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Rheology of emulsion-filled alginate microgel suspensions

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ABSTRACT

Emulsion filled polysaccharide gels can be used as carrier systems of lipophilic bioactives in the food, pharmaceutical and cosmetics industry. This carrier system can exist either as bulk or discrete gel systems. In this study the rheological properties of discrete emulsion filled alginate microgel suspension was examined as a function of volume fraction (ϕ) and oil content. Fine emulsion (220 nm) was encapsulated within alginate microgels (mean size 36.2–57.8 μm) by using the impinging aerosol technique. The microgels (containing 0–77% w/w oil total solids basis) produced were estimated to have particle modulus in the range of 150–212 Pa. An increase in oil content in the microgels led to more deformable microgels due to the reduction in gel density. The deformability of microgels influenced the bulk modulus and apparent viscosity of the concentrated suspension. At the same suspension volume fraction (ϕ), suspensions with more deformable microgels exhibited a lower bulk modulus. We also showed that the Carreau and Cross models were adequate in predicting the flow behaviour of the concentrated emulsion filled microgel suspension.

1. Introduction

Emulsions represent the most conventional and simple carrier for functional lipophilic compounds such as apolar bioactives, lipophilic drugs and fatty acids (McClements, 2010; Nanjwade, Patel, Udhani, & Manvi, 2011). However, the use of emulsions alone as a stable carrier system is limited due to the chemical environment (pH, temperature, ionic concentration) of different food systems and the destabilising conditions (enzymatic, pH) encountered in the human gastrointestinal tract after ingestion (Fatouros, Karpf, Nielsen, & Mullertz, 2007; Guo, Ye, Lad, Dalgleish, & Singh, 2014). Studies have shown that lipid digestion and bioavailability of emulsions and their bioactive contents are affected by factors such as droplet size, interfacial composition, lipid molecular structure and lipid physical state (Garaiova et al., 2007; Golding & Wooster, 2010; Haug et al., 2011; McClements, Decker, & Park, 2009; Nielsen, Petersen, & Mullertz, 2008).

The use of emulsion filled gels is an alternative technique to stabilise and protect emulsion in the food environment and during the passage through the gastric system. Emulsion entrapped within an alginate gel has been shown to retard lipolysis by digestive enzymes (Klinkesorn & Julian McClements, 2010). Flow behaviour (rheology), which directly affects mouth feel and textural properties, is a crucial consideration in the application of emulsion filled gels in food. In bulk protein or polysaccharide gel systems, gel behaviour is influenced by the interaction between the gel matrix and the emulsion droplets (Sala, de Wijk, van de Velde, & van Aken, 2008). Emulsion droplets act as fillers that either increase (active fillers) or decrease (inactive fillers) the elastic modulus of the bulk gel (bulk modulus) (Chen & Dickinson, 1999; Lorenzo, Zaritzky, & Califano, 2013). Active fillers increase the elastic modulus of gels through strong interaction between the filler particles with the gel matrix while inactive fillers have little or no interactions with the gel matrix (Vliet, 1988).

Emulsion gels can also exist in the form of discrete microgels. Although emulsion-filled microgel and bulk emulsion gel share fundamental similarities in their basic structure, the rheological behaviour of microgels differ significantly to bulk gels. The microgel system is a suspension, which constitutes a continuous phase (usually water) and microgel particles. Thus, rheology is influenced by three parameters: volume fraction, particle modulus (modulus of particles that make up the suspension) and interaction potential (Islam, Rodriguez-Hornedo, Ciotti, & Ackermann, 2004; Ketz, Prud'homme, & Graessley, 1988; Shewan & Stokes, 2012; Stokes, 2011). Volume fraction (ϕ) is defined as the volume of particles in suspension (V_P) as a proportion of the total volume of suspension (V_T), ($\phi = V_P/V_T$). At low concentration (low ϕ), the flow behaviour of microgel suspension follows hard particle suspension rheology where rheology is determined by the continuous phase. At higher ϕ, the microgels are packed tightly leading to deformation of microgels. At this high solid concentration, softer microgels (lower elastic modulus) will exhibit a lower viscosity compared to hard microgels (higher elastic modulus) (Adams, Frith, & Stokes, 2004). At even higher ϕ corresponding to a critical limit (0.64 for polydisperse samples), close packing of the microgel particles results in a microgel "paste" with viscoeleastic behaviour although still retaining their identity as single particles (Cloitre, 2011; Stokes, 2011).

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Understanding the rheology of microgel suspensions is crucial to the application of the microgel. In consumer personal care products, synthetic microgel such as Carbopol is widely used to impart thickness and yield stress to improve texture, stability and acceptability (Ketz et al., 1988). As a major component in topical drug delivery systems, such as nasal, dermal, ocular and rectal application, knowledge of the microgel rheological behaviour allows optimization of drug diffusion, spreadability and adhesiveness to the application area (Ducheˇne, Touchard, & Peppas, 1988; Tamburic & Craig, 1995). In food applications, microgel particles in the form of fluid gels are used for texture modification and fat substitution (Fernández Farrés, Moakes, & Norton, 2014). The study of rheological behaviour of microgel suspensions in food allows better prediction of product processability, product stability, texture control and handling properties.

Past studies have described the rheological properties of emulsion in proteins, starches and hydrocolloid gels (Firoozmand & Rousseau, 2013; Kim, Gohtani, & Yamano, 1996; Lorenzo et al., 2013; Sala et al., 2008). Rheological behaviour of synthetic and non-synthetic (colloidal and non-colloidal) biopolymer (e.g. agar, Carbopol, poly (*N*-isopropylacrylamide), poly (vinylpyridine)) microgel suspension has also been reported (Adams et al., 2004; Ketz et al., 1988; Lyon & Fernandez-Nieves, 2012; Senff & Richtering, 1999; Vincent & Saunders, 2011). To our knowledge, no studies have been reported on the rheological behaviour of emulsion filled alginate microgel suspensions.

We attempt to characterize the rheological behaviour of concentrated suspensions made up of emulsion filled alginate microgels. Alginate, a widely used polysaccharide, is made up of β-D-mannuronate and α-L-guluronate monomers. Gelation of alginate occurs in the presence of multivalent cations such as Ca^{2+}. The ionic interaction between the cations and carboxyl groups on the alginate monomers forms a gel network. The use of alginate microgels, which have been applied in biomedical, pharmaceutical, food and cosmetic industries, is attractive due to its stimulus responsive nature, ability to encapsulate and release functional compounds, thickening effect and bioadhesive nature (Matricardi, Di Meo, Coviello, & Alhaique, 2008). Most recently, a number of studies have focused on the gelation properties, rheology and tribology of alginate fluid gels, highly concentrated gelled particle suspension which are analogous to microgel suspensions, albeit with a smaller particle size range (Fernández Farrés, Douaire, & Norton, 2013; Fernández Farrés & Norton, 2014; Xu et al., 2013). In this study, viscosity, modulus and yield stress of the emulsion filled alginate microgel suspension were investigated using constant shear rate, constant shear stress and dynamic oscillatory experiments. The influence of oil concentration, particle size and microgel concentration on the rheological behaviour were also investigated. Macrogels (mm-sized) particles were used to study the effect of oil concentration on the gel particle modulus.

2. Materials and methods

Calcium alginate microgel particles were produced with sodium alginate (GRINDSTED® Alginate FD 155, Danisco, Australia) and calcium chloride. Canola oil was purchased from local supermarkets. Sodium caseinate (SCN) (NatraPro), supplied by MG Nutritionals (Australia), was used as an emulsifier. Nile red (0.1% w/v in acetone), a lipid soluble fluorescent dye, was used to stain the emulsion droplets. Deionised water was used as a diluent throughout the experiment.

2.1. Preparation of emulsion filled alginate microgels and microgel suspensions

To prepare the emulsion-filled alginate microgels particles, a fine oil emulsion was firstly made up followed by entrapment of the emulsion droplets in the alginate microgel particles. A 10% (w/w) coarse water-in-oil emulsion was created by emulsifying canola oil in a 1% (w/w) SCN solution with the Silverson (UK) mixer at 1500 rpm for 5 min. The coarse emulsion was passed through a two-stage homogeniser (Twin Panda, GEA, Australia)(1st stage — 25 MPa, 2nd stage — 0.5 MPa) twice, to form fine emulsion with a mean droplet size of 0.22 ± 0.01 μm (measured as per Section 2.5). Solutions containing different proportions of fine emulsion, water and sodium alginate were mixed with a lab mixer (5000 rpm) (T25 IKA-Werke, Germany) (Table 1) to create microgel particles containing different oil concentrations.

The fine emulsion filled calcium alginate microgel particles were formed from the emulsion-alginate solution based on the spray aerosol method described in International Provisional Patent No. 062,254, 2009 Bhandari (2009) and Ching, Bhandari, Webb, and Bansal (2015)(Fig. 1a). A fine aerosol mist of 0.1 M calcium chloride solution was created in the cylindrical reaction chamber using an air atomizing nozzle operated at liquid and air pressure of 0.15 and 0.2 MPa. Pressurized (0.5 MPa) mixture of sodium alginate and emulsion was counter currently atomized in the chamber using compressed air at 0.5 MPa. The resulting emulsion-filled alginate microgel particles were collected from an outlet at the base of the reaction chamber and passed through a 200 μm sieve to remove any larger or aggregated gel particles.

2.2. Determination of suspension volume fraction

The microgels were condensed by filtering (Advantec 5C filter paper) (<5 μm) under vacuum and washed twice with water to remove excess Ca^{2+}. The resulting "microgel concentrate" was redispersed in water. The moisture content of 0_{OIL}, 32_{OIL}, 52_{OIL}, 67_{OIL}, and 77_{OIL} microgel concentrate was 92.7, 89.5, 80.5, 78.3 and 71.8% (w/w) respectively. Due to difficulties in differentiating the volume of water bound to the microgels and water in the continuous phase, the volume fraction (ϕ) of the microgel concentrate was assumed to be 1. At $\phi = 1$, it was assumed that the microgel particles are packed tightly against each other with minimal interstitial space and no permanent deformation occurs. While this will result in a slight over- or underestimation of the exact volume fraction, this assumption allows microgels with slightly different shape and sizes to be compared (Hemar, Lebreton, Xu, & Day, 2011).

Water was added to the microgel concentrate to obtain emulsion filled microgel suspension with different volume fraction. The final volume fraction was determined using the equation below (Suzawa & Kaneda, 2010):

$$\phi = \frac{\frac{m}{\rho}}{\frac{m}{\rho} + v} \quad (1)$$

Where, ϕ = final microgel suspension volume fraction, m = mass of microgel concentrate, ρ = density of microgel concentrate, and v = volume of water added to microgel concentrate. ρ, the density of the microgel concentrate was measured with a 50 mL calibrated pycnometer. The suspension volume fractions remain the same as

Table 1
Sample formulation of sodium alginate-emulsion mixture solution prior to gelation. The sample names are given based on the concentration (% w/w) of oil (total solids basis).

Sample name	Sodium alginate total solution mass (% w/w)	Oil concentration total solution mass (% w/w)	Oil:solids ratio
0_{Oil}	2	0	–
32_{Oil}	2	1	0.5:1
52_{Oil}	2	2.5	1.1:1
67_{Oil}	2	5	2:1
77_{Oil}	2	10	3.3:1