Inulin Gels

Edible Crystalline Soft Matter

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In food, a very important class of materials are gels (soft liquid-rich solids), which have a wide range of applications due to their variety of textures. Their mouthfeeling ranges from soft and squishy to creamy to firm and elastic.

While well-known hydrocolloids such as gelatin or agarose form physically cross-linked polymer networks upon cooling, gels can also develop by aggregation of colloidal particles into three-dimensional networks. The textural properties of these so-called particle gels depend on the morphology of the particle network as well as on the interaction forces between the individual particles. These consist for example of protein aggregates as in yoghurt or cheese, but can also be made up of crystallites such as in solid fats as margarine or cocoa butter. Consequently, similar structures made up from molecules other than lipids have a high potential as fat replacers. Examples discussed in the following are inulin gels, which can be produced in a variety of textures.
Inulin
Inulin is an oligosaccharide, which can be easily extracted from several economically important plants, such as chicory (root), onion, garlic and wheat. Industrially it is almost exclusively obtained from chicory roots by a production process almost identical to the extraction of sugar from sugar beets. Chemically, inulin belongs to the family of fructans, and is built up from 2 – 60 β-(2,1) linked fructose units (Fig. 1) and, most often, a terminal glucose molecule [1]. The inulin molecule’s average degree of polymerization is dependent on the source it is extracted from. Nutritionally it is a dietary fiber with low calorie content and prebiotic properties which is suitable for diabetic nutrition [2, 3]. Inulin/water suspensions can form particle gels with a fat like structure [4, 5]. Depending on the inulin molecule’s DP (= degree of polymerization), nowadays inulin is commercially used as sugar replacement (low DP), texturizer (medium DP) and as fat replacer (high DP).

The Particle Gel Model
While the exact structure and formation mechanisms of inulin gels are not yet fully understood, a simple model can be used to describe the gel formation.

When a certain amount of long chain inulin is added to water, depending on the amount of inulin and the temperature of the solvent, inulin powder dissolves partially (Fig. 2). The dissolved polydisperse oligosaccharides can be approximately considered as rods of different lengths. Upon cooling the dissolved inulin molecules partially recrystallize. To start the crystallization process, seeding material is needed upon which the dissolved inulin molecules are able to recrystallize. If the complete amount of inulin is dissolved at higher temperatures, a percolating particle gel will not be formed upon cooling, due to missing seeding particles [6]. The molecules with a larger DP recrystallize first (due to the lower solubility in water), and the molecules with a smaller DP accumulate on the outer regions of the developing crystallites. According to [7] those crystallites act as primary particles...
of the particle gel network. When the crystallization process continues, the primary particles form aggregates, acting as secondary particles in the particle gel network. The primary and secondary particles are mainly attracted to each other by van der Waals forces [6], water is trapped in the interspaces and a particle gel is formed. The particle sizes as well as their packing density are strongly influenced by the chain length distribution of the dissolved inulin. Variations in those parameters have a significant impact on the mechanical properties of the final inulin gels. Due to the crystalline nature of the primary particles, gel formation can be followed by methods probing crystal structures, e.g. X-ray diffraction (XRD). This non-invasive method allows studying the crystal development inside inulin gels in-situ in real time.

X-ray Diffraction
In the XRD experiment, a monochromatic X-ray beam is scattered by the sample in transmission geometry (Fig. 3a). For crystalline materials, Bragg reflections can be observed at specific scattering angles 2θ. These Bragg angles depend on the symmetry and dimensions of the crystal lattice. Therefore, they can serve as fingerprint for substance identification. In our experimental setup, the intensity distribution of the scattered X-rays is recorded on a 2-dimensional area detector. By radial averaging of the 2D data sets, measured on samples with isotropic crystallite orientation, X-ray diffractograms are obtained. For further analysis the background-subtracted intensity is plotted versus the scattering angle 2θ (Fig. 3b).

With an increasing crystalline fraction within the sample, the integrated intensities of the Bragg reflexes increase too. Therefore, the areas of the diffraction peaks of the inulin crystals are representative for the development of the inulin particle gel network.

X-ray Diffraction of Inulin Gels
To study the slow kinetics of the gel formation, it is necessary to monitor the development of the gels over several hours. Therefore, the scattered intensity distributions of the gels were monitored for 22 h. Inulin gels are prepared in the following way: Inulin/water suspensions containing 20% inulin dry matter are prepared at 25 °C, and the sample is stirred at this temperature for 10 min in a sealed beaker. Approximately 50 µL of this suspension are pipetted into the X-ray sample holder. For the XRD measurements, roughly 1 mm thick samples of inulin suspensions were contained between two 16 µm thick aluminum foils. The measurements are performed at a self-made instrument using a rotating anode X-ray generator (Rigaku MicroMax 007), multilayer optics (Osmic Confocal Max-Flux, Cu Kα) and a 2D online image plate detector (Mar345). Diffraction patterns are obtained by radial averaging of the 2D data, for scattering angles 2θ between 5° and 25°.
The background-corrected diffraction patterns of an inulin gel (prepared at 25 °C) at different stages of gelation, are shown in Fig. 4. For further analysis of the time dependent development of the gelation process, the maximum intensities of the Bragg reflexes at 2θ≈12.1° are projected to the YZ-plane. The peak intensity increases with increasing aging time. This is caused by the crystallization of the gel primary particles, which is representative of the development of the gel network [8]. The time dependence of the gel formation process can be analyzed quantitatively, when the development of the integrated Bragg intensities is examined (see inset Fig. 4). The extracted peak areas from the reflection at 12.1° were normalized to the corresponding maximum intensity after 22 h of ageing. The main part of the crystallization takes place in the first two to three hours of the gelation. In those first hours, the intensity increases to over eighty percent of its final value. Since the integrated intensity is representative for the degree of crystallinity, we conclude that the particle gel formation is almost finished after three hours of ageing. However, a quasi-equilibrium stage is probably only reached after more than 22 h. This in-situ XRD method is also useful for further applications. Every process that depends on the crystallinity of a material could be monitored in-situ during production. Examples include fat crystallization in chocolate [9] and cocoa butter [10]. Nowadays it is possible to obtain a diffraction pattern, with adequate statistics and resolution, in only a few minutes measurement time. This enables the operator to supervise the crystallization of the sample almost in real-time during the production process.

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**References**


