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Direct measurement of the interaction of model food emulsion droplets adhering by arrested coalescence

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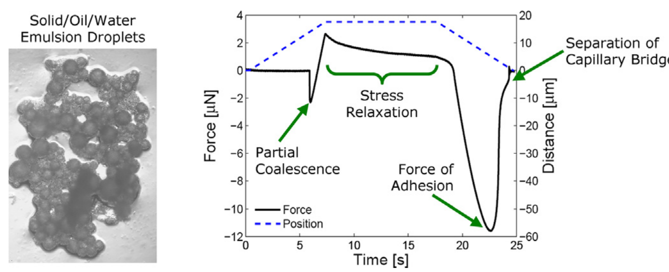
HIGHLIGHTS

- Individual solid-in-oil-in-water emulsion droplets are investigated.
- Forces of interaction are measured in new apparatus with nano-newton resolution.
- A capillary bridge is identified as the mechanism for adhesion of droplets.
- Rheological properties of the individual emulsion droplets are quantified *in situ*.

GRAPHICAL ABSTRACT



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ABSTRACT

A new instrument called a Cantilevered-Capillary Force Apparatus is used to characterize the interaction of two individual solid-in-oil-in-water (S/O/W) emulsion droplets. The droplets studied are intended to act as a model for understanding the physics of food emulsions and other similar suspensions of droplets. The formation of capillary bridges between emulsion droplets is identified as the physical mechanism for the adhesion of droplets with a high volume fraction of solid particles. This mechanism is supported quantitatively by direct measurements of the magnitude of the force required to separate the droplets. It is also demonstrated that some rheological properties of the individual emulsion droplets can be investigated *in situ*.

1. Introduction

Many emulsions, like milk and ice cream, as well as consumer products, like lotions and beauty creams, contain solid particles along with the immiscible fluid phases. The solid particles may be found in the aqueous phase, in the oil phase, and/or at the interface between the two phases. When the solid particles are surface active and, therefore, present at the interface, they form emulsions known as Pickering emulsions and have been widely studied [1]. When the solid particles are composed of fat, as is often the case in food emulsions, they tend to be found primarily within the oil phase. In the present work, the case of oil droplets dispersed in an aqueous solution is considered where the solid particles are completely wet by the oil (a solid-in-oil-in-water emulsion or S/O/W emulsion). In particular, S/O/W emulsions with a high volume fraction (>40%) of solids in the oil phase are investigated (see Fig. 1). This is different from many other studies involving S/O/W emulsions in which solid particles like fat crystals protrude from the drops [2].

The solid particles within the droplets in this type of emulsion can reduce phase separation of mixtures by preventing coalescence

Abbreviations: S/O/W, solid-in-oil-in-water; CCFA, Cantilevered-Capillary Force Apparatus.

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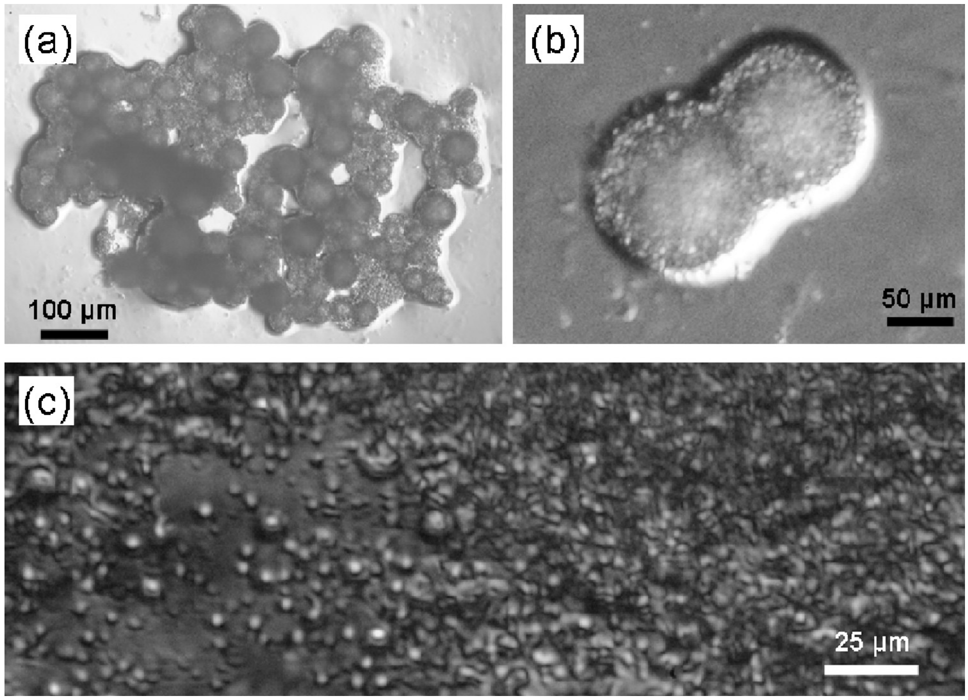

Fig. 1. Images of S/O/W emulsion taken using Hoffman modulation contrast microscopy. (a) Large aggregate of emulsion droplets. (b) Doublet of emulsion droplets. (c) Solid wax particles in hexadecane.

or arresting coalescence (also referred to as "partial coalescence" [2]) of the droplets. This may be desirable or undesirable depending on the final product of interest. In ice cream, for example, the S/O/W emulsion droplets help trap air bubbles that provide good texture and mouth feel [3]. Solid particles in waxy crude oil are normally problematic, because they can clog pipelines and reduce coalescence of oil droplets, making it more difficult to separate water from the crude prior to refining [4]. Even in the case of crude oil, however, the solid particles can be advantageous for other applications such as emulsion transport of gas hydrates [5]. Additional information about these materials can be found in the reviews by Rousseau [6] and Fredrick et al. [7].

Despite their prevalence and importance, S/O/W emulsions are very complicated systems and in need of more fundamental understanding. Current characterization methods are dominated by rheological measurements of bulk materials [4,5,8,9]. Only a few studies have also made investigations of individual S/O/W emulsion droplets in an effort to characterize these materials. Pawar et al. studied the resulting shape of two oil droplets in aqueous solution after arrested coalescence as a function of the volume fraction of wax crystals in the oil [10]. They find that when the volume fraction is large enough the droplets essentially "adhere" with little deformation allowing them to be used to form larger multi-particle structures such as doublets, rings, or chains in solution. Such structures can be useful for the formation of self-assembled materials from colloidal particles.

Tan et al. used a modified atomic force microscope combined with laser scanning confocal microscopy to measure mechanical properties of individual oil droplets coated with clay particles [11]. The droplets investigated by Tan et al. are more related to Pickering emulsions, but the technique suggests that force measurements on individual particles can be useful in characterizing these materials.

In this study a new instrument that is also capable of making force measurements called a Cantilevered-Capillary Force Apparatus (CCFA) [12] is used to investigate the interaction between two individual oil droplets containing a high volume fraction of solid wax particles in an aqueous solution. The CCFA can be used to directly measure the strength of the adhesive interaction between the droplets as well as interrogate some aspects of the rheology of the individual particles. The strength of the adhesive interaction will determine the stability of multi-particle superstructures that form intentionally or otherwise in the bulk S/O/W emulsion. This will, inevitably, be related to the bulk rheological properties of S/O/W emulsions and can be included in theoretical models [13].

2. Materials and methods

The S/O/W emulsion used in this work was prepared by Proctor & Gamble and shipped to the authors for study. The solid content of the droplets was made up of petroleum jelly (also known as petrolatum wax) which has a melting point range of 38–56 °C. A dispersion of 40 wt.% petrolatum wax in hexadecane was prepared by heating the materials to 70 °C to dissolve the wax and then mixing. The dispersion was then mixed manually with an aqueous solution containing ∼0.5 wt.% microfibrous cellulose and 20 mM sodium dodecyl sulfate at the same temperature. The purpose of the microfibrous cellulose is to give the suspending fluid a small yield stress (∼0.17 Pa) to prevent spontaneous creaming and aggregation of the droplets [12]. The resulting S/O/W emulsion was then allowed to cool to room temperature. Immediately after cooling, the solid wax particles in the drop fluid are typically crystalline rods with an aspect ratio (length/width) of around 10. After shipping and aging, however, the wax particles have changed in morphology to be approximately spherical as observed *via* Hoffman modulation contrast microscopy (shown in Fig. 1). Although it was not possible to fully capture *via* photographic images, direct microscopic observation of the structure of the droplets was used to verify that the oil phase completely wets the solid, wax phase.

As mentioned previously, a Cantilevered-Capillary Force Apparatus (CCFA) is used to measure the force of interaction between two individual S/O/W emulsion droplets. A full description of this instrument is presented in a previous paper [12]. In brief, the CCFA consists of two capillaries in which one of the capillaries is bent to a 90° angle near the tip to act as a force transducer (referred to as