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Development and characterisation of a continuous phase based on a fumed silica and a green surfactant with emulsion applications

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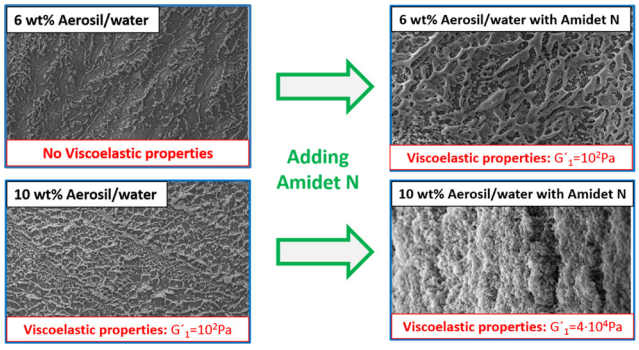
GRAPHICAL ABSTRACT



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ABSTRACT

Different ecological continuous phases were developed as a function of a green surfactant (Amidet N) and a fumed silica (Aerosil 200) concentration. The suitability of these systems was analysed by means of Small Amplitude Oscillatory Shear tests, flow curves, Cryo-SEM (Scanning Electron Microscopy) and the Multiple Light Scattering technique.

An important rheological change in viscoelastic and flow properties was detected from 8 wt% to 9 wt% for binary systems of Aerosil/water. This rheological change was related to the interaction of Aerosil chains, which was reflected through the Cryo-SEM. As a consequence of the microstructure and, therefore, rheological properties, an increase in the physical stability of the more concentrated systems was observed. The addition of Amidet N provoked an increase in viscoelastic properties related to the effective interaction between Aerosil chains. Finally, a stable lemongrass essential oil-in-water was developed. In this study, the role of Aerosil 200 as rheological modified and stabilizer has been studied. On top of that, the synergic rheological effect between this fumed silica and Amidet N has been proved.

1. Introduction

The microstructure of the continuous phase of an emulsion plays a very important role in, for example, reducing or inhibiting some destabilization mechanisms, such as creaming or coalescence [1,2]. The addition of thickeners to the continuous phase is one of the most common strategies used to improve their rheological properties and physical stability. These materials can act as structuring, thickening or

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gelling agents in the aqueous phase. Their influence on the physical stability of emulsions depends on their molecular characteristics, rheological properties and on their impact on bulk properties [3]. Polysaccharides, clays or oxide gels are the most common materials for the control of the rheology of the continuous phase.

The most used oxide gels are based on silica and can be divided into "fumed" and "precipitated" silicas. Fumed silica (e.g. Aerosil 200) are produced by the reaction of silicon tetrachloride($SiCl_4$) with steam [4]. Some aggregates linked by almost unbreakable bonds are irreversibly formed during the industrial fabrication of Aerosil 200 [5]. Siloxane bonds and isolated silanol groups compose the surface of fumed silica [6]. However, there is always an equilibrium existing between associated and dissociated silanols, i.e. SiO^- and SiOH [7]. Aerosil 200 is the most hydrophilic silica and is extraordinarily versatile; being used in rubbers, plastics, coatings, adhesives, cements, sealants and as a rheology modifier [5,8,9]. Its features include nano-size scale, chain-like structure and a high degree of water-absorption. Furthermore, the most interesting characteristic for its use in emulsions is its capacity to form chains and 3D gel networks with a yield value in water solutions due to the formation of weak hydrogen bonds [8]. These bonds are produced by the acid-base interaction between silanol groups and dissociated $Si-O^-$ groups [7]. In aqueous media, the influence of pH, ionic strength and particle concentration is relevant. Thus, an exhaustive control of these parameters must be considered. For instance, the double-layer repulsion is the predominant mechanism at pH = 7 and the abrupt increase in viscosity with particle concentration is due to the considerable repulsion between the particles. In contrast, this repulsion at pH 3 is not as significant as in pH 7 and the interaction takes place at higher concentrations [6]. In addition, it is well.known that silica particles show thickening and gelling properties. Its rheology is very sensitive to some additives such as electrolytes, polyvinyl alcohol (PVA) [6] and polyethylene glycols (PEG) [10]. Although Aerosil-200 suspensions have been relatively well-studied [6–8,11], relevant studies by means of Small Amplitude Oscillatory Shear (SAOS) tests, Cryo-SEM and Multiple Light Scattering have not yet been conducted at higher concentrations in the absence of salt at pH 7. This is expected to mimic the convectional conditions in the emulsion field.

AMIDET® N (HLB = 11), a green surfactant, is a low-viscosity ethoxylated fatty acid alkanolamide with a yellow liquid appearance. It is a vegetable oil mainly containing C18 unsaturated fatty acid from renewable European rapeseed oil. AMIDET® N shows good biodegradability and non-significant aquatic toxicity. In addition, it can be dispersed at room temperature. This emulsifier fulfils the new requirements of European environmental law and the principles of Green Engineering. Because of that, it has been used recently in "green" formulations [12].

The use of essential oils as dispersed phase in emulsions has attracted considerable attention lately since they come from natural resource and possess great functional properties. For example, lemongrass essential oil possesses important properties in cosmetic and medicinal field [13].

In this study, a new continuous phase with potential applications in emulsions has been developed step-by-step. The stability, viscoelastic behaviour and microstructure of Aerosil 200/Millipore water dispersions have been studied at pH 7 as a function of Aerosil concentration. Furthermore, the addition of Amidet N as a new eco-friendly surfactant to the dispersions has been explored for a further development of the continuous phase. Finally, the stabilizing role of Aerosil 200 has been proved by Multiple Light Scattering technique. This work demonstrates the suitability of Aerosil 200/Amidet N/water to tune rheological properties and to improve physical stability in emulsions.

2. Materials and methods

2.1. Materials

Aerosil 200 was supplied by EVONIK Industries (Germany) and used as received. These particles (12 nm diameter) have a specific surface area of 200 $m^2 g^{-1}$ and density of 2.2 g cm^{-3}. A non-ionic green surfactant (PEG-4 Rapeseedamide) was also used as emulsifier. Its trade name is Amidet N and it was received from KAO (Kao Corporation, Japan). All emulsions were prepared using ultrapure water in order to avoid added salt.

2.2. Suspensions preparation

The suspensions were solutions of ultrapure water and 6, 8, 9, 10 and 12 wt% of Aerosil 200. The green surfactant was added at 3 wt% to the 6 and 10 wt% Aerosil dispersion.

Continuous phases were prepared by mixing ultrapure water and Aerosil 200 using a magnetic stirrer at 600 rpm for 2 h. Then, systems were adjusted to pH 7 by adding NaOH. The slight change in volume caused by the addition of the small amount of NaOH was ignored. pH values were measured at room temperature using a basic pH meter (Hach 5050). Finally, the addition of the surfactant was carried out using a magnetic stirrer at 1000 rpm for 1 min.

2.3. Emulsion development

The dispersed phase (5 wt% Lemongrass essential oil) was added to the selected continuous phase using a Ultraturrax T50 (IKA, Staufen, Germany) for 90 s at 10,000 rpm.

2.4. Rheological measurements

Rheological tests were performed with a controlled-stress rheometer (Haake MARS, Thermo-Scientific, Germany). Suspensions studied were measured using a sandblasted double-cone geometry (angle: 0.017 rad; diameter: 60 mm) or serrated plate-plate geometry (60 mm) at 20 °C. Flow curves were carried out using a multi-step protocol (3 min per point). Stress sweeps were performed at a frequency of 6.20 rad/s for all Aerosil suspensions studied to estimate the linear viscoelastic range (LVR). Small Amplitude Oscillatory Shear (SAOS) tests were conducted from 20 rad/s to 0.05 rad/s at a stress within the Linear Viscoelastic Range. All the rheological measurements were carried out in triplicate with an equilibration time of 5 min.

2.5. Multiple light scattering

Physical stability of dispersions was studied and quantified using Multiple light scattering technique (Turbiscan Lab Expert). These measurements were carried out for 40–60 days at 20 °C. The following equation states the value of Turbiscan Stability Index (TSI):

$$TSI = \sum_j |scan_{ref}(h_j) - scan_i(h_j)| \quad (1)$$

where $scan_{ref}$ and $scan_i$ are the initial transmission value and the transmission value at a specific time respectively and h_j is a specific height in the measuring cell.

2.6. Cryo-scanning electronic microscopy (cryo-SEM)

The microstructure of dispersions was observed using a Cryo Scanning Electron microscope (Zeiss EVO) at 8–10 kV. Samples were prepared following the required protocol consisting of plunging into nitrogen slush. Subsequently, frozen samples were etched and coated with gold. Finally, the samples were kept at −120 °C for observation.

3. Results and discussion

3.1. Suspension characterisation

Fig. 1 shows the critical stress at 1 Hz for the onset of the Linear