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The effect of sugars on agar fluid gels and the stabilisation of their foams

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ABSTRACT

The rising demand to reduce sugar in foods has resulted in the need to better understand its structuring properties and contribution to the overall microstructure of products. The effect of sugars on the microstructure of agar fluid gels and their novel foams, including stability, has therefore been studied. Gelation kinetics and material properties of agar fluid gels with added glucose, fructose and sucrose have been explored. The addition of sugar did not notably affect the temperature of ordering during gelation however, it did cause a reduction in fluid gel particle size through changes in solution viscosity during gelation. At high concentrations of sugar (above 50%), the conversion of an overall brittle agar gel network to a more rubbery-like structure was inferred through rheology, as the glass transition of sugar was approached. Below 50% sugar, shear viscosity and G′ increased with concentration due to an increase in particle gel strength (observed through initial Young's modulus). These changes in material properties were overall observed to be independent of sugar type.

All systems showed good foaming properties where foam half-life increased with sugar concentration as a result of increased fluid gel yield stress. In order to increase understanding of the foam stability mechanism, fluid gel particle size was altered. When the continuous phase consisted of larger particles, the initial liquid drainage was considerably reduced as particles were more effective at accumulating in the foam channels preventing the flow of the bulk phase. However, foam half-life was ultimately dependent on fluid gel yield stress. This research has provided fundamental understanding of the effect of sugars on the microstructure of agar fluid gels and their use in foam stabilisation, allowing the development of an approach that can potentially be tailored to specific product requirements.

1. Introduction

Food foams have continued to attract interest in the food industry due to their ability to reduce the calorific value and cost of food whilst providing a luxurious texture desirable to consumers. Sugar is an important ingredient in many whipped products as it provides taste, texture and structure (Coultate, 2009). However, there are strong demands to reduce its content in food. The UK Government introduced The Sugar Reduction Program in 2017, which outlines guidelines for the food industry to achieve a 20% reduction in sugar across products aimed at children (*Sugar Reducion: Achieving the 20%*, 2017). These include desserts, sweet confectionary and ice cream. In order to achieve this reduction, it is essential to understand the role of sugar and how it contributes to the overall microstructure of products. Recent work by the authors revealed the ability of agar fluid gels to stabilise potential fat-free foams (Ellis, Norton, Mills, & Norton, 2017). The addition of sugar to these novel fluid gel foams has been investigated, focusing on its effect upon microstructure and foam properties.

Fluid gels are concentrated systems of gel particles dispersed in a non-gelled continuous phase, typically water (Norton, Foster, & Brown, 1998). They are produced when a biopolymer solution undergoes a sol-gel transition under an applied shear. Their interest within the food industry extends from the variety of structural requirements they can fulfil. For example, their textural and tribological responses can be manipulated to mimic those of oil droplets and therefore provide low-fat alternatives (Norton, Cox, & Spyropoulos, 2008). Furthermore, their development has also increased the functionality of hydrocolloid gels, for example the ability to be aerated.

To understand how sugar will affect the microstructure of an agar fluid gel it is useful to look at quiescently set agar gels. The effect on their material properties is already widely reported in the literature (Deszczynski, Kasapis, MacNaughton, & Mitchell, 2003; Maurer, Junghans, & Vilgis, 2012; Nishinari & Fang, 2016; Normand et al., 2003). Watase, Nishinari, Williams, and Phillips (1990) were the first to report how the addition of either glucose or sucrose, up to a critical concentration, increased the elastic modulus (as well as melting temperature and melting enthalpy) of agarose gel. They later found that this stabilisation of agarose was related to the number of equatorial

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hydroxyl groups on the sugar, n(e-OH) (Watase, Kohyama, & Nishinari, 1992); a zipper model approach was used to explain that a high n(e-OH) increased the number of junction zones whilst reducing both the size of each junction and the rotational freedom of a parallel link in a junction zone. Above the critical concentration of sugar, there is a lack of available water for the formation of stable junction zones and so the elastic modulus of agarose decreases (Watase et al., 1992). The mechanical properties of the system also begin to change from a rubbery to a glass structure (Deszczynski, Kasapis, MacNaughton, et al., 2003).

Despite the investigation of co-solutes (glucose and glycerol) on the tribological properties of agar fluid gels (Fernández Farrés & Norton, 2015), without particle imaging their material properties could not be analysed in great detail. The availability of particle imaging now provides the opportunity to study particle shape and size in relation to material properties as well as how different sugars affect them. The foaming properties of agar fluid gels have been previously studied (Ellis et al., 2017); initial drainage of the foams was prevented by the formation of localised plugs by particles accumulating in the foam channels. This mechanism has also been described by Lazidis, de Almeida Parizotto, Spyropoulos, and Norton (2017) and in great detail for model systems (Haffner, Khidas, & Pitois, 2014, 2015; Khidas, Haffner, & Pitois, 2014). Foam half-life was dependent on fluid gel yield stress, which was influenced by particle shape, elasticity and interaction. This reported dependence on yield stress is supported by the literature (Carn, Colin, Pitois, Vignes-Adler, & Backov, 2009; Dickinson, Ettelaie, Kostakis, & Murray, 2004; Rio, Drenckhan, Salonen, & Langevin, 2014; Zúñiga & Aguilera, 2008), for example, Guillermic, Salonen, Emile, and Saint-Jalmes (2009) reported unusual behaviours of surfactant doped laponite foams, where drainage was completely arrested after a period of time due to the confinement of laponite particles on foam ageing which altered the yield stress of the network.

This work will focus on the effect of sugar (type and concentration) on agar fluid gel microstructure and how this relates to their foam properties. The simplest monosaccharides and disaccharide (glucose, fructose and sucrose) were chosen to allow size effects to be investigated. Firstly, the influence of sugar on the gelation of agar fluid gels was studied to provide a foundation for exploring subsequent material properties, such as particle size. In addition, the gel strength of quiescent agar gels was measured to provide information on the intrinsic polymeric network of fluid gel particles, before examination of their bulk rheology and trends in foamability and stability. Finally, the manipulation of particle size through altering processing parameters was used to modify foam drainage.

2. Experimental

2.1. Materials

Agar (A7002), D-glucose (G7021), D-fructose (F0127), sucrose (S0389) and Tween 20 were purchased form Sigma Aldrich (UK) and used without further purification. All concentrations were calculated as weight percentage.

2.2. Preparation of agar fluid gels using pin stirrer

Agar (1 wt%) was dispersed in deionised water at room temperature, then heated to 90 °C. After complete dissolution, the solution temperature was lowered to 70 °C and Tween 20 (0.5 wt%) and the required concentration of sugar were added. The solution was transferred into the cooled jacketed pin stirrer through a peristaltic pump at 70 °C. The outlet temperature was controlled to 5 °C to ensure gelation occurred under shear (gelation temperature $\approx$ 30 °C). A retention time of 7.5 min was achieved through using a pump speed of 20 mL min^{-1}, resulting in a cooling rate of 8 °C min^{-1}. The shaft rotation speed was set to 1500 rpm to give a narrow distribution of particle size (Gabriele, Spyropoulos, & Norton, 2010). Fluid gels were stored at 5 °C.

2.3. Preparation of agar fluid gels using a rheometer

Solutions of agar (1 wt%) with Tween 20 (0.5 wt%) and sugar were prepared as described in Section 2.2. Fluid gels were produced using the vane geometry in a rheometer (Kinexus, Malvern, UK). Solutions at 70 °C were transferred into the pre-heated rheometer cup and the temperature allowed to equilibrate for 5 min. The temperature was then decreased from 70 °C to 5 °C at a cooling rate of 2 °C min^{-1}, under an applied shear of 500 s^{-1}. A slower cooling rate was used compared to preparation in the pin stirrer to increase the accuracy of gelation temperature determination through viscosity measurements. Experiments were carried out in three replicates and fluid gels were then stored at 5 °C.

2.4. Optical microscopy

Fluid gels were imaged using phase contrast microscopy (Leica Microsystems, UK). They were diluted with deionised water (1:4), placed onto a microscope slide with a coverslip and observed using objective lenses up to 20x magnification. ImageJ software was used to measure 300 fluid gel particles from 10 different micrographs in order to achieve a good representation of the particles.

2.5. Texture analysis of quiescent agar gels

Agar gels of 1 wt% agar +0.5 wt% Tween 20 and various concentrations (10–60 wt%) of fructose, glucose and sucrose were quiescently set and stored at 5 °C for 48 h. Tween 20 was added to keep the formulation the same as fluid gel production (Tween 20 was required for aeration). Compression tests were then carried out using a TA XT plus texture analyser (Stable Micro Systems Ltd, UK) with a 40 mm diameter cylindrical probe. Samples of 21 mm diameter and 10 mm height were compressed at a rate of 1 mms^{-1}. The force/distance data was converted to true strain (ε) and true stress (σ). From the gradient of the linear region at 0–5% strain, the initial Young's modulus was determined (Bradbeer, Hancocks, Spyropoulos, & Norton, 2014). Experiments were carried out in three replicates.

2.6. Bulk rheology

A Kinexus rheometer (Malvern, UK) was used to perform rheological measurements at 25 °C. Fluid gels were tested after 48 h to ensure post-production particle ordering completion (Gabriele, Spyropoulos, & Norton, 2009; de Carvalho & Djabourov, 1997). All measurements were conducted using a serrated parallel plate of 60 mm diameter set to a 1 mm gap. Shear viscosity at 1 s^{-1} was determined from viscosity profiles at shear rates of 0.1–500 s^{-1}. Amplitude sweeps were conducted at a frequency of 1 Hz as a function of applied oscillatory strain. All experiments were carried out in three replicates.

2.7. Aeration

Fluid gels of equal volumes were aerated using a Hobart mixing unit. The highest speed setting was used for 7 min as this ensured all systems were in the wet foam boundary (air fraction within 0.65–0.95). Air fraction was determined to assess foam ability using Equation (1), by weighting equivalent volumes of fluid gel and foam, using three replicates.

$$\text{Air fraction} = 1 - \left(\frac{m_{foam}}{m_{fluid\,gel}} \right)$$
(1)

The stability of foams was measured using foam half-life of three replicates. The reduction of the foam height was recorded using a CCD camera and the half-life was later calculated as the time taken to reduce the foam height by half.

2.8. Foam liquid drainage measurements

Liquid drainage measurements were conducted using a Krüss DFA100LCM foam analyser (Krüss, Germany). The corresponding fluid gel liquid was poured into the foam cell to cover the reference electrode followed by the externally produced foam. The decrease in liquid fraction was then recorded using electrical conductivity measurements at 7 pairs of electrodes along the cell height. Drainage profiles were recorded for the first 4 h from initial aeration. Experiments were carried out in three replicates.

3. Results and discussion

3.1. Effect of sugar on gelation

In order to explore the influence a variety of sugars have on the material properties of agar fluid gels, it is necessary to first understand their effect upon gelation. Agar is a mixture of agarose and agaropectin fractions, where agarose is responsible for gelation. The role of agaropectin is not as well understood, although recent work by Nishinari and Fang (2017) reported that it may enhance gelation rather than inhibit it. The gelation mechanism as described by the Domain model (Arnott et al., 1974) states that agarose molecules exist as random coils in solution, which undergo a coil-helix transition as the temperature is lowered. The helices, which are stabilised by hydrogen bonds with water (Foord & Atkins, 1989), then aggregate together. The formation of a wider 3D network occurs when these helical domains are linked through junction zones. During fluid gel preparation, this process occurs under shear resulting in the production of gel particles dispersed in a continuous phase, typically water.

Gelation during fluid gel preparation was studied by preparing 1 wt % agar fluid gels with varying concentrations of glucose, fructose and sucrose using a rheometer. It is important to note that solutions were prepared by first dissolving agar in water, followed by the addition of sugar. Yang et al. (2015) highlights the importance in the order of sugar addition by reporting a weaker and more inhomogeneous gel structure when sucrose (above 50%) was dissolved before agar. The solutions of agar were cooled from 70 °C to 5 °C whilst under a fixed shear rate (500 s^{-1}) and the viscosity was measured. The viscosity profiles of agar fluid gels with 0%, 20% and 40% glucose (Fig. 1a), fructose (Fig. 1b) and sucrose (Fig. 1c) all exhibited a sharp increase in viscosity just below 30 °C indicating the occurrence of considerable ordering and structuring. This occurred close to the gelation temperature of agar and so can be attributed to the formation of gel particles during the coil-to-helix transition (Norton, Jarvis, & Foster, 1999). This can be more clearly seen in the inset graphs in Fig. 1, which focus on the region between 20 °C and 40 °C. The inset graph in Fig. 1c highlights a difference between the onset temperature of ordering at different concentrations of sucrose, where ordering occurred at a higher temperature upon raising sucrose concentration. Similar results were observed for quiescent agarose gels; Watase et al. (1990) revealed that the presence of sucrose decreased the size and increased the number of cross-links during gelation, due to hydrogen bonds formed between sugar and agarose. This was enhanced by the high number of equatorial hydroxyl groups, n(e-OH), and therefore increased viscosity of sucrose (Nishinari, Watase, Williams, & Phillips, 1990). This theory can be translated to agar fluid gels and explains the increase in ordering temperature upon increased sucrose concentration. However, the onset temperature of ordering for glucose and fructose fluid gels (Fig. 1a and b) was similar regardless of sugar concentration. The difference in trend between these two sugars and sucrose is likely a product of the different sugar size; n(e-OH) increases in the order of fructose < glucose < sucrose.

The shear viscosity curves for 1 wt% agar fluid gels with 60% glucose (Fig. 1a), fructose (Fig. 1b) and sucrose (Fig. 1c), did not display a sharp increase in viscosity. This slower, more gradual transition from sol-gel suggests that 60% sugar was somewhat inhibiting gel formation.
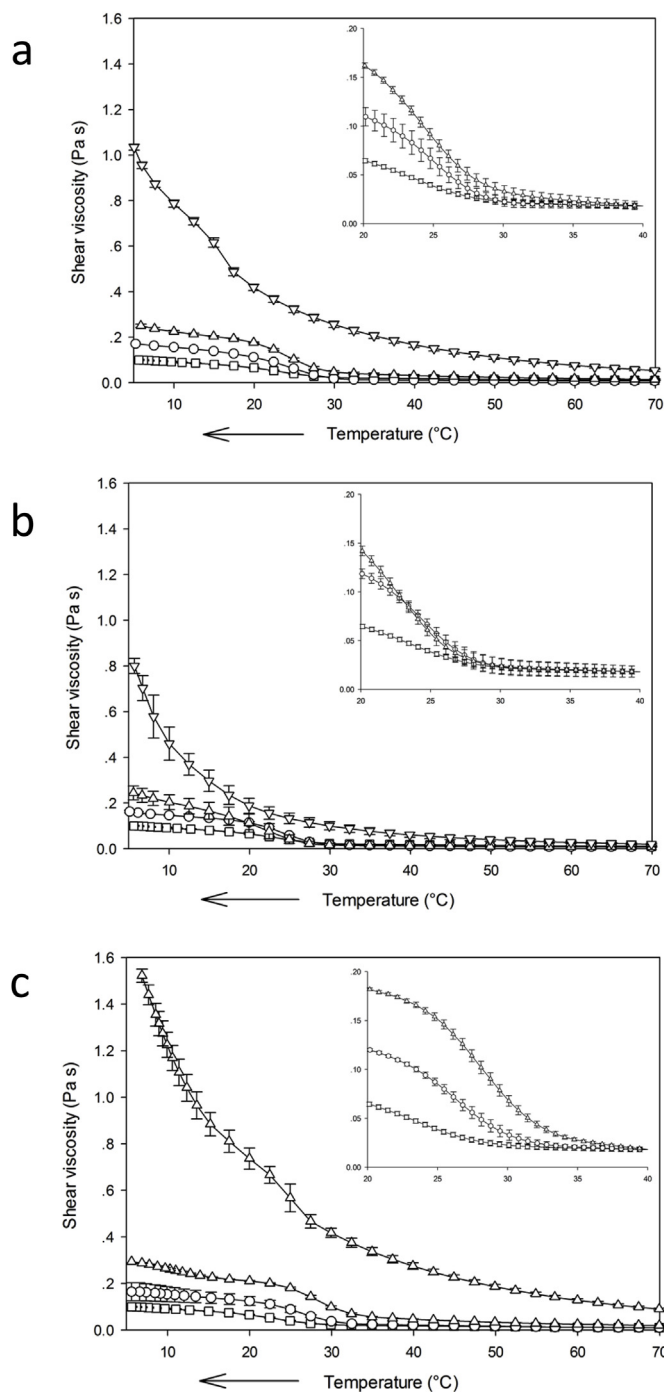

Fig. 1. Viscosity profiles during fluid gel preparation of 1 wt% agar fluid gels + 0.5 wt% Tween 20 with 0% (square), 20% (circle), 40% (triangle up) and 60% (triangle down) of (a) glucose, (b) fructose and (c) sucrose. The temperature was decreased from 70 °C to 5 °C at a cooling rate of 2 °C min^{-1}, under a fixed applied shear of 500 s^{-1}. The inset graphs focus on the region between 20 °C and 40 °C for the three lower concentrations of sugar, where viscosity was normalised at 40 °C. This allows the ordering transition and its onset temperature to be observed more clearly.

It is likely that at this concentration, the glass transition temperature, T_g, was close to the gelation temperature and therefore the sol-gel transition was hindered. A similar observation was observed by Deszczynski, Kasapis, and Mitchell (2003); upon gelation of agarose in the presence of high levels of co-solute (50:50 sucrose/glucose syrup), a broader temperature band of gelation was observed indicating a less co-operative process of coil-to-helix formation. This will be further
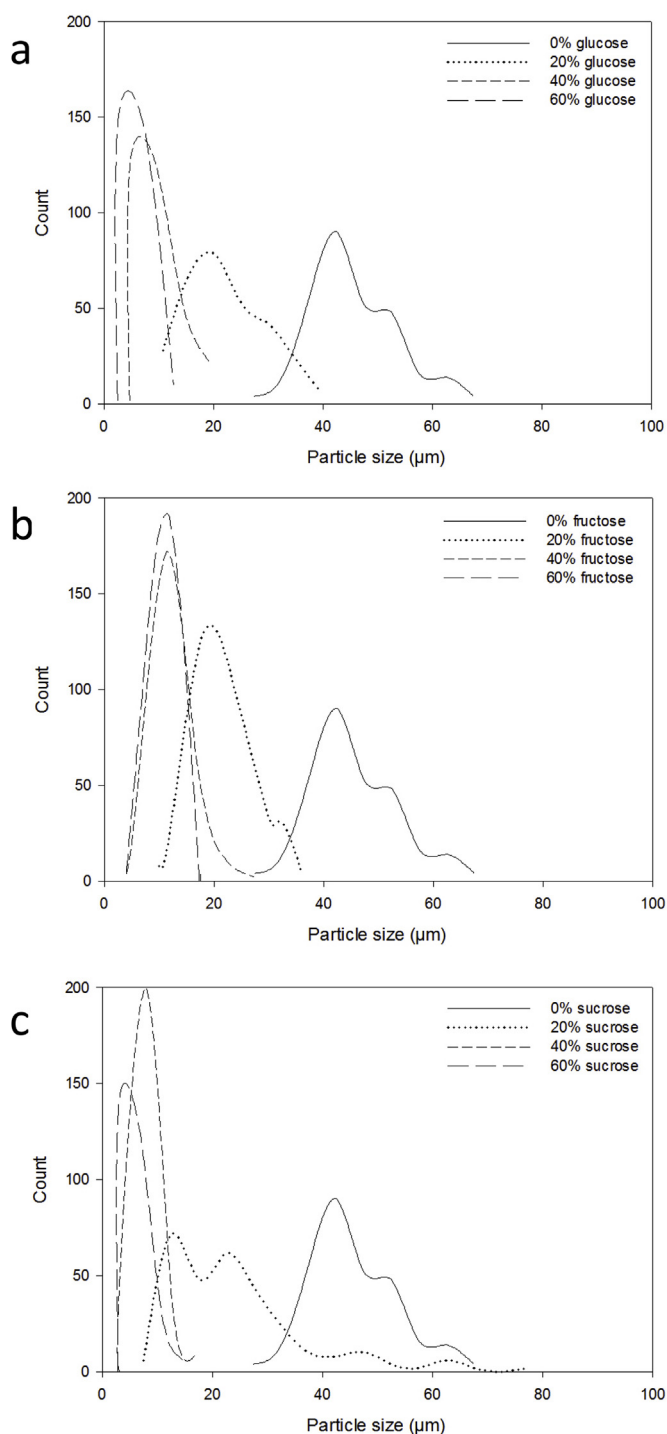
Table 1
Viscosity of glucose, fructose and sucrose solutions at 70 °C of concentrations 10–60 wt% from Telis et al. (2007). Figure adapted.

Concentration (wt%)	10	20	30	40	50	60
Sugar	Viscosity at 70 °C (mPa s)					
Glucose	0.44	0.65	0.81	1.32	1.7	4
Fructose	0.46	0.69	0.81	1.41	1.82	4.42
Sucrose	0.42	0.69	0.85	1.62	2.34	7.20

rheometer was used in Section 3.1 only to study gelation kinetics, therefore the difference between it and the pin stirrers shear environment on the properties of fluid gels produced is not relevant. Firstly, fluid gel particle size and shape were studied as it is important to consider their impact on foam stability. 1 wt% agar fluid gels with increasing levels of added sugar were produced and subsequently diluted and imaged using phase contrast microscopy. ImageJ software was used to measure particle size.

Fig. 2 shows particle size distributions for 1 wt% agar fluid gels with 0%, 20%, 40% and 60% of glucose (a), fructose (b) and sucrose (c) added. With no added sugar, the most abundant particle size was 40–45 μm in diameter. Upon addition of each sugar at 20%, a shift towards smaller particles was observed. At 40% and 60% addition, particle size distributions again shifted to smaller sizes and also narrowed (Fig. 2). To investigate this trend, it is important to consider the viscosity of the solutions entering the pin stirrer at 70 °C. Viscosity measurements for glucose, fructose and sucrose solutions from work by Telis, Telis-Romero, Mazzotti, and Gabas (2007) are therefore shown in Table 1. At higher concentrations of sugar the viscosity increased, for example from 10% to 60% sucrose, viscosity rose by a factor of 18 (Table 1).

In terms of fluid dynamics, the viscosity of the solution entering the pin stirrer will affect the resistance of the fluid to deformation. A solution of higher viscosity offers more resistance and consequently feels a lower shear rate (Gabriele, 2011), which would result in the formation of larger particles (Moakes, Sullo, & Norton, 2015). However, the opposite occurred here; increasing the viscosity of the solutions through sugar addition resulted in a decrease in particle size. The most influential factor in determining particle size was therefore likely to have been gelation kinetics. Normand et al. (2003) expanded the explanation given by Nishinari et al. (1992) relating the effect of sugar on gelation kinetics to viscosity; they describe a reduction in polymer chain mobility of agarose solutions caused by increasing sugar concentration and therefore viscosity. This in turn slowed down gelation, which favoured helix nucleation and inhibited the growth process. As the concentration of sugar and hence the viscosity of agar solutions entering the pin stirrer was raised, a reduction in polymer chain mobility was therefore expected. This would have likely resulted in a greater abundancy of initial gel nuclei, which were unable to grow to as large an equilibrium particle size, explaining the trends observed in Fig. 2. At 60% sugar addition, gelation was observed to be somewhat inhibited (Section 3.1), therefore during fluid gel production on the pin-stirrer, it becomes difficult to interpret particle size as a number of factors were involved. In addition, it is not known whether there is a minimum possible particle size and if there is, whether it's dependent on gelation kinetics or pin stirrer parameters.

The shape of particles was also explored; micrographs of 1 wt% agar with varying concentrations of sucrose are presented in Fig. 3. In the presence of no sugar, agar fluid gel particles produced on the pin stirrer have previously been described as spherical structures consisting of small fibrous particles (Ellis et al., 2017). This structure was confirmed by the micrograph in Fig. 3a. Upon addition of 20% sucrose, particles of the same conformation but smaller size were observed (Fig. 3b). From 40% to 60% sucrose addition (Fig. 3c and d), these structures begun to disappear leaving only the small fibrous particles. These observations

Fig. 2. Overlapping histograms showing particle size distributions for 1 wt% agar fluid gels + 0.5 wt% Tween 20 with 0%, 20%, 40% and 60% of (a) glucose, (b) fructose and (c) sucrose. Measured from micrographs using ImageJ software.

investigated in Section 3.4, when the rheological properties of fluid gels at higher sugar concentrations are explored.

3.2. Effect of sugar on microstructure

The investigation into the influence of sugar during gelation of agar fluid gels in Section 3.1 provides a good foundation to explore such effects on their microstructure. Fluid gels henceforth in the paper were prepared using a continuous pin stirrer, as described in Section 2.2. The
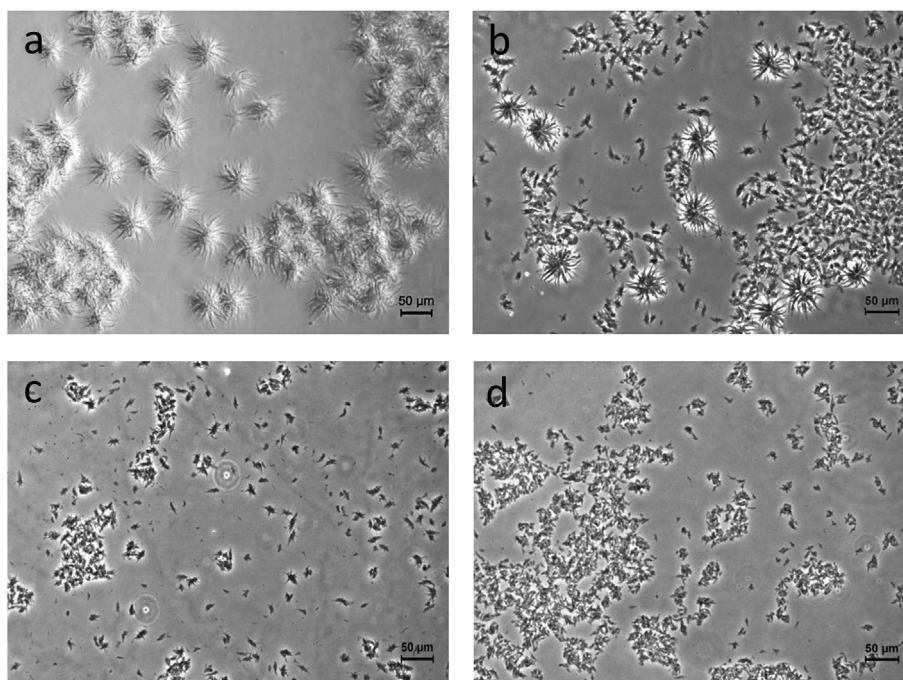
Fig. 3. Optical micrographs of diluted 1 wt% agar fluid gels + 0.5 wt% Tween 20 with 0% (a), 20% (b), 40% (c) and 60% (d) sucrose, using phase contrast microscopy.

support the theory that the more viscous solutions resulted in the greater abundance of gel nuclei and inability of particles to grow to as large a size; at 60% sucrose, only small fibrous particles existed but by decreasing sugar concentration and therefore viscosity, these fibrous particles were able to grow and form larger structures (observed at 20% and 0% sucrose). Together with the shape and size of the fluid gel particles, exploring their rheology will allow a greater understanding of the overall material properties.

3.3. Effect of sugar on quiescent agar gels

In order to understand fluid gel rheological properties, it is necessary to first understand the effect of sugar on quiescently set agar gels and in particular, gel strength. To measure this, texture analysis was conducted on 1 wt% agar quiescent gels with varying concentrations of glucose, fructose and sucrose (Fig. 4). The intrinsic polymeric network of agar fluid gel particles and therefore their textural properties can be inferred by their quiescently set counterparts (Frith, Garijo, Foster, & Norton, 2002). The gels were cold-set for 48 h and subsequently compressed to 50% strain. Initial Young's modulus was determined using the gradient of the linear region at 0–5% strain on a true strain (ε) true stress (σ) graph. It is a measure of the stiffness/deformability of the gel network, until structure failure occurs (Bradbeer et al., 2014). It is worth noting here that material properties of 1 wt% agar quiescent and fluid gels with glucose and sucrose were explored first at 10% concentration intervals from 0 to 60%. Once the trends had been revealed, it was considered unnecessary to test gels at 10% and 30% fructose.

The initial Young's modulus increased with concentration of each sugar until 50% addition (Fig. 4) and therefore resulted in stiffer agar gels. However, the addition of sugar at 55% and 60% resulted in a lack of available water for the formation of stable junction zones and consequently a fall in the initial Young's modulus was observed (Fig. 4). The enhanced elastic modulus of agar gels on addition of sugar can be explained by the increased number of junction zones and decrease in both the number of parallel links and their rotational freedom (Nishinari et al., 1992). In addition, the initial Young's modulus observed for agar gels with up to 30% sucrose was higher than those of fructose and glucose (Fig. 4). This again is likely to be a function of n(e-

OH), which increases in the order of fructose < glucose < sucrose (Nishinari et al., 1992). The trends in gel strength reported here will be comparable to particle stiffness in corresponding fluid gels.

3.4. Bulk rheological properties

The bulk rheology of the fluid gels was studied 48 h after production. At 55% glucose, and 60% fructose and sucrose, crystallisation of the samples began, thus these measurements were not taken as the sample was not homogenous and therefore not representative. This supports the explanation given in Section 3.1, where the inhibition of gelation at 60% sugar (Fig. 1) was said to be a result of the proximity to its glass transition. Fig. 5a and b shows viscosity and oscillatory data as a function of sugar concentration. Shear viscosity rose gradually upon increased concentration of sugar until 50% addition (Fig. 5a). At 50% glucose and fructose, shear viscosity appeared to be noticeably higher and the error bars were larger (Fig. 5a). The same observation can be made at 55% sucrose. The viscoelastic behaviour of the fluid gel systems was assessed using oscillatory rheological data and storage modulus (G′) has been plotted as a function of sugar concentration (Fig. 5b). A similar trend to viscosity can be observed for G′.

To explain these results, it is helpful to consider the data from Fig. 4. The addition of each sugar (up to 50%) resulted in more pronounced gel stiffness. This trend is reflected in the corresponding fluid gel particles and can therefore be attributed to the observed increase in viscosity and G′ with sugar concentration (Fig. 5a and b). Beyond 50% sugar, the lack of available water resulted in a decrease in quiescent agar gel strength (Fig. 4). However, viscosity and G′ of the corresponding fluid gels increased (Fig. 5a and b). At these high levels of sugar, upon cooling of the agar/sugar solution during the fluid gel formation process, the sugar will have approached its glass transition. The fluid gels produced were therefore rubbery exhibiting a high G′ and shear viscosity. Tsoga, Kasapis, and Richardson (1999) described how agarose prevents sugar crystallisation in high levels of co-solute through encouraging intermolecular interactions, leading to high viscosity glass mixtures. The larger error bars at higher concentrations are also likely to be a function of this behaviour.

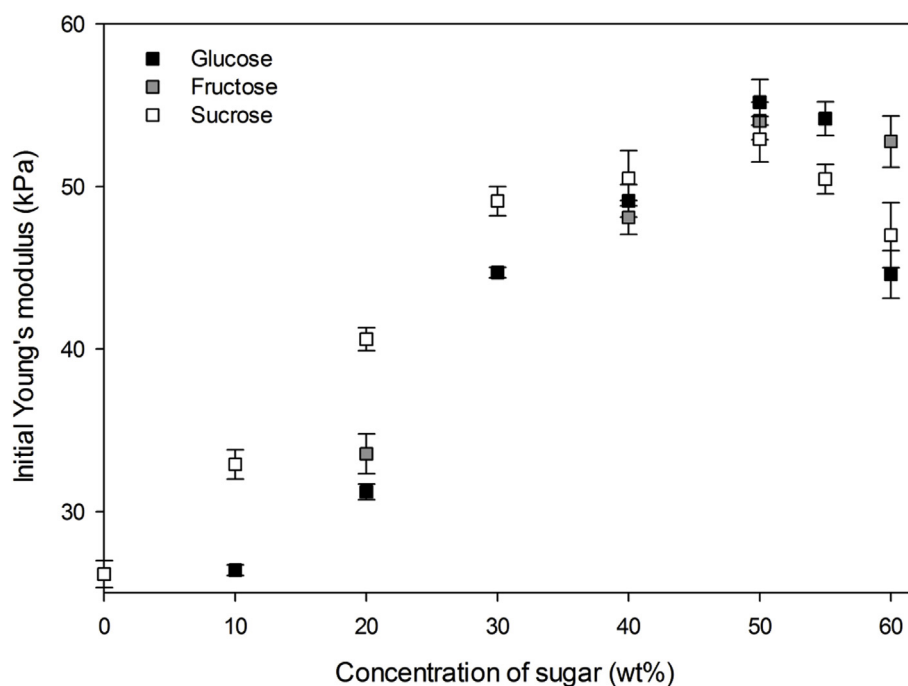This trend can also be identified when looking at the yield stress of

Fig. 4. Initial Young's modulus of quiescently set 1 wt% agar gels + 0.5 wt% Tween 20 when compressed to 50% strain at a rate of 1 mms^{-1} as a function of sugar concentration. This reflects fluid gel particle stiffness. Measurements were conducted at 25 °C.

the agar fluid gels. Yield stress was determined from an amplitude sweep with controlled strain as the stress required to decrease G' in the LVR by 5%. This corresponds to the disruption of particle-particle interactions within the system and the initiation of flow by particles "squeezing" past each other. Yield stress increased gradually from 0 to 50% sugar (Fig. 6), which can be attributed to greater particle stiffness. Particle size also plays an important role, as smaller particles with a higher surface area should facilitate more interactions. The decrease in particle size with increasing sugar concentration (Fig. 2) therefore resulted in greater particle-particle interactions and subsequently yield stress (Fig. 6). The large yield stress at 55% sucrose further confirms the conversion of the brittle agar gel network to a more rubbery-like structure.

3.5. Foam capabilities and stability

The functionality of agar fluid gels to produce stable foams was investigated and related to their material properties. The ability of the systems to incorporate air was characterised using air fraction measurements. The soft, elastic nature of the fluid gels allowed the incorporation of air despite the opposite being true for many particulate systems (Murray & Ettelaie, 2004). Agar fluid gels were aerated in a Hobart mixer for 7 min, which ensured that all foams were in the wet foam boundary (air fraction within 0.65–0.95). Foam stability is another important parameter to understand when producing food foams, as they age over time leading to reduced sensory characteristics. The stabilisation of aerated agar fluid gels discussed in previous work by the authors (Ellis et al., 2017) can be applied here. Tween 20 was used to establish short term stability and therefore creation of the foam through quick adsorption to the interface. Once the foam was generated, a large number of agar particles were confined in the foam channels. This accumulation of particles at Plateau borders and nodes resulted in an effective concentration increase which in turn caused a significant increase in the local rheology. This therefore reduced liquid drainage, which had a large impact on the overall foam stability. However, eventually foam coarsening led to the channels widening and the loss of confinement. Foam half-life was dependent on the yield stress of the fluid gel, which could be manipulated through altering particle

interaction and elasticity. Here, foam half-life, that is the time taken for foam height to reduce by half was measured and plotted as a function of fluid gel yield stress in Fig. 7. Foams only exhibited a very small amount of coalescence at the top where it was drying slightly; the reduction in foam height was therefore a result of a sudden decrease in liquid drainage. Yield stress at different concentrations of each sugar were plotted where data points correspond to concentrations in Fig. 6. The data points closely follow the same curve, independent of sugar type. Increasing fluid gel yield stress, resulted in the foam half-life rising until the necessary stress required to suspend air bubbles of this size by overcoming the gravitational stress acting on the fluid (1–2 Pa) was reached. At a fluid gel yield stress of 3–4 Pa, liquid drainage was considerably ceased and the half-life plateaued (Fig. 7). Even without the effect of liquid drainage, the foam was limited to a certain life time. This was likely due to coarsening of the gas phase; the size of foam channels would have started to increase causing loss of confinement of the fluid. The gravitational stress would then become larger than the yield stress and the liquid quickly drained through the foam causing its collapse. This data supports the trend seen for agar fluid gels with no sugar in previous work (Ellis et al., 2017). Yield stress was enhanced through increased particle elasticity and particle interaction. Previously, this was manipulated through altering agar concentration whereas in this work, it was influenced by changing solvent availability by adding sugar at various concentrations.

3.6. Effect of particle size on foam drainage

Foam stability firstly depends on the ability of particles to accumulate in Plateau borders and nodes to slow drainage. The role of fluid gel particle shape and size in this mechanism has not yet been explored. Haffner et al. (2014) however, report a strong dependence of particle size when studying the jamming transitions in aqueous foams of granular hydrophilic particle suspensions. Drainage velocity decreased continuously as particle volume fraction increased until eventually drainage stopped, revealing a strong effect of particle size. Here, the manipulation of production parameters provided the opportunity to investigate size effects. It was reported earlier in Section 3.2, that particle size was a function of solution viscosity entering the pin stirrer.
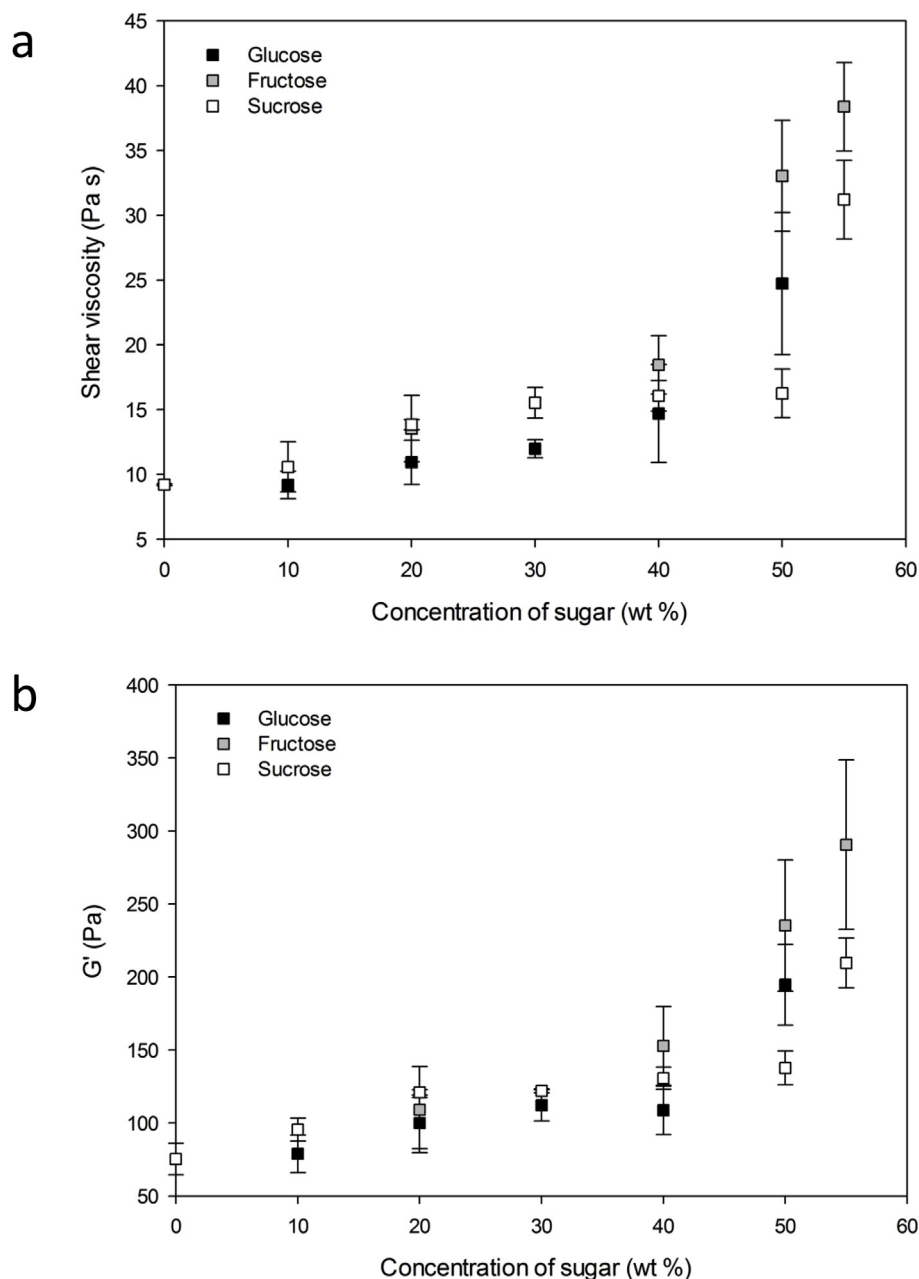
Fig. 5. Rheological measurements of 1 wt% agar +0.5 wt% Tween 20 fluid gels as a function of sugar concentration (glucose, fructose and sucrose). (a) shear viscosity at a shear rate of 1 s^{-1} measured from a flow curve (0.1 s^{-1} to 500 s^{-1}) and (b) storage modulus (G′) from the LVR region of a strain controlled amplitude sweep. Measurements were carried out using a serrated parallel plate 48 h after production at 25 °C.

The addition of an equivalent amount of sugar pre- and post-production would therefore alter solution viscosity and therefore final particle size, whilst keeping the formulation the same. Pre-production refers to the addition of sugar to the dissolved agar solution before it undergoes gelation in the pin-stirrer (pre fluid gel production) whereas post-production refers to the addition of sucrose to the fluid gel once it has been produced.

Sucrose at 20 wt% was added pre- and post-production and particle size was measured after 48 h (Fig. 8). The particles were observed for two weeks after production to investigate the possibility of changes due to osmosis but none were observed. Particle sizes, as expected, were considerably different (Fig. 8); the addition of sucrose pre-production resulted in fluid gels with a distribution of smaller particles (most abundant size approx. 10–15 μm in diameter) whereas addition post-production, yielded a distribution of larger particle sizes (most

abundant approx. 40–45 μm). The rheological properties of the two systems were controlled in order to eliminate any other differences. The fluid gels were diluted to the same yield stress (0.058 ± 0.019 Pa and 0.052 ± 0.005 Pa for pre- and post-production, respectively) and their elastic modulus (G′) was also similar (Table 2).

The two samples were aerated in a Hobart mixer to a similar air fraction, 0.87 ± 0.02 and 0.86 ± 0.02, as seen in Table 2. In order to evaluate particle size effect, liquid drainage measurements were recorded using a foam analyser (DFA100). The initial liquid fraction was determined by comparison to the reference liquid and its decrease was recorded by measuring the electrical conductivity at 7 pairs of electrodes along the cell height. Drainage profiles for the first 4 h after aeration at sensor 3 (half way down the foam) are plotted in Fig. 9. Both samples had a very similar liquid content initially but less liquid drained through the foam when the continuous phase consisted of
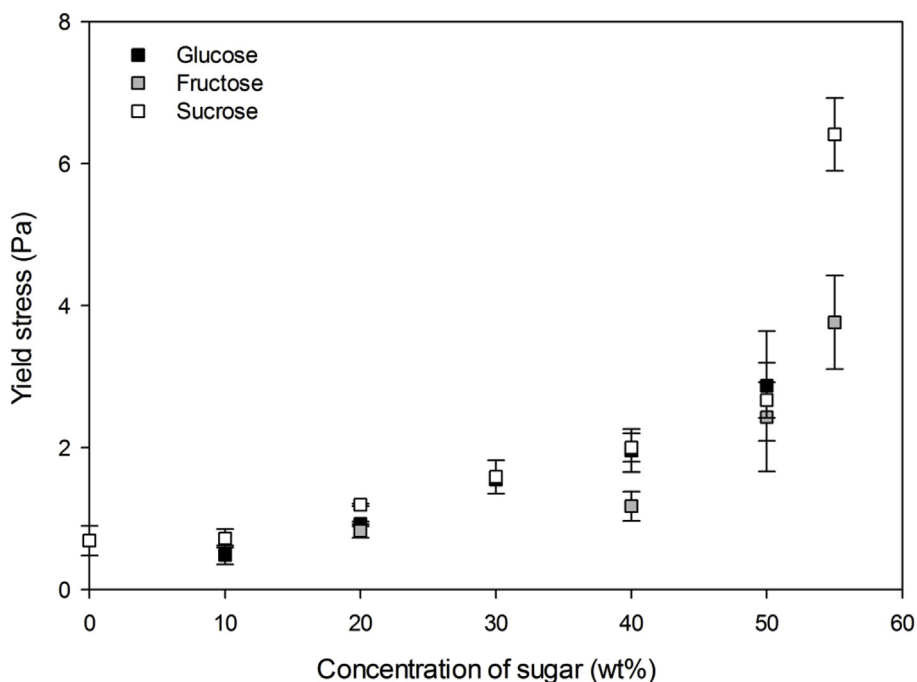
Fig. 6. Yield stress of 1 wt% agar +0.5 wt% Tween 20 fluid gels as a function of sugar concentration. Yield stress was measured as a 5% decrease in G′ during an amplitude sweep conducted 48 h after production at 25 ˚C.
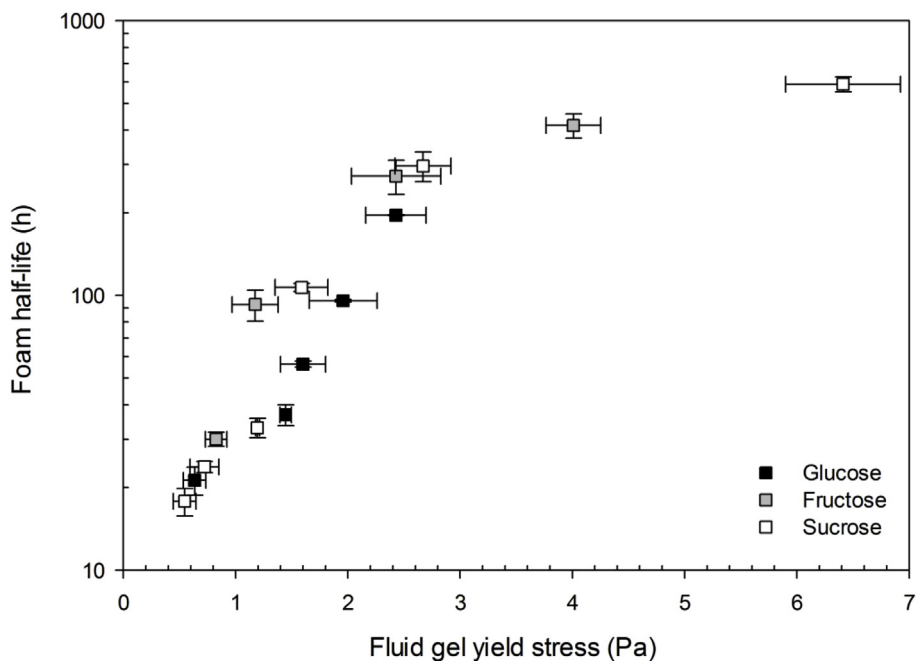

Fig. 7. Foam half-life as a function of agar fluid gel yield stress for 1 wt% agar +0.5 wt% Tween 20 with glucose, fructose and sucrose at various concentrations. The concentration of sugar to which each data point corresponds to can be determined from Fig. 6.

larger particles (post-production sucrose addition) than smaller particles (pre-production sucrose addition); 1.9% ± 1.0 compared to 6.4% ± 0.8 (Fig. 9). After initial aeration, the bulk phase would have began to flow through the foam channels causing them to narrow. It appears that the larger particles were more effective at accumulating in the foam channels and therefore reducing the flow of liquid. It was likely that the smaller particles were not so easily confined to the channels, resulting in a higher extent of drainage of the continuous phase before confinement occurred.

However, despite differences in drainage rates, the half-life of the

foams (Table 2) was very similar (9.4 ± 2.1 h for pre-production and 9.2 ± 1.1 h for post-production). A foam is a complex system and whilst drainage of the continuous phase is happening, coarsening of the dispersed gas phase and bubble re-arrangement is also occurring (Saint-Jalmes, 2006). Eventually, the size of the foam channels in these foams would have started to increase, resulting in the loss of confinement. The gravitational stress would have become larger than the yield stress causing an acceleration in liquid drainage, and in turn, the narrowing of channels and contact of bubbles leading to coalescence and ultimately foam collapse (Guillermic et al., 2009). As the two fluid gels had a
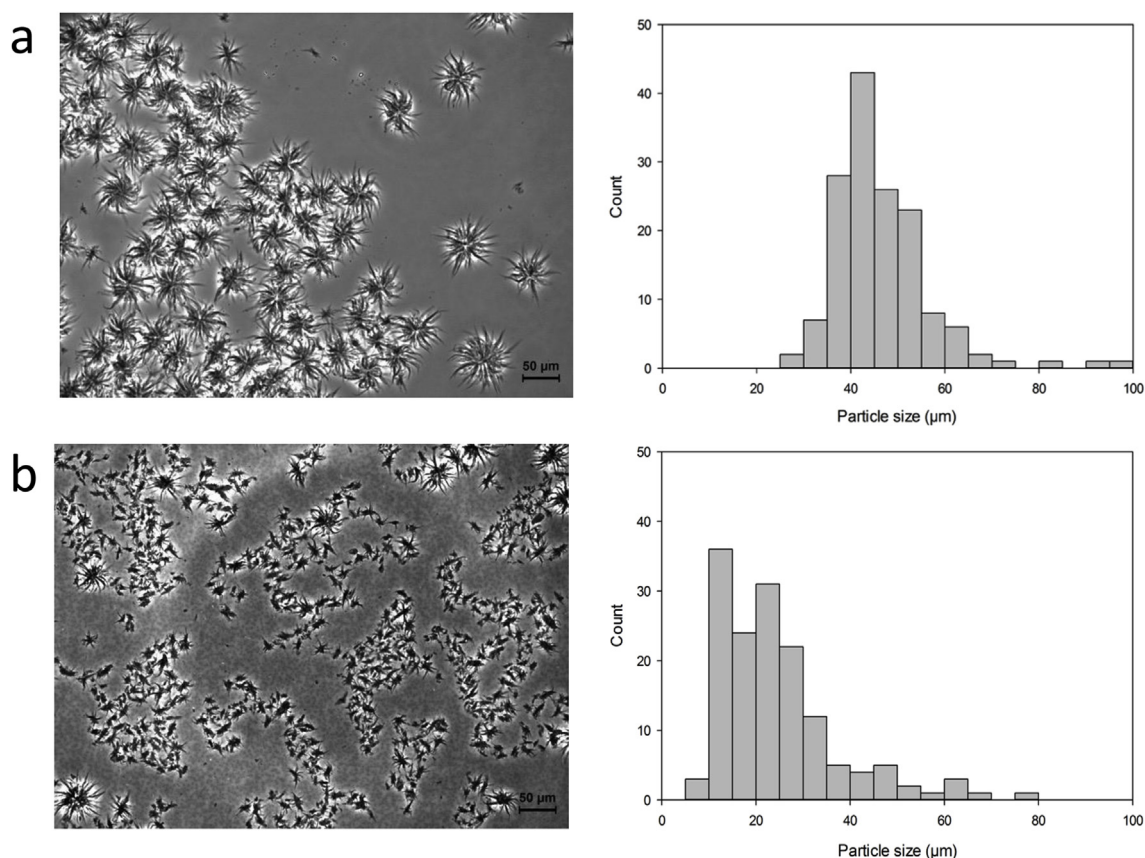
Fig. 8. Optical micrographs and corresponding particle size distributions for 1 wt% agar fluid gels with 0.5 wt% Tween 20 and 20 wt% sucrose added post-production (a) and pre-production (b).

Table 2
Properties of 1 wt% agar + 0.5% Tween 20 fluid gels with sucrose added pre- and post-production, as well as their properties once aerated.

	Sucrose addition	
	Pre-production	Post-production
G' (Pa)	12.8 ± 4.7	15.1 ± 0.8
Yield stress (Pa)	0.058 ± 0.019	0.052 ± 0.005
Air fraction	0.87 ± 0.02	0.86 ± 0.02
Foam half-life (h)	9.4 ± 2.1	9.2 ± 1.1
Decrease in liquid content over first 4 h (%)	6.4 ± 0.8	1.9 ± 1.0

similar yield stress, despite differences in initial drainage of the foams, they collapsed at similar times. The yield stress of the fluid gel measured pre-aeration to the time of foam collapse would have altered over time due to changes in confinement upon aeration and with foam ageing. However, these initial measurements showed a strong correlation with foam half-life (as seen in Section 3.5). Exploring the effect of particle size on foam stability in terms of liquid drainage and half-life has allowed the overall mechanism to be more clearly defined.

4. Conclusions

The influence of glucose, fructose and sucrose on the gelation, material and foaming properties of 1 wt% agar fluid gel have been investigated. The temperature of ordering during gelation was only affected by the addition of sucrose, where it increased with sucrose concentration due to an increase in number of junction zones provided through hydrogen bonding. All sugars at 60% somewhat inhibited gelation as the glass transition of sugar was approaching. The size of fluid gel particles decreased with increasing sugar concentration due to a higher solution viscosity entering the pin stirrer favouring helix nucleation and inhibiting the growth process. Particle size was not dependent on the type of sugar, only the viscosity change of the solution manipulated by sugar concentration. In order to infer particle strength, the strength of quiescent 1 wt% agar gel counterparts were measured. The addition of glucose, fructose and sucrose up to 50% resulted in increased initial Young's modulus of the gel. Above 50% sugar however, the lack of available water for gelation resulted in a lower gel strength. Again the type of sugar was not so important. Furthermore, the influence of sugar on bulk rheology was explored. At high concentrations of all sugars (above 50%), shear viscosity and G' were considerably higher, due to the conversion of an overall brittle agar gel network to a more rubbery-like structure occurred due to the glass transition of sugar. Below 50% sugar, shear viscosity, G' and yield stress increased with increasing concentration of all sugars, this was supported by the affect this had upon foam half-life measurements.

All systems showed good foaming properties, controlled by sugar concentration. Foam half-life was dependent on fluid gel yield stress and increased until the necessary stress to suspend air bubbles of this size was reached (3–4 Pa) and the half-life begun to plateau. This change in yield stress could only be a factor of increased sugar concentration and was independent of sugar type. These results supports the trend seen for agar fluid gels with no added sugar in previous work (Ellis et al., 2017). In both studies, yield stress was enhanced through increased particle elasticity and particle interaction. However, here we report the first example of influencing such parameters by changing solvent availability through the addition of sugar. In order to increase understanding of the foam stability mechanism, particle size was altered. The addition of sugar pre- and post-production allowed fluid gel particle size to be modified, whilst keeping the formulation the same. The addition of 20 wt% sucrose post-production resulted in the
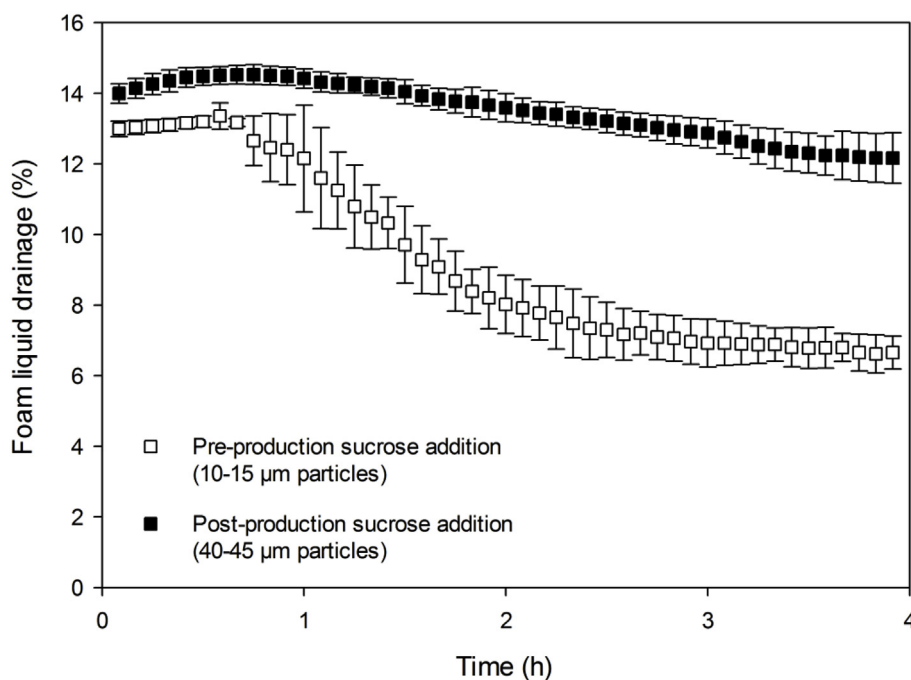
Fig. 9. Liquid drainage profiles of aerated 1 wt% agar + 0.5 wt% Tween 20 fluid gels with 20 wt% sucrose added pre-production and post-production. Liquid content is shown over 4 h from initial foaming at sensor 3 in the column (positioned half way down the foam).

formation of larger particles, which when aerated, considerably reduced liquid drainage. The larger particles were more effective at accumulating in the foam channels and therefore reducing the flow of liquid through the foam. Despite considerable differences in initial drainage, the half-life of the foams was very similar. The collapse of the foams was ultimately dependent on fluid gel yield stress. Exploring the effect of particle size on foam stability in terms of liquid drainage and half-life allowed the overall mechanism to be more clearly defined. Furthermore, this is potentially important when manufacturing products as the water released from foams during their lifetime needs to be considered as well as their half-lives. In addition, there are further potential approaches which could be used to modify particle size, for example altering the pin stirrer shaft speed.

This research has provided fundamental understanding of the effect of sugars on the microstructure of agar fluid gels and their foams. Increasing the understanding of the role of sugar in such systems will allow products to be engineered with alternative ingredients, which will help in the current drive for sugar reduction.

Acknowledgements

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