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The role of emulsifier in stabilization of emulsions containing colloidal alumina particles

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ABSTRACT

This paper focuses on the study on rheological behaviour of emulsions, stabilized by both differently modified dispersible colloidal Boehmite alumina nanoparticles and a non-ionic emulsifier. Hysteresis loop measurements and dynamic rheological measurements were carried out in linear and non-linear regimes on two different emulsion systems – water-in-oil (W/O) and oil-in-water (O/W) emulsions.

Emulsion stabilized by a combination of moderately hydrophobic particles and a non-ionic emulsifier is an O/W emulsion. The addition of emulsifier improved the stability, however, did not show a significant influence on the emulsion flow behaviour. The emulsion, stabilized by both – nanoparticles and emulsifier – showed a complicated behaviour, i.e. sometimes it exhibited thixotropy or antithixotropy and sometimes both of them.

Emulsion stabilized by rather hydrophobic particles and a non-polar emulsifier is a W/O emulsion. The emulsion is very homogenous and exhibited very weak thixotropy. Dynamic measurements showed that G' was almost equal to G" and both parameters were frequency-dependent, indicating a viscous liquid-like system with little network structure if any. With addition of emulsifier, the rather elastic solid-like emulsion structure may be changed into the viscous liquid-like structure.

In order to get a better understanding of relationships between rheological behaviour and microstructure, differential scanning calorimetry (DSC) results and optical microscopic images of the emulsions studied were discussed.

1. Introduction

Many soft materials of immense commercial importance, such as tooth pastes, concentrated emulsions and suspensions, colloidal gels, industrials slurries, pharmaceutical and cosmetic creams and a variety of soft food items, i.e., mayonnaise, demonstrate a time-dependent evolution of visco-elastic properties strongly affected by a deformation field [1]. This behaviour is termed as thixotropy [2,3] and is associated with build-up of a structure in these complex fluids under quiescent conditions and break-up of the structure under a deformation field. In antithixotropy, the descending curve rheograms are positioned above the ascending curve rheograms. According to Ghannam [4], when a shear stress is applied to an emulsion, the flow started, viscosity decreased, and the rate of aggregates dissociation increased while shear rate increased. On the other hand, because of the effect of the thermal agitation and shear induced, the rate of the aggregates association is increased, which increases the emulsion viscosity. The antithixotropy indicates that shearing can promote temporary aggregation rather than breakdown due to the collision of the solid particles and droplets [3].

Particle-stabilized emulsions exhibit highly variable rheological behaviour useful in a wide range of technological applications. Currently, there is a lot of interest in using thixotropy to control spreading, film formation, coating of emulsions containing active ingredients [5]. In our previous study [6], rheological behaviour of two different water–oil emulsion systems stabilized solely by modified colloidal alumina at different storage time was investigated. Pickering emulsions stabilized by moderately hydrophobic particles (oil-in-water emulsion) exhibited an inhomogeneous structure, relative large yield stresses and thixotropic flow behaviour, indicating a formation of a three-dimensional network. Emulsion stabilized by rather hydrophobic particles with a water contact angle around 90° (oil-in-water-in-oil multiple emulsion) was homogenous and showed thixotropy indicated the presence of a three-dimensional network. However, a phase

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Table 1
Composition of emulsions.

Sample	Particle	H_2O (ml)	Oil (ml)	Emulsifier (g/100 ml)	Particle (g/100 ml)	Emulsion type
S1	OS1	70	30	1	1.5	O/W
ES1	–	70	30	1	–	W/O
CP1	OS1	40	60	1	2.5	O/W
CS1	OS1	70	30	–	1.5	O/W
S2	OS2	65	35	1	1.5	W/O
CP2	OS2	60	40	1	2.5	W/O

separation slightly occurred in the storage time of both type of emulsions over one year evaluated meaning that the stability needs to be improved.

In this study, emulsions were stabilized by differently modified colloidal Boehmite alumina nanoparticles and a non-ionic emulsifier at different water/oil ratios. Then, rheological experiments on two selected emulsion systems, having the higher stability, were carried out. Additionally, the differential scanning calorimetry (DSC) results and microscopic images of these emulsion systems are discussed in order to get a better understanding of the relationship among the rheology, microstructure and stability of the emulsion systems.

2. Materials and methods

2.1. Materials

Emulsions were prepared using deionized water, technical oil and particles. Two modified dispersible colloidal Boehmite alumina powders, manufactured by Sasol (Germany), were used in this study. The particles were modified by manufacturer with *p*-toluene sulfonic acid (OS1 particles) and alkylbenzene sulphonic acid (OS2 particles). OS1 particles are moderately hydrophobic and OS2 particles are hydrophobic with a water contact angle of about 60° and 90°, respectively. For further details see [7]. Technical oil (Mygliol 812N) for pharmaceuticals and cosmetics applications, supplied also by Sasol (Germany), was selected as an oil phase for the preparation of emulsions. A commercial emulsifier (Imwitor 600) which is an ester from polyglycerin and from plant-derived condensed castor oil fatty acids (Sasol, Germany) was used. The emulsifier having an average molecular weight larger than 3000 g/mol is polyethylene glycol-free substance with a low HLB number of about 4 and is suitable for all kinds of water-in-oil (W/O) emulsions.

2.2. Preparation of emulsions

Emulsions were prepared by mechanical agitation with a household mixer (Bosch MSM 6300, 600W) at full power. Two different processes of emulsion preparation can be distinguished as follows:

(i) Emulsions **S1** and **CP1** were stabilized by OS1 particles and emulsifier at different water–oil ratios: OS1 particles were pre-dispersed in deionized water using the mixer for 180 s at room temperature of 23 °C. The emulsions were prepared by slow addition of an oil/emulsifier mixture, preliminarily mixed under 3 min agitation, to the suspension under continuous stirring during 30 s. Thereafter, the agitation was maintained for further 150 s.Emulsions **CS1** and **ES1** were stabilized only by OS1 particles or only by the emulsifier, respectively, at the same water/oil ratio.
(ii) Emulsions **S2** and **CP2** were stabilized by OS2 particles and emulsifier: the hydrophobic OS2 particles were pre-dispersed in oil to form a suspension and then water was slowly added to the suspension. After mixing the particles and oil, an appropriate amount of the emulsifier was added to the suspension and the mixture was stirred for 3 min.

A brief recipe description for the preparation of the emulsions investigated is given in Table 1.

2.3. Rheological measurements

The rheological tests were carried out by means of a stress-controlled rheometer Physica MCR 301 (Anton Paar, Germany) equipped with a cone and a plate sensor. The cone angle is 1°, and the cone diameter is 50 mm with a gap of 0.052 mm. All measurements were performed at a constant temperature of 25 °C using 6 samples of each kind of emulsions. The sample was placed on the plate using disposable pipettes, and allowed to come to thermal equilibrium for 3 min before rheological experiment was made. Two different rheological experiments were performed.

First, measurements of hysteresis loop were used to observe the thixotropy behaviour of emulsions. The experiment was carried out in a three-part cycle: the shear rate was firstly steadily increased from 0 to 5 s^{-1}, subsequently kept constant at 5 s^{-1} and, finally, progressively decreased from 5 to 0 s^{-1} for 1 min, respectively. The flow curve containing shear rates and stresses was formed.

Second, dynamic shear measurements were made to test the visco-elastic response. The dynamic strain sweep for determination of the linear visco-elastic (LVE) region of the emulsions was carried out at a fixed frequency of 10 rad/s. Thereafter, a strain of 0.04% within the LVE region was selected for the dynamic frequency sweep measurements with the frequency range from 1 to 100 rad/s. The frequency-dependent curves of G' and G" were recorded.

2.4. Optical microscopy

Optical microscopic observation of the emulsions was done using a usual optical microscope. An appropriate amount of freshly prepared emulsion was placed onto the microscopic slide. A cover slip was placed on the sample by ensuring that no air or bubbles were trapped between the sample and cover slip and the samples were tested with a 10× objective.

2.5. Differential scanning calorimetry (DSC)

DSC measurements were performed with a Setaram TG-DSC 111 calorimeter [8]. The samples were placed in aluminium pans of cylindrical geometry 300 mm^3 in volume. The mass of the samples was weighed using a Mettler AE200 balance, and then the samples container was sealed by means of an upper cap. Then, the sample container was placed into the calorimeter to begin the experiment. The average mass employed in a typical cooling experiment ranged between 0.015 and 0.022 g. All the DSC measurements started at an initial temperature of 25 °C. The samples were first cooled down to −50 °C, then they were heated steadily up to 25 °C. The scanning of temperature was carried out at a constant rate of 2 °C min^{-1}. The energy changes were recorded by the software in the form of a heat flow rate signal as a function of time and temperature, i.e. thermogram [8]. By the use of DSC technique, it is in general possible to determine [9] thermodynamic properties of melting and solidification of pure compounds or emulsion components (temperatures