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Role of gellan gum microstructure in freeze drying and rehydration mechanisms

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ABSTRACT

The role of LA (low-acyl or deacylated) and HA (high-acyl) gellan gum microstructure in freeze-drying and rehydration processes was investigated. Molecular configuration and three-dimensional network of gellan gels were evaluated in relation to the freeze-drying kinetics, dried structure and rehydration rate. Interestingly, it has been observed and not yet reported prior to this work that the freeze-drying process of LA gellan gum was considerably different from HA gellan, especially in terms of decrease in water activity over time. The former shows a higher rate in water activity reduction. The freeze-dried structures were different between the two gel types due to their molecular configuration, as indicated by total porosity and pore distribution. Overall, the freeze-dried high-acyl gellan gum gel presented slightly larger pores. Moreover, on the subsequent rehydration, LA gellan gum behaved differently from HA gellan, showing a high dependence on the polymer concentration. In this context, both the bulk and surface properties were examined.

The proposed reason for these trends refers to the different molecular and three-dimensional freeze-dried structures between the two gel types. In this light, it is the first time that a research paper reports the micro CT analysis to characterise the freeze-dried structures for both HA and LA gellan gels.

The deep understanding of the gellan behaviour in freeze-drying and rehydration processes can be applied to HA/LA gellan mixtures, especially in terms of gel structure design. Some properties of the gellan blends are intermediate to the two gel types (swelling), others are more similar to one or the other gel (drying kinetics and rehydration).

1. Introduction

The interest in the production of dried-gel structures from hydrocolloids has been increasing for applications in different sectors. In the food industry, hydrocolloids are often used in the product formulation to modulate material properties, acting as a stabiliser, thickener or gelling agent (Norton & Foster, 2002; Phillips et al., 2000; Renard, van de Velde, & Visschers, 2006; Williams & Phillips, 2002). The release of sugar or active compounds can be designed in both wet and dried systems (Lin & Metters, 2006; Nishinari & Fang, 2016; Tønnesen & Karlsen, 2002). Furthermore, dried-gel structures are widely used for pharmaceutical purposes (George & Abraham, 2006; Lee & Mooney, 2012; Tønnesen & Karlsen, 2002) and tissue engineering (Drury & Mooney, 2003; Kang, Tabata, & Ikada, 1999).

Drying allows the extension of the shelf life of products (Ratti, 2001; Van't Land, 2011) by reducing both the water content and water activity, making them ready for use when requested. Water activity (a_w) is an essential parameter to measure in drying mechanisms (Barbosa-CÃ, Fontana, Schmidt, & Labuza, 2008). It provides information about the free water in materials, available to participate in chemical, physical and microbiological reactions (Barbosa-CÃ et al., 2008; Labuza, 1980). Considering food spoilage, it is used to define a stability map (Barbosa-CÃ et al., 2008; Rahman, 2009), since the bound water to the material structure (Aguilera et al., 1999; Mathlouthi, 2001) is not involved in reactions. In addition to food preservation, transport becomes cheaper (Sagar & Kumar, 2010), due to the weight reduction of the dried product. Drying should be carried out considering potential induced alterations in terms of mechanical properties and nutrient content (Fellows, 2009). For more complex products, such as dairy, it is necessary to preserve the whole structure and all the ingredients inside them. Therefore, if additives or gelling agents are used as

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ingredients (de Vries, 2002), they need to be treated appropriately on drying, considering their high capability to retain water (Milani & Maleki, 2012). Since the dried food structure plays an important role in some product properties (e.g. colour, texture and shape) (Aguilera, 2005), dried gel systems require investigation, as they act as effective ingredients. Rehydration is also affected by the drying process and the generated structure. Since a lot of products must recover water before their use, the water uptake mechanism has been extensively studied (Lewicki, 1998; Vergeldt et al., 2014).

A widely investigated drying technique that allows both gel shape and volume to be better maintained, decreasing the occurrence of shrinkage, is freeze drying. This is made possible by the absence of the liquid – vapour interface during the process, which is based on the sublimation of water (Scherer, 1990) from the matrix. By contrast to the common air drying, it works at low temperatures (Evans, 2008; Krokida, Karathanos, & Maroulis, 1998), avoiding product damage due to thermal treatment (Avila & Silva, 1999; Ratti, 2001). Therefore, freeze-dried products can achieve a high quality structure (Ratti, 2001).

In this context, the microbial polysaccharides LA (low-acyl or deacylated) and HA (high-acyl) gellan gum are widely used hydrocolloids in the food industry (Gibson & Sanderson, 1997; Morris, Nishinari, & Rinaudo, 2012; Saha & Bhattacharya, 2010) for modifying texture and giving structure (Chandrasekaran, Millane, Arnott, & Atkins, 1988), for the preservation of flavours or taste/appearance enhancement of foods (Morris et al., 2012).

In parallel to food applications, gellan gum is widely used in tissue engineering (Gantar et al., 2014; Silva-Correia et al., 2011), microbiology and for pharmaceutical formulations (Morris et al., 2012; Shah & Jani, 2010) and for cosmetic products, such as lotions and creams, conditioners and shampoos (Kubo, Miyazaki, & Attwood, 2003).

The gellan gum molecular configuration completely affects the three-dimensional structure of the gel, having an effect on its properties. The acyl substituents (acetate and glycerate) along the HA gellan polymer chain are well-known to lead to a softer and more flexible gel (Mao, Tang, & Swanson, 2000; Phillips et al., 2000). In particular, the acetate hinders the helix aggregation, introducing an entropic barrier (McClements, 2015; Morris et al., 2012), while the glycerate enhances the stabilisation by adding new hydrogen bonds, yet leading to the disruption of the binding site for cations by orientation change of the adjacent carboxyl group (Morris et al., 2012) and consequently the junction zone alteration. The acetyl substituents do not modify the overall double helix geometry (Chandrasekaran & Thailambal, 1990; Morris et al., 2012), while the L-glyceryl groups lead to a mechanical strength drop (Morris et al., 2012).

Freeze-dried LA gellan gum gels have already been investigated in terms of generated structure (Silva-Correia et al., 2011; Tiwari, Chakkaravarthi, & Bhattacharya, 2015), although the analyses reported are only based on SEM results, without providing information about pore distribution throughout the entire bulk volume. A micro CT analysis can provide a deeper understanding at the macroscopic level. Interestingly, there is a lack of information about freeze-dried HA gellan gum structure, or a clear comparison with LA gellan gum. Furthermore, the freeze-drying kinetics for gellan gum systems has not yet been investigated, especially highlighting the role of the molecular configuration. Abramovič and Klofutar (2006) suggested that the water absorption on gellan gum polymer is strictly dependent on its molecular structure, providing a useful support for drying kinetics modelling. However, in that study these considerations are applied for a generic drying process, and without considering the 3D macrostructure. Gantar et al. (2014) investigated the rehydrated gellan gum after freeze drying in terms of final water uptake. Nevertheless, in the same work the rehydration kinetics has not been proposed and HA gellan gum has not been considered.

In this work, the study of freeze-drying and rehydration mechanisms for both LA and HA gellan gum gels from a molecular and structural point of view is proposed. Different polymer concentrations were compared. Mixtures of LA (low-acyl or deacylated) and HA (high-acyl) gellan gum were investigated for the design of products in freeze-drying and rehydration mechanisms. Specifically, true-quiescent gels (Morris et al., 2012) were examined to clearly assess the effect of the molecular/network structures on freeze-drying and rehydration processes. However, this work can be applied to smaller aggregates as well, e.g. a fluid gel system (Banerjee & Bhattacharya, 2012; Norton, Jarvis, & Foster, 1999).

2. Materials and methods

2.1. Gel preparation

In this study, low acyl (Kelcogel F, CPKelco, UK) and high acyl (Kelcogel LT100, CPKelco, UK) gellan gum were used as gelling agents. All materials were used with no further treatment or purification. To prepare the gel solution, distilled water, obtained by a milli-Q water system, was heated up to 85 °C and then gellan gum powder was slowly added to avoid clump formation. Different polymer concentrations (1.5, 2, 2.5, 3% w/w) were used to prepare gels.

To have complete hydration, the solutions were stirred for two hours at constant temperature.

The pH was evaluated at 80 °C, equal to 5.1 ± 0.1 for LA gellan gum and 5.2 ± 0.1 for HA gellan gum, and were not dependent on the polymer percentage, from 1.5% w/w to 3% w/w.

The solutions were poured into sample moulds (22 mm in diameter and 65 mm in height) and left to cool down at room temperature (20 °C) to allow gel formation. After the gels were set, they were stored at room temperature (20 °C ± 1 °C) for 24 h.

Afterwards, the gels were cut, and from each mould, four samples were obtained (22 mm in diameter and 15 mm in height).

2.2. Freeze drying

The gel samples were put into a −18 °C freezer for 24 h to freeze, applying a 0.2 °C/min freezing rate, previously measured by using thermocouples at both the sample surface and core. Afterwards, they were placed into the freeze dryer (SCANVAC 110–4 PRO, LaboGene, UK) onto the shelf trays. The chamber pressure was lowered to 0.18 mbar by a rotary pump and the temperature of the condenser was set at −110 °C.

These process parameters were kept constant for all experiments, to highlight the effect of the gel structure.

The process was run for different times (1, 3, 6, 18, 24, 30) up to 48 h, after which the samples were stored under low vacuum conditions in a desiccator with silica gel beads until characterisation.

2.3. Water activity

Water activity is mathematically defined as the ratio of the equilibrium vapour pressure in a food or in the product (P) over the vapour pressure of pure water (P_o) at the same temperature (Labuza, 1975):

$$a_w = P/P_o$$

To measure the water activity, the Aqualab dew point water activity meter 4te (Labcell LTD, UK) was used and set at 25 °C