T_g$ of various types of inulin was investigated using differential scanning calorimetry (DSC), and the effects of MW, crystallinity, and moisture on $T_g$ of inulin were revealed in order to predict $T_g$ and $T'_g$ of fructan. These results were compared with those of a glucan reported in previous studies (Kawai, Hagiwara, Takai, & Suzuki, 2005; Levine & Slade, 1988; Orford, Parker, Ring, & Smith, 1989; Roos, 1995).

## 2. Materials and methods

### 2.1. Materials and sample preparation

Three types of inulin reagent, Instant® (native), fiblose® (low-MW), and XL® (high-MW) were provided from San-ei Sucrochemical, Co., Ltd., Aichi, Japan. It was preliminarily confirmed that the average molecular weight of low-MW, native, and high-MW inulins was 1197, 2175, and 4395 g/mol (DP = 7, 13, and 27), respectively, by gel permeation chromatography (HLC-8220GPC; Tosoh Co., Ltd., Osaka, Japan).

First of all, crystallinity of the inulin reagents was investigated by X-ray. As shown in afterwards, it was found that only the high-MW inulin was a semi-crystal polymer, and thus amorphous high-MW inulin was also prepared, according to previous studies (Zimeri & Kokini, 2002, 2003b; Ronkart et al., 2009). In brief, a high-MW inulin–water mixture (40%, w/w) was hydrolyzed thermally at 90 °C, and then quenched by dropping it into liquid nitrogen. The frozen mixture was freeze-dried for 2 days, and the obtained solid was disintegrated using a rotary mixer. Four types of inulin samples (native, low-MW, non-treated (NT) high-MW, and pre-melted (PM) high-MW) were employed in this study.

### 2.2. X-ray diffraction (XRD)

The crystallinity of the inulin samples was investigated using X-ray diffraction (RINT-UltimaIII; Rigaku Co., Tokyo, Japan). The sample was placed in the aluminum sample stage. XRD measurement was carried out with 40 kV × 40 mA wavelength of CuKα = 1.54 Å and scanned at a rate of $2\theta = 10^\circ$/min with a 3–30° scanning range of the diffraction angle.

### 2.3. Isothermal water sorption

The samples were vacuum-dried at 60 °C for 48 h for sufficient water removal, and then held under various relative humidity (RH) conditions at 298 K. The equilibrium of water sorption was confirmed gravimetrically. A portion of the samples was used for DSC measurement, as is shown below. The others were used for the measurement of moisture content. The samples were dehydrated at 105 °C for 12 h, and the moisture content was evaluated gravimetrically.

### 2.4. DSC measurement

$T_g$ and $T'_g$ of the inulin samples were investigated using a DSC (DSC8230; Rigaku Co., Tokyo, Japan). In order to investigate the effect of moisture content on $T_g$, the inulin samples held under various RH conditions were prepared as mentioned above. Furthermore, 3–10% (w/w) aqueous solution was prepared in order to investigate $T'_g$ of the inulin samples. An empty aluminum pan was used as a reference, and the temperature and heat flow were calibrated using indium and distilled water. The sample (2–10 mg) was placed in an aluminum pan and hermetically sealed. In order to evaluate anhydrous inulin $T_g$, inulin that had been vacuum-dried at 60 °C for 12 h was put into the pan and held at 105 °C for 2 h prior to sealing. DSC measurement was performed at 5 °C/min in the temperature range of −40 and 180 °C.

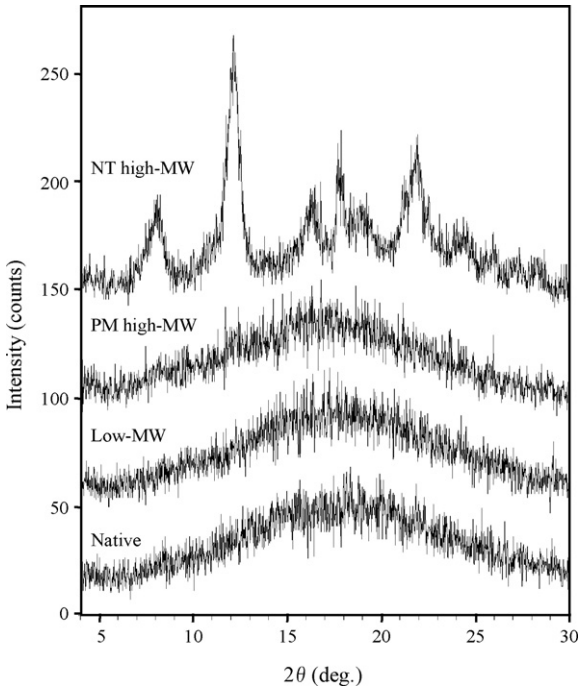


**Fig. 1.** X-ray diffraction pattern of inulin samples.

## 3. Results and discussion

### 3.1. Crystallinity of the inulin samples

The results of XRD are shown in Fig. 1. The native and low-MW inulins showed a halo pattern, indicating an amorphous form. NT high-MW inulin, on the other hand, showed some peaks indicating the existence of ordered structure in the XRD pattern. The peaks disappeared in PM high-MW inulin. From these results, it was confirmed that low-MW, native, and PM high-MW inulins were amorphous and NT high-MW inulin was in a semi-crystal state.

### 3.2. Isothermal water sorption behavior

The results of isothermal water sorption are shown in Fig. 2. The solid line was obtained by fitting the Guggenheim, Anderson and de Boer (GAB) equation (Eq. (1)) to the data,

$$W = \frac{W_m CK(RH/100)}{(1 - K(RH/100))(1 - K(RH/100) + CK(RH/100))} \quad (1)$$

where $W_m$, $C$ and $K$ represent the moisture content of the monolayer, a factor correcting the sorption properties of the first layer with respect to the bulk liquid, and a factor correcting the properties of the multilayer with respect to the bulk liquid, respectively (Zimeri & Kokini, 2002, 2003b). The obtained GAB parameters are listed in Table 1. It was found that the GAB parameters were affected by inulin MW and crystallinity. The $W_m$ of PM high-MW inulin was much larger than that of low-MW, native, and NT high-MW inulins. This can be attributed to the difference in the number of hydration-sites. The $C$ and $K$ increased and decreased with increase in MW, respectively. Increases in crystallinity caused increases in $C$ and $K$. The moisture content of low-MW and native inulins was much higher than that of NT and PM high-MW inulins at a RH > 60%. The drastic increase in the moisture content of low-MW and native