Microstructure and reconstitution of freeze-dried gum Arabic at a range of concentrations and primary drying temperatures

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Microstructure and reconstitution of freeze-dried gum Arabic at a range of concentrations and primary drying temperatures

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Title page**Microstructure and reconstitution of freeze-dried gum arabic at a
range of concentrations and primary drying temperatures**

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Abstract

Freeze-drying is an energy intensive unit operation used for the production of dehydrated foods, such as instant coffee and dried fruits, and results in high sensorial, nutritional and reconstitution properties of the final products. Understanding the relationships between operating conditions and product quality is essential to design processes that are energy efficient, whilst producing high quality dried foods.

In this work, the properties (microstructure and reconstitution) of freeze-dried gum arabic samples (with initial concentrations ranging between 20 and 60% solids by weight) were evaluated. The materials were dried at three different primary drying shelf temperatures, T_s (-20, -30 and -40°C).

Sample temperatures recorded throughout freeze-drying were close to the pre-set T_s , with the exception of the 60% initial concentration system, where the sample was hotter than the shelf by 10-15°C, in particular on increasing T_s . This was attributed to a combination of local temperature and pressure conditions that may have resulted in partial melting of the material. For the 20-50% systems, the properties of the freeze-dried materials were mainly affected by the initial concentration of the system, with increasing initial concentration generally resulting in lower porosities (ranging between 20-40%) and higher reconstitution times (ranging between 0.5-10min for 95% reconstitution). Pores were generally needle-shaped and <200µm. Large (200-1800µm), circular pores were observed in high initial concentration systems, and they were dominant in the microstructure of the freeze-dried 60% sample. The presence of these large bubbles was linked to the partial melting of the material, which enabled its expansion and puffing. For the 60% system, primary drying temperature had a profound effect on the properties of the freeze-dried solid, with samples dried at higher temperature showing higher porosity (e.g. 60-70% for $T_s = -20^\circ\text{C}$) and faster reconstitution rates (e.g. 3min for 95% reconstitution at $T_s = -20^\circ\text{C}$).

Overall, this study demonstrates the significance of formulation and shelf temperature on the porous structure of freeze-dried samples, which directly influences product performance.

Keywords: *Freeze-drying; Gum arabic; Concentrated formulations; Primary drying temperature; Porosity; Microstructure; Reconstitution*

1.0 Introduction

Drying is an important process in the food industry, historically used to extend the shelf-life of food products but also to create a range of dried foods. Food can be dehydrated using a variety of traditional methods including heat from the sun, hot air, osmotic and freeze-drying techniques. In addition, novel drying technologies such as microwave, ultrasound, super critical, superheated steam, infrared, high electric field drying have been proposed with a focus on improving the energy requirements and sustainability of the processes (Kumar et al. 2014; Moses et al. 2014; Huang et al. 2009; Reyes et al. 2008). The mass and heat transfer phenomena involved during water removal induce changes in the physical, chemical and biochemical characteristics of the raw materials producing dried food of diverse forms (e.g. powder and tablets). Often, physical changes are related to the structural properties, which also have implications on the bioavailability of nutrients, sensorial and functional properties as well as storage stability.

Among the different drying processes, freeze-drying remains popular for dehydration of delicate, thermally sensitive, biological materials including antibiotics, microorganisms (Nireesha et al. 2013; Chang & Patro, 2004; Tsinontides et al. 2004), encapsulated aroma or flavour, coffee, fruits and vegetables (Ciurzyńska & Lenart. 2011; Ratti, 2001; Sagara & Ichiba, 1994). In freeze-drying, water is first solidified and the solid state (ice) is then removed by means of sublimation. The material is generally dehydrated in three consecutive steps starting with freezing, followed by sublimation (primary drying) and ending with evaporation (secondary drying). The phase transitions of water from liquid to solid and finally to vapour are caused by a combination of low temperature (less than 0°C) and pressure (less than 0.006atm). However, one of the concerns in operating at such low temperatures and pressures is the heavy usage of refrigeration and vacuum systems leading to 4-8 times higher operational costs than spray and air drying (Ratti 2001). Studies on drying pre-treatments (Pardo & Leiva 2010; Huang et al. 2009), operational models (Liu et al. 2008; Luo & Zhou 2008) and controlling process parameters such as shelf temperature (T_s) and chamber pressure (P_c) (Parker et al. 2010; Lewis et al. 2010; Krokida et al. 1998) have been carried out in an effort to reduce drying time and energy expenditure whilst producing product of an acceptable quality.

With a continuously increasing demand for wholesome foods, freeze-drying stands out in consumer preference for its high food quality aspects such as maximising nutrients, flavour, aroma, and structure retention. In terms of microstructure, freeze-dried products are

recognized for being light weight and highly porous, often with instant reconstitution attributes (Meda & Ratti 2005; Marabi & Saguy 2004). The final microstructure and functional properties of freeze-dried materials are in part dependent on the material's initial concentration and the operating shelf temperature (T_s) during sublimation. These process variables significantly influence the simultaneous mass and heat transport properties throughout the operation (Tsinontides et al. 2004). For instance, the collapse temperature (T_c) and glass transition (T_g) points are typically used as indicators of the highest drying temperature during freeze-drying, and they are a function of product formulation (e.g. solid fraction or composition) (Ciurzyńska & Lenart 2016; Harnkarnsujarit et al. 2012; Tsourouflis et al. 1976). These investigations suggest that selection of suitable operating temperatures is indirectly controlled by the composition of the materials being processed. Extensive work on understanding the importance of eutectic, glass transition, melting and collapse temperature (Ruiz-Cabrera et al. 2016; Sacha & Nail 2009; Tang & Pikal 2004; Levi & Karel 1995; Roos & Karel 1991; Pikal & Shah 1990; Roos & Karel 1990; Tsourouflis et al. 1976) has led to the design of appropriate freeze-drying cycles for different formulations (Esfandiary et al. 2016; Harnkarnsujarit et al. 2012; Parker et al. 2010; Khalloufi & Ratti 2003; Overcashier et al. 1999; Karathanos et al. 1996). Sublimation of the ice is a major part of the freeze-drying process, with most of the water within the material being removed at this stage. The sublimation stage has the longest duration and is the highest energy consumer compared to freezing and secondary drying (Ciurzyńska & Lenart 2011; Ratti 2001). For this reason, primary drying has long been the focus area in process design usually through manipulation of T_s and pressure chamber (P_c) (Patel et al. 2010; Barresi et al. 2009; Hammami et al. 1999; Sadikoglu et al. 1998).

Gum arabic is a natural gum that contains arabinogalactan, arabinogalactan-protein complex and glycoprotein. It is widely used as an emulsifier in the food industry. As a food additive it influences the viscosity, body and texture of the food (Sanchez et al. 2017). The nutritional aspects of gum arabic have also been highlighted in several articles, and it has been suggested as a natural source of dietary fibre, thus improving the gut health (Khalid et al. 2014; Phillips & Phillips 2011; Glover et al. 2009).

In our previous work, the effect of different freezing conditions on the properties of freeze-dried highly concentrated (50 and 60% initial solids content by weight) gum arabic was studied (Malik et al. 2018). The current investigation focuses on investigating the effect of formulation (20-60% w/w initial concentration) and primary drying temperature (-20, -30,

-40°C) on the properties of the freeze-dried gum arabic systems, in an attempt to contribute further in the understanding of the link between operating conditions and structure/performance properties of freeze-dried hydrocolloid-based systems.

2.0 Materials and methods

All concentrations mentioned in this work refer to w/w solid content of the material.

2.1 Sample preparation

Gum arabic powder from Sigma-Aldrich Co. Germany was used to prepare solutions with concentrations of 20, 30, 40, 50, and 60%. The required amount of powder was slowly added to distilled water under mixing (250rpm with magnetic stirrer) to avoid lump formation and the mixture was heated between 45-50°C until all the powder was dissolved. Prepared solutions were then degassed to remove excess air bubbles incorporated during dissolution. Air bubbles were removed manually after overnight gravimetric separation at room temperature (20°C). Solutions were then left at room temperature and were used within 24 hours.

2.2 Viscosity

Viscosity of the investigated gum arabic systems was measured using an Ametek Brookfield DV2T extra Viscometer, Spindle RV-04, speed measurements 20rpm (with the exception of the 60% solution that was measured at 2rpm due to the operational limitations of the device and the viscosities of the samples), single point measurement, end condition (time) at 1min. Volume of sample was 80mL.

2.3 Differential scanning calorimetry (DSC)

Thermal analysis was performed using a Differential Scanning Calorimeter, DSC (Metler Toledo 821e with liquid N₂ cooling, Leicester, UK). Samples (7-18 mg, exact weight recorded) were placed on 40mL DSC aluminium pans (Metler Toledo, Leicester, UK) that were then hermetically sealed. The samples and a reference pan containing air were transferred to the DSC device and were cooled and scanned from 20°C to -80°C at 1°C/min, then held at -80°C for 5 min and finally scanned during heating to 20°C using the same rate. Duplicate samples were used and the average onset melting temperature T_m was determined

from the heating endotherm recorded during scanning from -80 to 20°C. This was considered as the equilibrium freezing temperature (T_f) (see section 3.2). The endothermic melting curves were further analysed to determine the percentage of frozen water in the systems (FW%). The area under the melting peaks was estimated using Origin 9.0 and it was used to determine the enthalpy of the phase transition by dividing with the heating rate. Equation 1 was then used to calculate the FW% (Xanthakis *et al.*, 2014).

$$FW\% = \frac{Q \times 100}{H_f \times m}$$

Equation 1

Where,
 Q = Enthalpy of endothermic melting (J)
 H_f = heat of fusion of ice-water (333.50 J g⁻¹)
 m = mass of the sample (g)

2.4 Freeze-drying cycles

28mL of each gum arabic solution was poured into carbon steel baking tins (9.5cm in diameter and 2.5cm in height) to reach a fill depth of approximately 0.5cm and were placed inside a benchtop freeze-drier (VirTis AdVantage Plus 2.0, SP Industries, Warminster, PA, USA). Samples were cooled to -40°C at 1°C/min at ambient pressure (~1bar) (temperature measured by thermocouple placed at the centre of the sample) and were kept at this temperature for 6h. Primary drying was performed for 12hrs at three different shelf temperatures (-20, -30 and -40°C). This was followed by secondary drying at 20°C for 6hrs. The chamber pressure and condenser temperature was kept at 0.1mbar and -80°C, respectively during the primary and secondary drying stages for all freeze-drying cycles. The freeze-drying conditions are schematically shown in figure 1.

Figure 1. Investigated freeze-drying cycles with primary drying temperatures of -20, -30 and -40°C.

2.5 Structural analysis

Freeze-dried cakes were fractured carefully lengthwise by hand and a section from the middle of the cake, representing the cake's morphology alongside its height, was analysed with X-Ray Computer Tomography (Skyscan 1172, Bruker MicroCT, Kontich, Belgium) under medium camera settings (2000 × 1048 pixels) with the X-ray source set to 50-70 kV (100 μ A). Before scanning, the cut sample was carefully mounted on a sample holder and an adherent material (blue tac) was used to prevent the sample from moving while rotating. The selected distance between the X-ray source, the object, and the camera produced images of size 8 μ m pixel. Three frame averaging with a rotation step of 0.40° and exposure time between 200-300ms was chosen to minimise the noise. This covered a view of 180°. A typical scan took around 25-30min. NRecon software package (Bruker MicroCT) was then used for reconstruction of the 2D cross-section images. Representative cross-section images were converted to binary images by thresholding using the CTAn software package (Bruker MicroCT).

The acquired binary images were analysed using imageJ to determine the sizes of the porous structures within the material. Similar images were then used for quantification of total porosity, defined as the ratio of pore area to the total area of image (Malik et.al 2018). The average pore sizes were determined using Sauter mean diameter (D_{32}), which is defined in equation 2 where $p=3$ and $q=2$. In the equation, n_i refers to the number of pores with diameter equal to D_i .

$$D_{pq} = \left(\frac{\sum n_i D_i^p}{\sum n_i D_i^q} \right)^{\frac{1}{p-q}}$$

Equation 2

2.6 Reconstitution properties

Reconstitution rates of the freeze-dried gum arabic samples were evaluated using a Thermo Scientific™ Orion™ Star A212 conductivity meter, which measures changes in conductivity values over time. A conductivity probe was inserted in a 250ml beaker filled with 100ml distilled water. Conductivity recordings commenced and 0.2-0.4g (volume of about 1cm³) of a freeze-dried sample was then added to the distilled water under mixing (magnetic stirrer, 1000rpm). Readings of the conductivity values were taken every 5s until the sample was completely dissolved. For comparison, the reconstitution rate of untreated gum arabic was also measured. A schematic of the experimental setup is shown in figure 2. Reconstitution of all freeze-dried samples was measured in three replicates.

Figure 2. Illustration of the set up used for the conductivity measurements.

Reconstitution was determined as the total amount of solute released from the material with time, expressed as the percentage ratio of the conductivity measured at the corresponding time over the maximum conductivity value measured, using equation 3:

$$\text{Solute released (\%)} = \frac{C_t}{C_o} \times 100$$

Equation 3

C_t = conductivity at time t ; C_o = constant conductivity value measured on complete reconstitution of the material.

Experimental data were fitted to Weibull's equation as described by equation 4 (Skrdla 2007).

$$\frac{y}{y_{max}} = 1 - e^{-kt^n}$$

Equation 4

Where;

 y = solid dissolved at time t y_{max} = solid dissolved on completion of reconstitution t = time (s) k = scale parameter (s^{-n}) n = shape parameter

3.0 Results and discussion

3.1. Viscosity

Figure 3 shows that the viscosity of the gum arabic solutions increased as the solids content increased. The values of figure 3 are comparable to those reported in the literature for the range of 20-35% gum arabic (Williams & Phillips, 2009). The viscosity appears to increase exponentially ($R^2 = 0.9963$), and as a result, the viscosity of the 60% system was markedly higher than the viscosities of the lower concentration systems (about 5 times higher than the viscosity of the 50% system and about 35 times higher than the viscosity of the 40% system).

Figure 3. Viscosity of the 20-60% w/w gum arabic solutions

3.2. DSC

Thermal analysis was performed to determine the equilibrium freezing temperatures T_f of the materials. Samples were first cooled (to -80°C) to induce crystallisation and then

heated (to 20°C). The heating curves (figure 4a) were used to determine the melting temperatures, T_m , which are equal to the equilibrium T_f . It is noted that the freezing temperatures of the cooling curves are typically lower than the equilibrium values due to the supercooling required for crystal nucleation.

All investigated systems showed an endothermic melting peak during heating (figure 4a), indicating that crystallisation took place during cooling even at the highest investigated concentrations. The associated onset melting temperatures T_m (or equilibrium T_f) are shown in figure 4b. As expected, as the concentration of gum arabic in the solution increased, the onset T_m decreased (freezing point depression), which has also been reported in the literature (Homer et al. 2014; Arvanitoyannis et al. 1993). For example, onset T_m of the 60% solution was 10 times lower than that of the 20% system (-15°C, compared to -1.5°C, respectively). It is noted that while gradual freezing temperature depression was observed as concentration increased from 20 to 50%, the effect was greater on the further increase to 60% solids. The onset T_m values reported here are within the range of data reported in the literature for mixtures of fructose, glucose and sucrose (Ruiz-Cabrera et al. 2016), where onset T_m of the low molecular weight sugar mixtures was reportedly reduced from -1.6 to -15.8°C when solid content varied from 0.2 to 0.65 g solid/g of sample.

Figure 4. Thermal properties of the 20-60% w/w gum arabic solutions; a) DSC thermogram during heating at 1°C/min; b) Effect of concentration on the onset melting temperature (T_m) of gum arabic solutions; c) Percentage of frozen water during cooling of the different concentration gum arabic solutions.

The percentage of frozen water at the investigated gum arabic concentrations, as estimated from the melting peaks of figure 4a, is shown in figure 4c. As expected, the ice fraction reduces with increasing solids content because of the decreasing water availability (see for example Pongsawatmanit & Miyawaki, 1993).

3.3. Freeze-drying cycles

Figure 5 shows temperature recordings of the samples as the investigated systems were first frozen on the freeze-drier's shelf (-40°C, 6h) and were then subjected to freeze-drying cycles with primary drying temperatures of -40, -30, and -20°C. It is noted that for initial concentrations <40%, sample temperature followed closely the operating shelf's temperature throughout the freezing and freeze-drying cycles in all investigated conditions (data not shown).

Figure 5. Temperature profiles during freeze-drying of a) 40% gum arabic and b) 60% gum arabic at -20, -30 and -40°C.

At 40% solids (figure 5a), the sample's temperature still followed closely that of the shelf, showing only a few degrees (3-5°C) difference between them. At 60% solids, however, the sample's temperature was evidently higher than that of the shelf, in particular during primary drying at -30°C and -20°C, where it reached -15°C and -10°C, respectively. It appears that the temperature and pressure conditions during these freeze-drying cycles were such as to allow for localised temperature increase of the sample to occur. This may be linked to the following series of events. As drying commenced, the top layer of the cake dried first, leading to the formation of a dried crust. At 60% solids, this crust was dense, as there were only few crystals to sublimate due to a combination of low water content (see also figure 4c for the % of frozen water in the system) and high viscosity (low molecular mobility, see figure 3) in the liquid system that limited ice crystal formation during freezing. As sublimation continued in regions below this dried layer, new vapour was formed. However, its passage towards the top and out of the cake was obstructed by the lack of a porous network in the previously formed dense cake crust. This resulted in vapour being entrapped in the cake's inner structure causing sites with local pressure increase inside the cake. As the (local) pressure increased, it may have caused the (local) temperature to rise. When the shelf temperature was -40°C, the cake's temperature was maintained below the system's melting point (determined at -15°C in figure 4b). However, a shelf temperature of -30°C and -20°C was insufficient to cool down the sample at a rate that would prevent (local) melting. As a result, partial melting may have occurred at the inner structure of the cake. The combination of a melted, flexible structure with an increased inner pressure and a low environmental pressure in the freeze-drier (0.006bar) may have further contributed to the puffed, aerated patterns observed in the next section. At increasing concentrations (e.g. 60% solids), it has been reported that there is

greater possibility to experience overheating during freeze-drying, particularly when the system is exposed to high primary drying temperatures (Roos 1997; Franks 1998).

Furthermore, in figure 5a, there is a notable temperature fluctuation at the early stages of the secondary drying in the 60% gum arabic solutions dehydrated at -20°C, followed by a gradual increase in the temperature. This temperature variation may be due to the partially melted, flexible material allowing uncontrolled movements and relocations of the probe during this stage of drying that caused temperature fluctuation recordings. It may further be linked with physical changes occurring during the secondary drying. The risk of collapse during early secondary drying when product temperature exceeds T_g has been previously reported (Patel et al. 2017; Pikal et al. 1990).

3.4. Microstructural properties of the freeze-dried cakes

3.4.1 Morphology

Photos of the central region of the obtained freeze-dried cakes, cut in a vertical direction, are shown in figure 6. They indicate that as the initial concentration of the gum arabic increased, puffing occurred at the bottom of the cake during freeze-drying resulting in the formation of large pores.

Figure 6: Photos of the obtained freeze-dried cakes

The porosity of the materials was further examined using X-ray CT. This technique provides microstructural features of the material based on differences in the X-ray absorption capacity of different elements within the material's structure. This is directly related to differences in their densities. Thus, the cross-sections of figures 7 and 8 reflect the pores (black entities) and the solid network (white matrix) formed after freeze-drying.

Figures 7 and 8 show representative images of the investigated freeze-dried materials taken from the middle of the cake at different angles: vertically (throughout the cake's height, figure 7) and horizontally (parallel to the cake's base, figure 8). Images similar to those in figure 7 were used to determine the pore sizes and total porosity of the materials, discussed in sections 3.4.2 and 3.4.3, respectively.

The morphology of the freeze-dried 20 and 30% gum arabic solutions was that of needle-like pores, with minor signs of cracking, present in particular when the primary drying temperature was set to -20 or -30°C (see figure 8). On increasing the initial solid content to 40% and 50%, large, circular-type bubbles were observed at the bottom of the freeze-dried cakes (see figure 7), and the presence of cracks intensified. At an initial concentration of

367 60%, the circular-type voids dominated the freeze-dried cake's microstructure, in particular
368 when drying at higher temperatures (-20°C, -30°C). These features will be discussed below.

369 The presence of circular-type pores indicates that the structure of the material changed
370 during freeze-drying. In the literature, structural instabilities during freeze-drying are often
371 associated with collapse or shrinkage (see for example Patel et al., 2017; Levi & Karel 1995).
372 In this work, it appears that the material puffed up during drying. This "pop-corn" effect
373 suggests that the local pressure/temperature environment of the material allowed for partial
374 melting (decrease in viscosity) during drying, which combined with the increased pressure
375 difference between the inner local pressure and the near-vacuum operating pressure of the
376 freeze-drier, prompted the observed volume expansion and formation of the circular-type
377 voids, as discussed above (in section 3.3). In the literature, viscosity in the range of 10^4 to
378 10^7 Pas has been proposed as the critical range that can cause the loss of structure in freeze-
379 drying (Karathanos et al. 1996) At 40% and 50% initial solids content this happened at the
380 bottom of the cake – the region most distant from the surface and therefore more likely to
381 accumulate the higher level of water vapour. At 60% solids, the system with the denser crust,
382 puffed structure was dominant. Puffing has previously been linked with an internal pressure
383 development in the drying material (Malik et al. 2018; Tsourouflis et al. 1976). Local
384 pressure build up has been reported by Sagara & Ichiba (1994) during freeze-drying of
385 coffee, and it was linked with the formation of a skin layer at the drying interface, preventing
386 the water vapour from the sublimated ice crystals escaping from the materials being dried.
387 Entrapment of the water vapour within the material eventually increased the internal pressure.
388 The effect was found to intensify with increasing the initial concentration of the coffee
389 solution, which corresponds well with the present findings.

390

Figure 7. Vertical cross-section of the freeze-dried gum arabic solutions dried at -20, -30 and -40°C.

For the 60% systems, the degree of puffing appeared stronger when drying occurred at higher (-20 and -30°C), compared to lower (-40°C) drying temperatures, as the high shelf temperature was insufficient to adequately cool down the cake, thus resulting in temperatures that may exceed the melting point (see figures 4b and 5). Previously, Khalloufi & Ratti (2003) showed an increased risk of structural instability with higher drying temperatures during freeze-drying of apples and pears. It was found that dried fruits obtained with high drying temperature displayed discolouration and pores with weak interconnectivity.

Figure 8. Horizontal cross-section of freeze-dried gum arabic solutions dried at -20, -30 and -40°C.

The binary images of figures 7 & 8 further indicate the formation of cracks in the freeze-dried cakes with direction normal to the cakes' base, the effect being more obvious on increasing concentration. This cracked appearance may be in part due to the release of entrapped vapour from the inner structure, driven by the pressure difference between the inside and the outside of the cake. As the entrapped vapour travelled towards the top and out of the cake, it may have ruptured the rigid, dried top crust creating the observed passages. Cracks may have also been developed due to stresses associated with the evaporation of

unfrozen water in the secondary drying stage as suggested in recent studies by Ullrich et al. (2015) and Patel et al. (2017). As unfrozen water is evaporated at high temperature (20 °C), pressure within the solid matrix could have increased, which is then released when tensile stress exceeds the tensile strength, allowing unfrozen liquid to be removed.

3.4.2 Pore sizes

Binary images of the vertical cross sections (such as the examples shown in figure 7) were further analysed to estimate the pore sizes of the materials. It is noted that 'pores' here refers to all the voids present in the structure, including the cracks, without any further differentiation. The size of a pore was defined as the diameter of a circle with area equal to the pore area. Bar charts of pore size distributions of the freeze-dried gum arabic cakes are shown in figure 9 for all investigated concentrations and drying temperatures. Sauter mean diameters (D_{32}) of the voids in the materials are presented in Table 1.

In figure 9, the puffed 60% freeze-dried cakes showed overall the largest pores (of the order of 200-1800 μm), in agreement with the observations in figure 7 where the puffed 60% system displayed large, circular pores. Pores of the dried 20-50% systems were about 80% smaller, according to their D_{32} values. Excluding the 60% system, freeze-dried materials of higher concentrations (40 and 50%) had 60-80% of their pores distributed at sizes <100 μm due to the small pores created in the non-puffed regions of the cakes, where pore sizes are largely determined by the sizes of the crystals formed during freezing and sublimated during freeze-drying.

With the exception of the 60% systems, primary drying temperature had a marginal effect on the pore sizes and pore size distributions under the investigated conditions. This probably indicates that the systems were stable during freeze-drying even at the highest drying temperature. For the 60% system, low primary drying temperature (-40°C) resulted in the presence of smaller pores (approx. 80% of the pores had sizes $\leq 600 \mu\text{m}$) compared to those observed when drying at higher temperatures (-20 and -30°C), where 70% of the pores had sizes between 600 and 1800 μm . This resulted in a 20% reduction in the Sauter mean diameters of the (respective) samples. It appears, therefore, that drying at -40°C resulted in a lower degree of material puffing than drying at -30 or -20°C, which is also evident in the images of figure 7.

Figure 9. Pore size distribution of freeze-dried gum arabic (A-E: 20-60% w/w) processed at different primary drying temperatures (-20, -30 and -40°C).

Table 1 Sauter mean diameter (SMD), D32 measured for freeze-dried gum arabic solutions (20-60% w/w) dried at -20, -30 and -40°C

Freeze-dried gum arabic	-20°C	-30°C	-40°C
20% w/w	192	201	182
30% w/w	196	173	178
40% w/w	174	170	174
50% w/w	164	174	215
60% w/w	973	924	745

3.4.3 Porosity

Figure 10. Overall porosity of freeze-dried gum arabic at different concentrations (20-60% solid w/w) and primary drying temperatures (20, 30 and 40°C).

Porosity, defined as the ratio between the pore area and the total area within the images (Silva et al. 2015), of the investigated systems (estimated from the vertical cross-sections of the materials) is shown in figure 10. The porosity of the 60% freeze-dried solid was largely determined by the puffed microstructure observed in the binary images (figures 7 & 8). When dried at -20 and -30°C, the 60% freeze-dried gum arabic showed a higher degree of puffing (figures 7 & 8) and higher porosity values (i.e. 70% for drying at -20°C and 60% for drying at -30°C, figure 10) than when dried at -40°C (30% porosity).

The freeze-dried systems of 20-50% initial concentration had reduced porosities compared to that of the 60% system dried at -20 and -30°C, by 30-70%, depending on the conditions. The 20 and 30% samples showed similar porosity values, of about 45%. However, a further increase of the initial solution concentration resulted in a gradual porosity reduction of the final freeze-dried cakes, with the 40 and 50% systems showing porosities of about 35% and 25%, respectively. Overall, primary drying temperature had a marginal effect on the porosity of the samples under the investigated conditions, although the 30% system showed unexpectedly low porosity when dried at -30°C.

3.5. Reconstitution behaviour

Reconstitution of the freeze-dried gum arabic systems was determined based on changes in the conductivity values as the material dissolved in distilled water. The values were used to derive the amount of solid dissolved as a function of time (see section 2.6). For this analysis, freeze-dried cakes were cut throughout their height and samples were taken from the central part of the cake. Reconstitution kinetics of the investigated systems are presented in figure 11 together with the fitted curves from Weibull's equation (see section 2.6). It is noted that Weibull's equation is regularly used in dissolution kinetics of pharmaceuticals (Cascone et al. 2017; Ramteke et al. 2014; Martinez et al. 2009; Kosmidis & Marcheras 2007) and has also been suggested for modelling rehydration of porous foods, which often involve different physical mechanisms of water uptake (Wallach et al. 2011; Marabi et al. 2003). The estimated Weibull's scale and shape parameters, k and n respectively, are shown in table 2 and were used to calculate the time required for reconstitution of 95% and 99% of the material (table 3). The shape parameter depicts the shape of the curve: $n > 1$ denotes sigmoidal curves, while $n < 1$ indicates curves with an initial slope that is steeper than that of an exponential (Ramteke et al. 2014; Costa & Loba 2001). In the case of $n = 1$, reconstitution follows first order kinetics and the curve is represented by an exponential. The scale parameter, also known as rate parameter, shows dependency with time. When $n = 1$, the scale parameter is equal to the dissolution rate parameter. However, when $n \neq 1$ then interpretation of k is difficult.

Figure 11. Effect of freeze-drying cycles and concentrations on dissolution profiles of freeze-dried gum arabic (A-E: 20-60% solid w/w). Data is fitted with Weibull's equation.

Figure 11 shows that reconstitution rates were initially fast followed by a gradual decrease. With the exception of the 20% system, the estimated Weibull's shape parameters, n (table 2), are approximately equal to unity or slightly higher (up to 1.442 and with an average of 1.305 ± 0.244), indicating that reconstitution is close to an exponential with a tendency towards a sigmoidal shape. The n values of the 20% systems are of the order of 1.7, and therefore indicate a higher tendency towards a sigmoidal compared to the remaining systems. However, it is noted that these samples are practically dissolved (99% reconstituted) within 0.7min, and fitting of the slope was performed using a small number of points. It has further been suggested that the n values also indicate the mechanisms involved during dissolution (Papadopoulou et al. 2006; Marabi & Saguy 2004; Marabi et al. 2003). In particular, these studies suggested that $n \leq 0.75$ signifies a diffusion controlled process while higher n is

associated with combined dissolution mechanisms, including molecular diffusion, capillary imbibition and molecular relaxation (swelling).

For the 20-50% initial concentration systems, reconstitution rates of the freeze-dried material were practically unaffected by the primary drying temperature under the conditions investigated, as evidenced in table 3. The time required to achieve 95 and 99% dissolution of materials with equal initial solid concentrations but dried at different primary drying temperatures is similar, with a 3-13% estimated difference. This observation is in agreement with the porosity data shown in figures 9 & 10, which indicates that pore sizes and total porosities were largely independent of the primary drying temperature for these systems.

Interestingly, reconstitution kinetics of the freeze-dried 60% solids did not follow the above trend. For these systems, reconstitution rates were markedly affected by the primary drying temperature. Drying at lower temperature resulted in materials that reconstituted faster than those dried at higher temperature. As such, the sample dried at -20°C showed the fastest reconstitution rate whereas the sample dried at -40°C showed the slowest reconstitution rate. This contradicts the faster rehydration recorded by Barresi et al. (2009) for carbohydrate components freeze-dried at -50°C when compared to those freeze-dried at -32°C and is closely related to the observed microstructures of the cakes. The materials dried at -20°C had the highest degree of puffing (figures 7 & 8), largest pores (table 1), and highest porosity (figure 10) compared to those dried at higher primary drying temperatures, which led to faster dissolution rates.

The effect of initial solids concentration on the reconstitution kinetics of the freeze-dried cakes is also evident in figure 11 and table 3. Higher initial solids content resulted in dried cakes with faster reconstitution rates. In particular, freeze-dried 20 and 30% systems had similar reconstitution rates and were 95 and 99% dissolved in about 1.5min and 2.5min, respectively. Increasing the initial solids content to 40% resulted in reduced porosities (figure 10) and increased the time to dissolve 95 and 99% of the material to 7 and 10min, respectively, while further increase to 50% had a small effect on both the porosities and the reconstitution kinetics of the material.

However, cakes produced from freeze-drying 60% solutions at -20°C dissolved faster than systems of lower initial solids content (40, 50%, figure 11 and table 3) due to their porous microstructure. Enhanced water uptake with increasing pore size has been found during

rehydration of freeze-dried carrot and dissolution of freeze-dried rice porridge (Koh et al. 2011; Marabi & Saguy 2004).

Table 2. Weibull's function parameters derived from dissolution data of gum arabic.

Concentration (%)	-20°C			-30°C			-40°C		
	k	n	R ²	k	n	R ²	k	n	R ²
20	0.0060	1.797	0.998	0.0079	1.684	0.998	0.0163	1.629	0.994
30	0.0315	1.02	0.996	0.038	0.971	0.992	0.0105	1.229	0.998
40	0.0017	1.232	0.988	0.0021	1.227	0.987	0.0051	1.031	0.994
50	0.0016	1.179	0.990	0.0006	1.321	0.989	0.0004	1.392	0.986
60	0.0054	1.195	0.993	0.0007	1.442	0.987	0.0010	1.228	0.991

Table 3. Time (in minutes) required for the reconstitution of 95 and 99% of the total solid

Concentration (%)	-20°C		-30°C		-40°C	
	95%	99%	95%	99%	95%	99%
20	0.5	0.7	0.6	0.7	0.4	0.5
30	1.5	2.2	2.0	3.3	1.3	1.9
40	7.2	10.2	6.2	8.8	8.1	12.3
50	9.8	14.2	9.9	13.7	9.7	13.3
60	3.3	4.7	5.5	7.4	11.6	16.4

For comparison, reconstitution of untreated gum arabic was also performed. The system was 95 and 99% reconstituted in 8 and 14 minutes, respectively, which is similar to the 50% system (table 3). It is noted, however, that there are limitations in comparing the reconstitution data for the untreated and freeze-dried gum arabic. For example, the former is in the form of powder, whereas the latter is in the form of a “single” piece, and therefore their surface/volume ratio is different.

4.0 Conclusion

This work is a continuation of previous efforts (Malik et al., 2018) to study the links between formulation (initial solution concentration), freeze-drying conditions, and properties (porosity, reconstitution kinetics) of the resulting freeze-dried materials in hydrocolloid-based systems (gum arabic). Here it is demonstrated that increasing the initial concentration (from 20 to 50% by weight) resulted in a decrease of the porosity and the reconstitution rates of the freeze-dried gum arabic cakes. However, at 60% initial solids content, the material puffed

during freeze-drying resulting in the formation of large, circular pores that prompted faster reconstitution rates. This popcorn-like effect was associated with partial melting of the material due to the local temperature and pressure conditions within the cake during freeze-drying. Primary drying temperature had a marginal effect in the properties of the investigated systems with initial concentration up to 50%, however it strongly affected the properties of the 60% freeze-dried solid.

Overall, this work highlights that product formulation and shelf temperature each may have a role in governing the porous structure of freeze-dried cake, which directly influences product performance. Understanding the microstructure formation at different processing conditions helps to identify the key factors contributing to the design of more efficient freeze-drying processes, with the potential to reduce water and energy use during processing.

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Highlights

- 20-60% gum arabic was freeze-dried at -20, -30 and -40°C primary drying temperature
- 20-50% systems: lower porosities & slower reconstitution as concentration increased
- Volume expansion observed for the 60% systems
- Degree of expansion increased as primary drying temperature increased
- Expanded solids had high porosities and fast reconstitution rates

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Declarations of interest: none

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