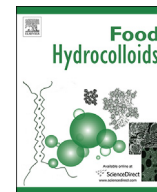




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Whey protein fluid gels for the stabilisation of foams

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ABSTRACT

The ability of whey protein fluid gels to produce very stable foams was demonstrated. These systems were prepared by heat induced gelation within the turbulent flow field of a pin stirrer at pH 5 and 8. The effect of pH and final protein concentration on the morphology of the particles, the bulk, interfacial and rheological properties and finally the foaming properties of their aqueous suspensions were investigated. Whey protein fluid gels, when produced close to the isoelectric point, consist of small spherical protein aggregates without significant functionality. Micrographs taken suggest that the protein aggregates created have the ability to adsorb at the air/water interface. Nevertheless, the lack of further increase in interfacial viscosity or elasticity indicates that either the adsorption is easily reversible or that it is only partial due to lack of material available to provide complete coverage. By increasing the pH of these systems the protein entities present acquire a negative charge, which causes an increase to both the bulk and interfacial viscoelasticity and increase of the stability of foams. The proposed mechanism is that during foaming, the smaller and mobile protein entities diffuse fast to the interface and provide the necessary interfacial tension reduction to facilitate foam formation. Subsequently, the larger protein particles fill the free space between the air bubbles and increase the local bulk viscosity, which improves foam stability mainly by preventing drainage. Whey protein fluid gels were able to create the same amount of foam as non-treated whey proteins but with substantially increased stability.

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1. Introduction

Aeration of foods is a process that is used both in traditional food products like bread and whipped cream but also in contemporary ones such as aerated chocolate, hot beverages and gourmet dishes. The presence of air, usually in the form of bubbles, throughout the volume of food provides a unique texture, which is frequently associated with luxury and high quality. Furthermore, when aeration is used effectively it can reduce the caloric value and the cost of foods by introducing an ingredient that costs nothing and has no nutritional value.

Aerated materials where the gas, in most cases atmospheric air, is distributed throughout an aqueous continuous phase are colloidal dispersions known as foams. These are thermodynamically unstable systems that generally have significantly shorter lifetime when compared to other colloidal dispersions such as emulsions (hours or even minutes compared to months) (Walstra,

2003). The main reason for the high instability lies to the fact that the interface between the dispersed and continuous phase, also called film, is larger in size when looking at bubbles in contrast to emulsion droplets. Moreover, the interfacial tension on the air–water interface (surface tension) is larger compared to the one between oil and water by a factor of 5 (Dickinson, 2010). The main mechanisms responsible for destabilising foams are drainage, disproportionation (the equivalent of Ostwald ripening in emulsions) and coalescence (Kinsella, 1981). In practice, these mechanisms reinforce each other commencing a snowball effect towards the breakdown of the foam structure. For instance, the larger bubbles formed due to disproportionation increase the size of the films which accelerate drainage and escalate instability (Walstra, 2003).

Foams are stabilised by amphiphilic entities, which can adsorb at the air/water interface and reduce the surface tension. Food foams are usually stabilised by high molecular weight surfactants or particles. Milk and egg proteins are very common ingredients present in foods that contain bubbles. Particle stabilised foams on the other hand are only present in whipped cream and ice cream where the foam structure is stabilised by a particulate matrix of

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either partially coalesced fat or ice crystals or both (Dickinson & Murray, 2006). Particles have shown an increased potential in producing ultra stable foams but in most of the cases the material used is non food (Dickinson, 2010). Trying to fulfil this need for finding food grade materials than can produce particles with foam stabilising properties, several studies have focused on plant carbohydrate materials (starches and cellulose derivatives) in combination with surfactants like proteins. These systems have demonstrated potential (Murray, Durga, Yusoff, & Stoyanov, 2011). Particles present in foams can provide stability whether they adsorb on the interface or remain on the continuous phase. In case of adsorption, they form rigid films that are stable against drainage and disproportionation, which is evident from an increase of the interfacial elasticity and viscosity. When there is no adsorption the particles either go through a percolation process and create a gel-like network or act as corks reducing the drainage of the continuous phase due to gravity (Rullier, Novales, & Axelos, 2008).

As the recent consumer trend demands foods to be 'natural' and 'wholesome' accompanied by a 'clean label', there is a need of producing particles from readily available food ingredients (Brockman & Beeren, 2011). A solution lies on the ability of several proteins to produce aggregates and gels when a set of conditions are met. In this study the heat denaturation of whey proteins is being explored as a mechanism to create micron sized aggregates or gel particles that will entail the necessary surface properties to adsorb on the air/water interface and produce very stable foams. Similar systems containing discrete gel protein particles created by freeze drying quiescently gelled whey protein isolate (WPI) suspensions prepared at a range of pH (5–8) has shown prominent results (Lazidis et al., 2014). The whey protein gel particles when rehydrated were able to produce foams with an increased stability by up to an order of magnitude compared to native proteins at the same concentration. That method allowed a significant proportion of whey proteins to remain in their native form and potentially in a form of soluble aggregates. It has been demonstrated in the past that the foaming properties of mixtures of soluble proteins with insoluble aggregates have enhanced foaming properties (Zhu & Damodaran, 1994).

This study focuses on exploring a process of producing gel micro particles that has a potential in future upscaling for manufacture through an industrially applicable process. The ultimate goal is to produce micro particle suspensions that will be in a state which will allow transport through a pump to a drying operation in order to achieve a powder formulation. The route chosen was the implementation of the well established method of producing fluid gels by subjecting a polymer solution to gelling conditions (pH, ionic strength, concentration, temperature) while being under a shear field (Norton, Jarvis, & Foster, 1999). In this case WPI solutions were heated at the critical gelation temperature while subjecting them to the turbulent flow field of a pin stirrer device. In this context, the effect of processing conditions (heating and mixing rate) along with the effect of environmental conditions (pH) on the physicochemical characteristics and foaming properties of the WPI gel particulates were assessed.

2. Materials and methods

2.1. Manufacture of WPI fluid gels

WPI BiPro (Davisco, MN, US) suspensions were prepared at 12 wt% protein concentration using reverse osmosis (RO) water and 0.001 wt% sodium azide (NaN_3) (Sigma Aldrich, Dorset, UK) to prevent microbiological growth. The suspensions were left stirring overnight at 4 °C to fully hydrate. The pH of the solutions was then adjusted to the desired value using 5M NaOH or 5M HCl (Sigma

Aldrich, Dorset, UK). For creating the fluid gels the solutions were pre-heated to 40 °C and then fed through a peristaltic pump to a series of two jacketed pin stirrers of well defined geometries (Gabriele, 2011). The first pin stirrer device was set to 80 °C and 2000 rpm rotation speed. The speed of the feed pump was adjusted in order to provide a retention time inside the pin stirrer corresponding to a heating rate of 2 °C min^{-1} . The outlet of the first pin stirrer was connected to an identical second pin stirrer rotating at 2000 rpm and set to a temperature of 5 °C that was used for cooling and diluting the primary fluid gel. For diluting the primary fluid gel RO water at room temperature (25 °C) was fed through a second inlet of the second pin stirrer at a rate that would allow the final dilution of the initial 12 wt% to 5, 3 and 1 wt% which represented more relevant concentrations to the study of foaming. The final fluid gel was stored in glass bottles at 4 °C until further characterisation.

2.2. Preparation of foams and determination of foam stability

Foams were prepared with two different methods, gas sparging and mechanical whipping. When foam stability and rate of drainage was assessed, foams were prepared by bubbling using a method adapted from literature (Waniska & Kinsella, 1979). Foam was created inside a clear acrylic circular column (75 mm internal diameter and 500 mm in height) by air sparging at a rate of 3 l min^{-1} and pressure of 2 bars through the bottom of the column where a porosity 3 (15–40 μm pores) glass sintered plate is located. A sample of 150 ml suspension was placed in the column and then air sparging was initialised until the production of a foam head of 20 cm. The reduction of the height of the foam head was then recorded with a CCD camera and the foam half-life was later calculated. All measurements were carried out in four replicates.

For all other measurements, foams were produced by mechanical whipping using a commercial milk frother with a spiral impeller of 10 mm diameter rotating at approximately 2000 rpm. For the means of foam production, 20 ml of sample was placed in a 100 ml glass beaker and whipped for 30 s. All measurements were performed at 25 °C unless otherwise stated.

2.3. Determination of foam overrun

The foaming ability of the systems studied was investigated by measuring the amount of air that was able to be incorporated after foaming by mechanical whipping. This was done by weighing equal volumes of the original dispersion and the corresponding foam and calculating the overrun through Eq. (1). The experiments were repeated in a set of five replicates.

$$\% \text{ overrun} = \frac{m_{\text{dispersion}} - m_{\text{foam}}}{m_{\text{foam}}} \times 100 \quad (1)$$

2.4. Determination of foam drainage from conductivity data

A conductivity column was developed in house based on the concept from (Barigou, Deshpande, & Wiggers, 2001) where the conductivity was measured at different heights of the foam across the side and the centre of the column. Alternating current (AC) in a square waveform with a frequency of 1 kHz and a max voltage of 10 V was fed through the volume of the foam and the drop of the root mean square value of the AC voltage (AC_{RMS}) was monitored. A calibration curve (Fig. 1) of different AC_{RMS} values of known liquid fractions of a foam were plotted and a two parameter logarithmic

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