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Droplet deformation and break-up under shear: Hydrocolloid solution vs. suspension of starch granules

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ABSTRACT

Shear induced deformation and rupture of two types of droplets, hydroxypropyl methylcellulose (HPMC) aqueous solution and modified waxy maize suspension, were studied and compared using a counter-rotating rheo-optical set-up. The motivation of the work was to explain the difference observed in flavour perception of food products thickened by these two fluids. A droplet of either fluid was placed into silicon oil and deformation and break-up were monitored as a function of applied shear stress and strain. It was found that starch suspension droplets broke up at lower deformation stress and strain than HPMC solution droplets despite viscosity ratio and capillary number suggesting the opposite. It is hypothesised that the ease with which droplets thickened by starch break-up is responsible for their rapid mixing with saliva.

1. Introduction

Starch and hydrocolloids are widely used as thickeners to vary the viscosity of food products. However, the introduction of these additives modifies the release of tastants which are sensed by the taste buds on the tongue. Numerous studies have been performed in order to understand the parameters influencing taste perception. In general perception depends on tastant type, concentration and its physico-chemical interactions with the thickening agents and the taste receptors in the mouth. It also depends on the properties of the thickening matrix itself and its behaviour under mastication, i.e., under mechanical stresses coupled with dilution due to saliva. The viscosity behaviour of the thickener influences diffusion and transport of tastants in the mouth.

It is now accepted that when a system is thickened with a polysaccharide solution, taste perception decreases when the polymer concentration is above the critical overlap concentration, C^* (see, for example, Baines & Morris, 1987; Cook, Hollowood, Linforth, & Taylor, 2002). For several hydrocolloids (for example, hydroxypropyl methylcellulose (HPMC), guar gum, λ-carrageenan) it was demonstrated that the Kokini oral shear stress can be used to predict sweetness and aroma perception (Cook, Hollowood, Linforth, & Taylor, 2003). For food gels, maximum sweetness intensity was shown to be closely correlated to its mechanical properties. In strong gels that do not easily break in the mouth, tastants will remain trapped and sweetness appreciation will be low (Bayarri, Rivas, Izquierdo, & Costell, 2007; Koliandris, Lee, Ferry, Hill, & Mitchell, 2008; Morris, 1994).

Process dynamics, i.e. kinetics of tastant release and mixing with saliva, also plays an important role in flavour perception (Bayarri et al., 2007; Dijksterhuis & Pigott, 2000). Recently it was shown that systems prepared with various thickeners at equivalent shear viscosity measured at 50 s^{-1} impart significant differences in taste perception. Starch thickened products suppressed tastant perception to a smaller extent than HPMC solution. The best mouthfeel and maximum perceived taste were obtained for starches which keep their granular integrity above their gelatinisation temperature (Ferry et al., 2006). It has been suggested that the mechanism responsible for the frequently reported reduction in taste perception as a result of an increase in hydrocolloid solution viscosity is restricted mixing with saliva above C^* (Baines & Morris, 1987). Chain entanglement limits tastant diffusion and slows convective mixing with saliva which is not the case for starch thickened systems which from a material science point of view represents a suspension (of granules) dispersed in a low viscosity medium phase (Ferry et al., 2006). The difference in microstructure of the fluids, polymeric solution vs. suspension, could explain very early studies reporting that the mouthfeel was less slimy with solutions thickened with granular starches than for solutions thickened with molecularly dissolved hydrocolloid (Mitchell et al., 2008; Szczesniak & Farkas, 1962).

In this work the break-up of droplets made of HPMC solutions and of starch granule suspensions are reported. This study was

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motivated by the thought that mixing efficiency is related to the ease with which droplets of fluid break-up. Rheo-optics was used to study droplet deformation and rupture as a function of shear stress and strain. In order to visualise the droplets silicon oil was used as a suspending matrix.

2. Materials and methods

2.1. Materials

A physically modified waxy maize starch (heat-moisture treatment), Novation 2600, was provided by National Starch, UK. It will be referred to as "starch" throughout the paper. This starch does not burst during gelatinisation, forming a well-defined suspension of soft swollen granules. Hydroxypropyl methylcellulose of the type K4M ($M_n = 90\,000$ g/mol) was supplied by Dow Chemical, UK.

To study shear induced droplet behaviour in the rheo-optical experiment, high viscosity polydimethylsiloxane (PDMS V 200 000, purchased from Rhodia) was used as suspending fluid. Its viscosity was 220 Pa s at 20 °C (see Results section) and it will be referred to as "PDMS 220" in the following. Silicon oil was chosen because it is transparent and inert towards the studied systems, and PDMS 220 is sufficiently viscous to generate stresses able to deform and break-up the droplets. For interfacial tension measurements, PDMS of a lower viscosity (0.1 Pa s, purchased from Sigma Aldrich, UK) was used.

2.2. Methods

2.2.1. Sample preparation

Starch suspensions were prepared by adding starch to water followed by heating the slurry until it reached gelatinisation temperature (73 ± 1 °C), the temperature at which the granules have lost their Maltese cross under polarized light as determined with an optical microscope (Desse, 2008). First, the average maximum swelling degree Q_{max} was determined using optical microscopy. Dry granules were placed in excess water and heated at their gelatinisation temperature for 30 min after which no further swelling of the granules occurred. The lengths of the dry (L_{dry}) granules and the swollen ($L_{swollen}$) granules were measured using image analysis software Ellix (Microvision, France). Maximum swelling degree was calculated as $Q_{max} = (L_{swollen}/L_{dry})^3$. Based on averaging data acquired for several hundred granules, a value of 12.5 ± 3.5 was found. The high deviation, about 25%, is due to heterogeneity of the granules in terms of their swelling ability. The values of Q_{max} obtained with optical microscopy were confirmed by separate measurements of the weight of dry and swollen granules. This was done by preparing the samples in excess water which was then removed by centrifugation (2700 g for 20 min).

Knowing Q_{max}, starch suspensions of two concentrations, both with granules swollen at maximum, were prepared. One was a dilute suspension of 1% w/w, with an approximate granule volume fraction of 13% (calculated as the product of Q_{max} and the concentration in weight percent). The other was a concentrated one, of 8% w/w, which corresponds to a theoretical granule volume fraction of 100%. Quantitative studies were only performed with concentrated suspension droplets as it was not possible to place a dilute suspension droplet with a well-defined starch volume fraction into the shear gap of the rheo-optical device. Results reported on dilute suspension droplets are of qualitative nature.

For the concentrated suspension with the theoretical volume fraction of 100% it could be expected that there should be no continuous liquid phase. However, the behaviour of the suspension revealed that the volume fraction was only close to 100% since, when a suspension droplet was immersed in the PDMS to conduct the rheo-optical experiments, the droplets were found to be of perfect spherical shape at rest (see Results section). Hence, it was concluded that a small fraction of continuous phase fluid was present. As shown in Desse, Ang, et al. (2009), this liquid was a dilute aqueous solution of a low molecular weight amylopectin. Thus, the 8% starch suspension used as the droplet fluid in the rheo-optical experiments can be described as an extremely closely-packed suspension of soft particles (swollen granules) in a very low viscosity aqueous medium.

This low viscosity aqueous solution was used for the determination of the interfacial tension between a starch droplet and PDMS. Since it was not possible to collect a sufficient amount of this liquid from the 8% w/w starch suspension even after severe centrifugation (2 h at 4000 g), a less concentrated starch suspension (6% w/w) was used instead. The 6% w/w starch suspension was centrifuged 15 min at 2700 g at 20 °C followed by recovery of the supernatant and disposal of the sediment. The supernatant was re-submitted to centrifugation for a further 20 min at 2700 g to ensure that there were no remaining starch granules. The recovered supernatant was used to measure its interfacial tension with the PDMS. This approach is valid since the amylopectin concentration in the supernatant was sufficiently low (<1% for the starch concentrations used, see Desse, Ang, et al. 2009) and the differences in amylopectin concentration observed were negligible when varying the initial starch concentration within a few percent.

HPMC solutions of 3.25 and 3.75% w/w were prepared by dispersing the polymer in water at 70 °C followed by continued stirring while the sample was allowed to cool. To prevent microbial bacteria growing, 0.05% of sodium azide was added to the HPMC solutions. The samples were then stored at 4 °C for two weeks to ensure full hydration.

2.2.2. Interfacial tension and density

The interfacial tension Γ between the droplet phase (3.25 and 3.75% HPMC solution or 6% starch suspension supernatant) and the suspending medium of the rheo-optical experiment, silicon oil, was measured at 20 °C with a pendant drop tensiometer (PAT-1, Sinterface, Germany). In order to avoid measurement problems caused by the high viscosity of silicon oil PDMS 220, a much lower viscosity silicon oil (0.1 Pa s) was used. This approach is valid as far as the interfacial tension does not depend on silicon oil viscosity (Bergeron et al., 1997). Interfacial tension between water and silicon oil was also determined. All results reported are equilibrium values calculated as the mean of 10 independent measurements.

The method used to obtain the interfacial tension requires the knowledge of the density of the two liquid phases. These were determined at 20 °C using a densitometer (DMA 5000, Anton Paar, Germany); the results are presented in Table 1. The error is less than 1%.

2.2.3. Rheology

Flow curves and first normal stress difference of the studied samples were obtained using a rotational rheometer (MCR 301, Anton Paar, Germany) with a cone and plate geometry (50 mm diameter, 1° cone angle). The shear stress was increased stepwise between 1 and 1000 Pa and steady-state data were acquired at each shear stress applied. For the starch suspension different geometries were tested in order to rule out slip (vane, plate/plate, cone/plate and roughened plate/plate), and only data acquired with the cone/plate configuration are shown in the following. As starch suspensions are known to be thixotropic, and this has previously been

Table 1
Density values for all components.

System	Water	0.1 Pa s PDMS	Starch supernatant	3.25% HPMC	3.75% HPMC
Density, kg/m^3	998.2	968.3	1027.9	1008.0	1011.1