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Modification to the lubrication properties of xanthan gum fluid gels as a result of sunflower oil and triglyceride stabilised water in oil emulsion addition

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ABSTRACT

A range of xanthan gum fluid gels and fluid gel emulsion mixtures have been constructed and their lubrication behaviour compared to high oleic sunflower oil. In addition, the lubrication properties have been measured after the addition of oil to the fluid gel, along with the effect of dispersing 10% (wt/wt) of a stabilised and un-stabilised oil continuous emulsion into the fluid gel postproduction.

This study has highlighted a method of producing xanthan gum fluid gels as well as a fat mimetic formulation based on a xanthan gum fluid gel/oil formulation, which has lubrication properties equivalent to that of standard sunflower oil during soft tribology experiments. The final formulation was shown to have similar initial lubrication behaviour as sunflower oil with a 93% oil reduction.

1. Introduction

The presence of fats is a vital component in foodstuffs due to its contribution to oral properties such as flavour, palatability, mouth feel and lubrication. (de Wijk, Terpstra, Janssen, & Prinz, 2006; O'Quinn et al., 2012) The consumption of excessive quantities of dietary fat has been shown to increase the risk of medical conditions such as obesity, high blood pressure and coronary heart disease. (Willett, 2012) The food industry in an attempt to facilitate healthier diets has adopted several methods of fat replacement. One such method is the use of hydrogels with lipid-like properties. Hydrocolloids are increasingly becoming key components in food industry formulations and have been widely discussed as potential systems in fat reduction/replacement applications. (Farres, Moakes, & Norton, 2014; Gidley, 2013) In order to be successful in emulating the attributes of fat systems, it is important to gain an understanding of the lubrication behaviour of these systems so that the impact of fat reduction on oral perception is minimised (Selway & Stokes, 2013).

The disruption of the molecular ordering of a biopolymer during its gelation is the primary method of forming fluid gel systems. (Cassin, Appelqvist, Normand, & Norton, 2000; Garrec, Frasch-Melnik, Henry, Spyropoulos, & Norton, 2012) A method commonly used is the application of shear forces to the gelling mixture leading to the separation of gel nuclei's, limiting aggregation. (Farres, Douaire, & Norton, 2013; Garrec & Norton, 2012) Xanthan gum is a naturally occurring polysaccharide widely used as a thickening/stabilisation agent in the food, cosmetic and pharmaceutical industries due to its highly pseudoplastic behaviour (Fitzpatrick, Meadows, Ratcliffe, & Williams, 2013; Sworn, 2009).

The production of fluid gels that possess properties similar to that of oil emulsion systems is a viable method of fat replacement but unfortunately, the vastly different oral perception of water/gels to that of oil means that fat replacement systems of this type can be easily distinguished from their full fat counterparts, necessitating the inclusion oil into formulations. (Chojnicka-Paszun, de Jongh, & de Kruif, 2012; Nishinari, 2006; van Aken, Vingerhoeds, & de Wijk, 2011)

This study aims to investigate the production of xanthan gum fluid gels and how the rheological behaviour differs from xanthan gum hydrated and sheared at room temperature. Once produced the effect of the addition of sunflower oil on the lubrication behaviour of the xanthan gum fluid gels is shown. Comparisons

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between sunflower oil and xanthan gum formulations where oil dispersed around the particles have been measured by ball on disk tribology. Finally, the effect on lubrication the mixing of a 30% water in oil (w/o) triglyceride stabilised emulsion system into the fluid gel postproduction was assessed.

2. Materials and methods

2.1. Materials

The sodium form of xanthan gum was obtained from MH Foods, Nile red was purchased from Sigma–Aldrich, and sunflower oil was obtained from a generic source. Glyceryl monostearate (Dimodan HP Kosher), Tri-palmitate (Edenor C16-98 MY), and Polyglycerol Polyricinoleate were provided from Danisco, Emery Oleochemicals, and Palsgaard, respectively. All materials were used as received and without further purification.

2.2. Methods

2.2.1. Xanthan gum fluid gel production

Dry pre-weighted xanthan gum powder (1.5% wt/wt) was added slowly and under constant agitation to heated distilled water (approximately 80 ± 5 °C). The pre gel solution was kept isothermal (above the literature ordered–disordered transition temperature) until complete hydration was achieved, then stirred for a further 30 min under cover to prevent evaporative losses. (Mannion et al., 1992) Xanthan gum fluid gels were produced by flowing the pre-gel solution through a thermally controlled pin stirrer set to a shaft rotation speed of 2000 rpm (schematic shown in Fig. 1.).

The pin stirrer consists of a rotor shaft with evenly distributed pins along its length, which is inserted into a thermally controlled jacket with stators running the length of the inside wall. The arrangement is such that when assembled the rotor pins are positioned between the stator pin of the jacket. In operation, areas of high shear are developed in the gaps between the pins when the centre shaft is rotated. Further details of the construction of the pin stirrer is described in Garrec et al. (2012) For fluid gel production, prior to being subjected to the shear field the fluid temperature remained at ~ 80 °C and was reduced to 20 °C during transit through the unit. The reduction in temperature provided the driving force for ordering whilst the shear between pins limited overall gelation of the solution volume as a whole.

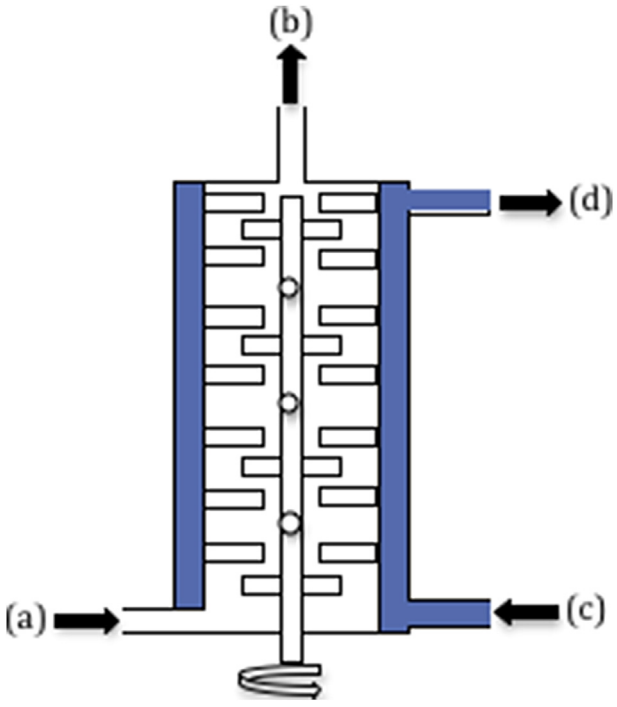

Fig. 1. Schematic representation of the pin stirrer unit (a) sample inlet (b) sample outlet (c) inlet for thermal jacket (d) thermal jacket outlet.

2.2.2. Water/Oil emulsion production (w/o)

As described by Frasch-Melnik et al. and Garrec et al. particulate emulsions were produced by pumping the pre-emulsion (at a flow rate of 150 ml min^{-1}) through a jacketed scraped surface heat exchanger, followed by a pin stirrer, both of which were set to a shaft rotation speed of 2000 rpm and cooled to 5 °C with water. (Frasch-Melnik, Norton, & Spyropoulos, 2010; Frasch-Melnik, Spyropoulos, & Norton, 2010; Garrec et al., 2012) Prior to production, a mixture of nucleation agent (Glyceryl monostearate, 1%), solid fat (Tri-palmitate, 3%) and emulsifier (PGPR, 1%) were added to the oil phase, and the bulk temperature raised to ca. 95 °C. Once the oil reached the required temperature and a homogeneous dissolution was obtained, water (heated to 60 °C) was added to the stirring oil mixture to produce a pre-emulsion that was 30% w/o (by mass). This pre-emulsion was maintained at 80 °C, before being pumped firstly through both the units, collected then passed through the system a second time at the same rate, in order to induce fat network break-up and reduce the particle size of the final emulsion.

2.2.3. Characterisation

Optical light microscopy, Light microscopy was performed using a Brunel SP300-fl (Brunel Microscopes Ltd, UK) fitted with a DSLR camera (Cannon EOS Rebel XS, DS126 191). For the purpose of imaging particles 20× or 40× objective lens were used. Post image processing was made using the software package ImageJ.

Confocal scanning laser microscopy (CLSM), CLSM was performed using a Leica TCS-SPE (Leica DM2500, Leica Microsystems Ltd, UK) fitted with an argon laser. Lipid based particles and sunflower oil were dyed with Nile red. Dyes were excited at 488 nm and detected between 500 and 550 nm, and image slices were collected at 1 μm intervals through the samples under 40x magnification. UV transparent/fluorescence free immersion oil (Sigma–Aldrich, UK) was placed between the lenses and coverslip of the sample slide during imaging. Image processing was made using the software package ImageJ.

2.2.4. Rheology measurements

Oscillatory measurements, Storage and loss modulus measurements were made at 20 °C using a Kinexus pro rotational rheometer (Malvern instrument, UK) with a parallel plate geometry (diameter 60 mm, gap set to 1 mm) calibrated with pure water (at 20 °C). Solution of xanthan gum fluid gel and gels hydrated at 20 °C were transferred to the geometries, and the temperature allowed to equilibrate for 5 min. The percentage strain on the sample was varied between 0.1 and 100%. All measurements were made at 1 Hz in triplicate and the average reported on a plot of modulus versus strain percent.

Viscosity measurements during production of fluid gel and gels hydrated at 20 °C, Single shear viscosity measurements during fluid gel production were made using a Kinexus pro rotational rheometer (Malvern instrument, UK) with a vane geometry (internal cup diameter 27 mm, vane rotor 25 mm) calibrated with water (at 20 °C). The required mass of deionised water was added to the vane and the temperature allowed to isotherm either at 20 °C or 80 °C depending on experiment type. Dry powdered xanthan gum was