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Microscale study of particle agglomeration in oil-based food suspensions: The effect of binding liquid

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ABSTRACT

In highly concentrated oil or fat-based suspensions, the addition of a secondary immiscible liquid binder results in the agglomeration of particles and formation of a spanning filling network. This network gives rise to a transition in the flow behavior of suspensions which can, in turn, be used to create tailored food products.

This agglomeration of particles is related to the formation of liquid bridges. The present work investigates this agglomeration process on a microscale. The effect of two binding liquids with different properties (viscosity, interfacial tension and wetting characteristics) on the adhesion of a particle and a flat surface inside oil medium is investigated. Forces due to water and anhydrous glycerol bridges between a spherical glass particle and a flat glass surface inside purified high oleic sunflower oil were measured with an atomic force microscope (AFM), using the colloidal probe technique. Dispersions of droplets of the secondary liquid (water, glycerol) in the continuous phase (oil) were prepared so that bridges between the particles and the glass surface could be created and force curves measured.

The measured forces were dominated by capillary attraction when a liquid of high interfacial tension and low viscosity such as water formed the liquid bridges. When a highly viscous liquid formed the bridge (glycerol), a dynamic viscous interaction contributed to the adhesion leading to a higher force, which was less dependent on the volume of the bridge.

1. Introduction

Wet agglomeration, or wet granulation, of powders refers to a particle size enlargement which occurs once individual primary particles adhere to each other due to the use of a liquid binder. This process has been extensively used to improve characteristics of powders such as flowability, handling and ease of use [1].

A similar concept to wet agglomeration can be applied to suspensions, where a liquid constitutes the continuous phase instead of air. The addition of small quantities of a secondary liquid to highly concentrated suspensions leads to the formation of a spanning network of particles connected by liquid bridges and a consequent change in the flow behavior of such samples [2–4].

Suspensions and pastes where oil or fat constitutes the continuous media are widely present in the food industry (e.g. peanut butter and other types of spreads). In such products, texture/flow behavior, stability and appearance are important attributes to the consumer. Therefore, the agglomeration of particles in suspensions by the addition of a secondary binding liquid could be used to match products with consumer needs, once the mechanisms and adhesion phenomena are understood. This agglomeration of particles triggered by the addition of a secondary binding liquid is related to the formation of liquid bridges between particles. Although static capillary forces have been widely studied theoretically and experimentally, the detailed study of liquid bridges by different immiscible binding liquids inside a viscous non-polar continuous phase such as vegetable oil has not been studied. The majority of studies have focused on liquid bridges with air as the continuous phase [5–10]. Some research into systems of particles in the presence of immiscible liquids has also been carried out [11–13]. One technique that has enabled the direct and experimental measurement of forces between micron-sized particles is atomic force microscopy (AFM) [14]. AFM has been used to measure normal capillary forces [9,15,16], and also the effect of relative humidity on these forces [17,18], in air. It has also been employed to study forces in liquids [19], forces between a particle and a bubble [20, 21] and adhesion of particles to thin liquid films [22]. Nevertheless, there is a lack in the experimental study and measurement of forces related to liquid bridges in an oil continuous phase.

The present work examines the effect of two binding liquids with different properties (viscosity, interfacial tension and wetting characteristics) on the adhesion between a particle and a flat surface using

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Table 1
Liquid properties (25 °C).

Liquid		Density, [kg/m^3][a]	Interfacial tension with HOSO, γ [mN/m][b]	Dynamic viscosity, η [mPa·s][c]	Contact angle with a glass surface inside HOSO, θ [°][b]
Continuous media	HOSO	919	–	65	–
Secondary liquids	Water	998	26	0.9	39
	Anhydrous glycerol	1250	17	840	64

[a] Density was measured with a liquid pycnometer.

[b] Measured using the drop method (pendant drop for interfacial tension, sessile drop for contact angle) with a goniometer (FTA125, First Ten Angstroms, United States).

[c] Viscosity was determined experimentally with a rotational rheometer (Kinexus, Malvern Instruments, UK) using the cone and plate system (4°/40 mm) and shear rate table ranging from 0.1 s^{-1} to 100 s^{-1}. All the three fluids showed Newtonian behavior.

colloidal probe AFM and discusses this effect in terms of the forces acting between them.

2. Materials & methods

A commercial atomic force microscope (NanoWizard III, JPK Instruments, Germany) was used to measure force curves between a spherical glass particle and a flat glass surface inside oil medium over separation distance. A glass particle and surface were used as model food materials due to their hydrophilic and also inert characteristics. A spherical soda–lime glass bead (Spheriglass®, code 20035, Potters Industries LLC, United Kingdom) was attached to the tip of an AFM cantilever (AppNano ACT-TL, nominal specifications: length 125 μm, thickness 4.5 μm, width 30 μm) using epoxi-glue. The particle attachment was performed using the AFM and its integrated inverted microscope. The cantilever spring constant and sensitivity were calibrated using the thermal noise method [23]. The NanoWizard III AFM has a thermal noise acquisition of up to 3.25 MHz; which enabled the calibration of the spring constant of the stiff cantilevers used with the thermal noise method (measured resonance frequency of 300–305 kHz). The measured sensitivities of the cantilevers used ranged from 13.9 to 15.7 nm/V and the spring constants were between 52.7 and 61 N/m. Both the glass particle and surface (soda–lime glass cover slip, 24 mm diameter, 0.20 mm thickness, Menzel-Glaser, Germany) were washed in absolute ethanol in an ultrasonic bath prior to use.

Purified high oleic sunflower oil (HOSO; Sofinol Specialty Oils, Switzerland) was used as the continuous medium. Commercially available oils, such as sunflower oil, may naturally contain certain amounts of minor components such as free fatty acids, phospholipids and tocopherols which may act as surfactants [24]. Therefore, the oil purification was aimed to reduce the effect of these surface-active agents on the interaction between particles. The purification process, based on the method described by Gaonkar [25] and Babin [26], consisted of dispersing 5–10% of activated magnesium silicate (Florisil®, 100–200 mesh Sigma-Aldrich, United Kingdom) in the HOSO under agitation for at least 30 min followed by filtration. Deionized water (Milli-Q) and anhydrous glycerol (Sigma-Aldrich, United Kingdom) were used as the secondary immiscible liquids. The properties of the liquids used are described in Table 1.

In order to measure the adhesion forces between glass surfaces due to the formation of liquid bridges of different liquids inside oil, one has to first create small droplets of the secondary (bridging) liquid inside the continuous phase. The height of these droplets (or droplet caps) on the glass surface should be smaller than the particle on the colloidal probe (Fig. 1) so that the cantilever would not sink in the secondary liquid. For this reason, a dispersion of secondary liquid droplets in oil was prepared. In order not to have an excessive number of droplets, a low concentration of secondary liquid was required. The liquid dispersions were prepared by thoroughly mixing the secondary liquid with purified high oleic sunflower oil at a concentration of 0.1% w/w with a homogenizer (L4R model, laboratory high-shear mixer, Silverson, UK) for 2 min at high speed (nominal speed of 2400 rpm).

Fig. 2 shows a schematic representation of how the AFM cycle measurements were conducted. After adding the liquid dispersion to the AFM liquid cell (BioCell, JPK Instruments, Germany), the system was left undisturbed for few minutes so that the droplets of the secondary liquid could settle on the lower glass surface. The colloidal probe (a glass sphere glued to a cantilever) was then positioned on top of one droplet and the force was measured on its approach, set point load force application and subsequent retraction from the surface. During this procedure, the vertical deflection of the cantilever was recorded versus the displacement in the vertical direction (normal to the surface). The force data could be obtained based on Hooke's law, i.e. by multiplying the deflection of the cantilever by its calibrated spring constant. The force curve was corrected according to the calibrated sensitivity of the cantilever. The approaching and retracting speed was kept constant at

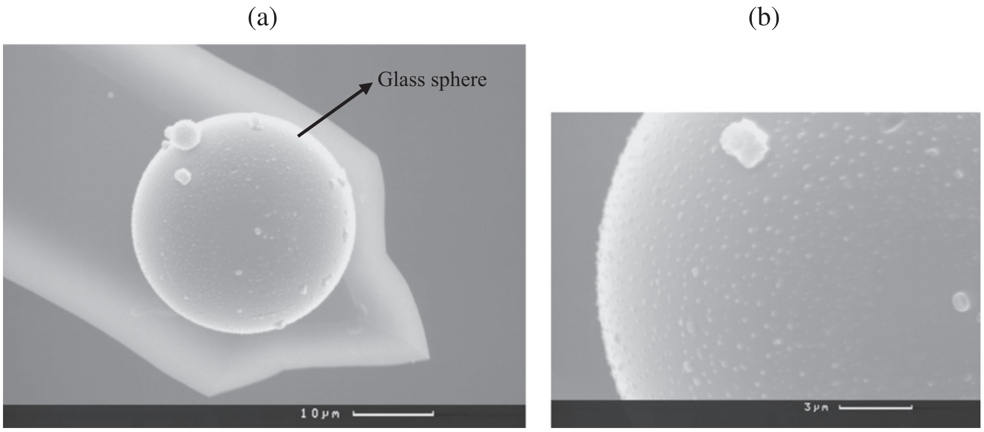

Fig. 1. Scanning electron micrograph (SEM) of an AFM colloidal probe: glass sphere (~28 μm diameter) glued to the tip of a cantilever (a) and detail of the glass sphere (b). The image was taken after the probe was used and cleaned with hexane and ethanol to remove excess oil. The SEM image was taken using the CamScan Mk. II SEM from the Sorby Centre for Electron Microscopy and Microanalysis from the University of Sheffield.