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Factors affecting inulin crystallization after its complete dissolution

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ABSTRACT

In this study, we analyzed inulin crystallization during one year after its complete dissolution and an effect of inulin crystal seeds concentration on rheological and textural properties of inulin gels. 20% and 25% solutions of three different inulins, one native and two high performance (crystal and amorphous), were prepared by heating at 100 °C for 5 min. During one year of storage at 20 °C, inulin did not form a gel structure, but only precipitates and a crystal layer on the walls of the containers. Addition of crystal seeds (0.02–2%) caused formation of gel structure. Minimal concentration of the crystal seeds necessary to form a strong inulin gel was 0.4%. Crystallographic structure of inulin powder did not have an influence on the formed gels. The obtained results allow inulin gelation to control which can be crucial in novel foods, the structure of which is based on inulin.

1. Introduction

Inulin is a polyfructan consisting of fructose (F) residues usually terminated by a glucose (G) moiety. Its simplified formula can be described as GF*n* and F*m*, where *n* or *m* is between 2 and 60, and represents the number of fructose units (Ronkart et al., 2006). Industrially inulin is mainly produced from chicory (Franck, 2002). Global production of inulin is estimated at 100 000 tons per year. Inulin is applied in food industry as sugar and fat substitute as well as gelling substance or bulking agent. Substitution of fat by inulin was successfully applied in milk drinks, cheese and meat products (Hennelly, Dunne, Sullivan, & Riordan, 2006; Mendoza, Garcia, Casas, & Selgas., 2001; Mittal & Bajwa, 2012). Such substitution caused significant decrease in caloric value of the final product (Glibowski & Kowalska, 2012; Mittal & Bajwa, 2012). Due to β (2–1) glycosidic bonds, inulin is not digestible by human enzymes and is classified as a soluble dietary fiber (EFSA, 2010). Moreover, inulin has prebiotic properties stimulating growth of pro-healthy bacteria in the colon (Gibson & Roberfroid, 1995).

Usually, inulin is purchased as a white powder, however sometimes it can be sold in a syrup form. The most important parameter describing inulin properties is average degree of polymerization (DP). Oligofructose (OF), native inulin and high polymerized (high performance) inulin has DP about 4, 10 and 23 respectively. Native inulin and OF are slightly sweet (up to 30% of sucrose) thus HP inulin is not sweet at all (Franck, 2002).

15–20% solution of HP inulin is able to form particulate gel mimicking fat (Kim, Faqih, & Wang, 2001). Besides DP and concentration, formation of inulin gel depends on pH, heating temperature and time, the presence of crystal seeds and crystallographic form of inulin powder (Glibowski & Pikus, 2011; Glibowski & Wasko, 2008). Inulin is hydrolyzed at pH below 4. The longer time, the higher temperature and the lower pH the faster hydrolysis takes place. Above pH 5, inulin is not hydrolyzed even after one hour of heating at 100 °C (Glibowski & Bukowska, 2011).

Recent studies showed that crystallographic form of inulin powder is quite important functional property (Glibowski & Pikus, 2011). Nowadays, inulin can be purchased in two forms – amorphous and semi-crystalline. Semi-crystalline form is easily dispersed. Fast addition of amorphous inulin powder to water causes very hardly dissolving clumps. This phenomenon results from a rapid bounding of water moieties by inulin to form crystal structure which energetically is more favorable than amorphous one (Glibowski & Pikus, 2011; Ronkart et al., 2009). As a consequence, dispersion of amorphous inulin powder in water at ambient temperature can cause a formation of strong inulin gel. To form similar gel, crystal inulin powder solution needs to be heated up to 72 °C (Glibowski & Pikus, 2011).

In the case of amorphous inulin, gel formation results from swelling inulin powder particles due to water binding. Crystal

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inulin powder forms a weak gel when dispersed at ambient temperature, probably because the crystals already exist in the powder and the formed gel structure is based on much less connection points between the present crystals than the primary structure formed by amorphous inulin. To form gel, crystal inulin has to be dissolved nearly completely (Glibowski & Pikus, 2011). When inulin solution reaches sufficient concentration (about 20%), gelation is possible as long as crystal seeds are present (Bot, Erle, Vreeker, & Agterof, 2004; Glibowski & Wasko, 2008). HP inulin dissolves poorly. At 50 °C, solubility of HP inulin is 1.2%. Further temperature increase causes significant increase in solubility (Kim et al., 2001). At 70–80 °C, 20% inulin solution is clear thus some microscopic inulin particles are still not dissolved. These particles, called crystal seeds, are necessary to form white creamy inulin gel after cooling. However, excessively long heating at 80 °C and above, can cause some problems with forming the compact gel structure (Glibowski & Wasko, 2008; Kim et al., 2001). Heating of 20% inulin solution at 100 °C for a few minutes makes formation of a gel structure impossible because of complete dissolution of inulin including most resistant particles. As Glibowski and Pikus (2011) mentioned in their studies, when such a solution is stored for several weeks at room temperature, gradual inulin precipitation occurs, but the gel structure is not formed even after a year of storage. However, to the best of our knowledge, there are no studies analyzing this phenomenon more deeply.

In spite of complete dissolution of native crystal seeds, inulin gelation can be initiated by addition of a small amount of inulin. Glibowski and Pikus (2011) showed that 5% addition of inulin (percentage calculated as a share in the total amount of inulin present in the sample) allowed the solution to turn into gel. These results were confirmed by Arcia, Navarro, Costell, and Tárrega (2012) in their studies concerning model desserts. They proved that seeding technique favored a faster formation of a greater amount and more regular sized inulin particles.

Because the knowledge about inulin crystallization in water environment is still lacking, the aim of this study was the estimation of inulin crystallization dynamic during one year after its complete dissolution and analysis of the impact of inulin crystal seeds concentration on rheological and textural properties of inulin gels.

2. Experimental

2.1. Materials

Inulin Frutafit® IQ (IQ) and Frutafit® TEX! (TEX) were kindly delivered by Sensus Operations C.V. (Roosendaal, The Netherlands). Inulin Beneo™ HP (HP) and Beneo™ HPX (HPX) were purchased from Orafti (Oreyle, Belgium). Inulins were extracted from chicory root and their average degree of polymerization is ≥23 with the exception of native inulin Frutafit® IQ with DP 9-12 (producer's data).

2.2. Preparation of samples

2.2.1. Long term observation

Inulin IQ, TEX and HPX (20% and 25%) was suspended in distilled water (20 °C) using a magnetic stirrer. To avoid clump formation inulin was gradually added to the beaker, which took approximately 2 min. The suspensions were stirred for 5 min. Subsequently, inulin suspensions were heated in conical flasks on an electric cooker up to boiling and boiled 5 min. After heating, the evaporated water was filled up with hot distilled water. Afterwards, the solutions were poured into plastic cylindrical containers of 35 mm inner diameter and the lids were twisted on to prevent evaporation. The containers were stored at 20 °C in a thermostatic cabinet. The whole procedure was repeated three times for each inulin and concentration.

2.2.2. Effect of crystal seeds addition on inulin gel formation

Inulin HP and HPX (18–20%) was suspended in distilled water as it was described in Section 2.2.1. The suspensions were heated up to boiling point and boiled for 5 min. Subsequently, the evaporated water was filled up with hot water and the solutions were cooled in a tap water to 40 °C. Afterwards, further inulin was added to reach 20% concentration in the final samples. The additional inulin, called crystal seeds, was added in the same way as it was described earlier. After 5 min of stirring, the solutions were poured into containers and stored as it was described above. The samples were analyzed after one week of storage. Some of the solutions were poured into rheometer cup for monitoring of gelation process.

2.3. Rheological measurements

Rheological measurements were conducted using a Haake RS 300 rheometer (Haake, Karlsruhe, Germany). Temperature control was maintained by a Haake DC30 circulator water bath (Haake, Karlsruhe, Germany). All rheological data were collected and calculated by Haake Rheowin software version 3.61.0004 (Haake, Karlsruhe, Germany). All measurements were done at 20 °C. The apparent viscosity was measured at 20 s^{-1} shear rate for 120 s. For analytical purposes the average value was calculated from the 90th, 105th and 120th second of measurement (Glibowski, Zarzycki & Krzepkowska, 2008). Dynamic oscillatory rheological measurements were conducted using parallel plate geometry (both 35 mm diameter and serrated). These measurements were carried out at 1 mm gap. Dynamics of the gelation process were conducted using rotating vane (22 mm diameter, 112 mm height). Measurement began when the sample was poured into the cup, 7 ml of oil was put on the surface of the sample to prevent evaporation, the lift moved and the vane took the measuring position (8 mm clearance to bottom). The oscillatory measurements were conducted at a frequency of 1.0 Hz and a strain of 0.001. Used strain corresponded to the maximum found within the linear viscoelastic region of the studied material (Glibowski & Pikus, 2011).

2.4. Hardness analysis

Hardness analyses were performed according to the method previously described by Glibowski (2009). Briefly, samples were punched by a cylindrical stainless steel probe (1 cm diameter) with the crosshead speed 1 mm s^{-1} at 15 mm depth, using a TA-XT2i texture analyzer (Stable Microsystems, Goaldming, England). The maximal peak value after punching the sample 15 mm down was considered as gel hardness. The analysis was performed without removing the samples from the containers.

2.5. Wide angle X-ray scattering

The wide angle X-ray scattering (WAXS) investigations were performed according to the method previously described by Glibowski and Pikus (2011). Briefly, we used Seifert URD-6 diffraction instrument. X-ray diffraction patterns were taken within the range of 2θ from 6° to 35°, at the increments of 0.02°, and at counting intervals of 6 s. Crystallinity indexes were calculated according to Ronkart et al. (2007) from the ratio of the integrated intensity of the crystalline peaks to the total integrated intensity of coherent scattering after appropriate baseline subtraction.