



Oil-in-water Pickering emulsions stabilized by phyllosilicates at high solid content



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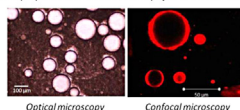
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HIGHLIGHTS

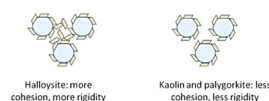
- Pickering emulsions are stabilized with phyllosilicates at high solid content.
- Rheological measurements in steady state and oscillatory modes are compared.
- Rheological properties of emulsions are strongly controlled by the initial suspension.
- The rheological behavior depends on particle surface interactions and particle shape.
- Halloysite leads to the highest rigidity, and palygorskite to the lowest.

GRAPHICAL ABSTRACT

Pickering emulsions were prepared with three different phyllosilicates: kaolin, halloysite, palygorskite



Rheological behavior depends on particle-particle interactions



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ABSTRACT

The present study aims at investigating the preparation and characterization of oil-in-water (O/W) Pickering emulsions stabilized using three different phyllosilicates: kaolin, halloysite, and palygorskite, and at high solid content (15 wt.% in the aqueous phase). Stable O/W emulsions could be obtained with no additional surfactant or surface treatment. The maximal oil fraction that could be introduced without phase separation was determined. The resulting oil/water ratios of 0.32, 0.44 and 0.60 were found for kaolin, halloysite and palygorskite, respectively. The O/W character of the three emulsions was confirmed by a simple “droplet test” and by confocal microscopy, which confirmed the positioning of the clay particles at the oil/water interface. These three phyllosilicates led to a limited coalescence mechanism that promoted the long-term stability of the Pickering emulsions. The rheological behavior of these emulsions was studied and showed that halloysite led to a more rigid structure. This trend could be justified by the formation of a strong network of clay particles due to strong surface interactions combined with an elongated particle shape.

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1. Introduction

Emulsions are used in many different fields, such as cosmetics, paints, food industry, or coal treatments. The mixing of two immiscible fluids to obtain oil-in-water (O/W) or water-in-oil

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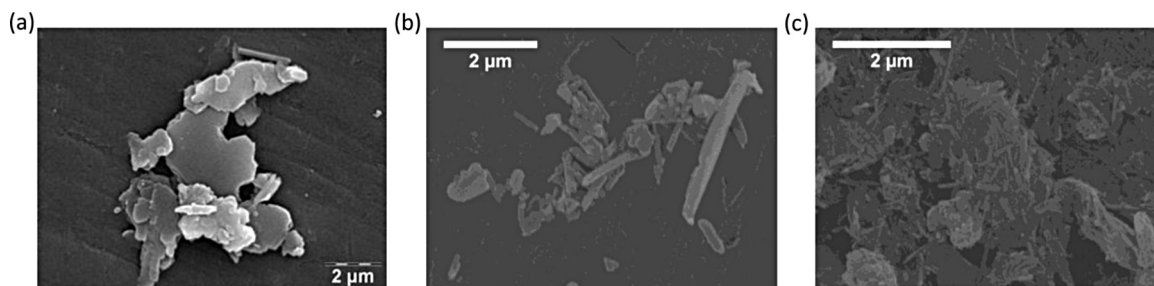


Fig. 1. High-resolution SEM micrographs of clays: (a) kaolin BIP, (b) halloysite, and (c) palygorskite.

(W/O) emulsions is thermodynamically unstable. The long-term life of emulsions required for these industrial applications is generally achieved by a proper use of organic materials, such as low molecular weight surfactants, or surface active polymers [1].

The development of solid-stabilized emulsions, also called Pickering emulsions, has been known since the beginning of the last century, with primary works attributed to Ramsden [2] and Pickering [3]. However a growing interest for this type of emulsions has emerged in recent years [4] supported by a better insight into the mechanisms that governs the size distribution and the stability of these emulsions [5].

The first mechanism considers that solid particles are adsorbed at the oil–water interface to form a particle monolayer acting as a rigid film and providing a mechanical barrier to coalescence [6,7]. The particle attachment at the oil–water interface is non-reversible, leading to a more efficient stabilization than surfactant adsorption. This mechanism was extensively supported by a theoretical approach and thermodynamic calculations, which can be found in very well-detailed publications [8–10]. The type of emulsion (O/W or W/O) is determined by the particle wettability at the oil–water interface: the less wetted liquid becomes the dispersed phase [11]. The contact angle (θ) of the particles with the aqueous phase will lead to O/W emulsion if $\theta < 90^\circ$ (e.g. silica, clay), and to W/O if $\theta > 90^\circ$ (e.g. carbon black). However if the particles are either too hydrophilic or too hydrophobic, they may remain in either the aqueous or oil phase, and thus may not be able to act as an emulsion stabilizer. Therefore several methods were investigated to modify particle hydrophilicity. For example, silica could be rendered partially or completely hydrophobic by an appropriate treatment with dichloromethylsilane, leading to a controlled amount of hydrophobic groups attached at their surface, that controls the contact angle [12,13]. Some other studies report some methods for particle surface modification through the adsorption of organic surfactants or amphiphiles, like propionic acid for alumina, hexyl gallate for silica, and octyl gallate for iron oxide [14], or CTAB (cetyl trimethylammonium bromide) for silica, bentonite or kaolin [15].

The second mechanism that governs Pickering emulsion stabilization is based on particle–particle interactions leading to the formation of a three-dimensional network of particles in the continuous phase. An enhanced stability is obtained through the increase of viscosity. This has been observed particularly in clay-based systems [16,17].

The term of clay actually covers a long list of materials, with different chemical compositions, structures, sizes and morphologies. They are characterized by a layered structure built by sheets of Si–O tetrahedra (tetrahedral silica sheets), alternating with aluminum- or magnesium-oxygen-hydroxyl octahedra sheets (octahedral alumina or magnesia sheets) or some other types of polyhedra of cations such as Fe^{2+} , Mg^{2+} , Al^{3+} , and Fe^{3+} with higher coordination numbers. Sharing 3 of the 4 oxygen atoms in the silica sheets with alumina sheets results in several layer types, such as: 1:1 layer type kaolinite formed of one tetrahedral sheet linked to an octahedral one by apical oxygen, 2:1 layer type montmorillonite in which

an octahedral sheet shares oxygen atoms with two silica sheets [18–20].

Clays are mostly natural silicate minerals, they are readily available cheap resources, and thus their use is considered with great interest from both economic and environmental considerations in new chemical processes. There is currently a growing interest for clays in the colloid science community, as their colloidal sizes, their anisotropy and their surface chemistry make them good candidates for the development of new colloidal processes.

Some reports have mentioned the use of clays such as montmorillonite [21], mica [22], hectorite and bentonite [16,17], or laponite [23] (a synthetic clay) in Pickering emulsions, where the content of solid particles is always relatively low (less than 5 wt.%). Moreover they are mostly used in combination with surfactants, or their surface is modified through a chemical treatment. In the present work, the formulation and properties of emulsions stabilized by natural non-modified phyllosilicates at a higher solid content (15 wt.%) were investigated. Three different phyllosilicates were studied: kaolin, halloysite, and palygorskite, which are different in their structure and morphology. Kaolin is a well known and commonly used platy clay, which serves as a reference clay. Halloysite is chemically similar to kaolin, from the family of 1:1 type phyllosilicates, but its sheets are rolled into tubes. Palygorskite (also called attapulgite) is characterized by a 2:1 structure with continuous two-dimensional fibrous-like tetrahedral sheets together with discontinuous octahedral sheets [24,25]. Therefore the structure of palygorskite exhibits ribbons with periodic inversion and the terminal octahedral cations complete their coordination sphere with water molecules (coordinated-water). The use of this fibrous clay is relevant to its specific structure and its large use for pharmaceutical and oil depollution purposes [26,27]. The aim of this article is to exploit these natural inorganic particles to stabilize oil-in-water emulsions, and study their influence on the emulsion properties, namely stability, size, and rheological behavior.

2. Experimental methods

2.1. Solid phase: phyllosilicates

Three types of clays were used as solid-stabilizers: halloysite (Imerys), kaolin BIP (Kaolin de Beauvoir, France), and palygorskite (Hangzhou Dayangchem Co. Ltd., China). The morphology and sizes of these particles are illustrated in Fig. 1 by SEM micrographs. Kaolin BIP is mainly composed of kaolinite, a 1/1 type phyllosilicate (stacks of several sheets that consist of alternating tetrahedral (T) and octahedral (O) layers). It consists of platelets of a few micrometers in size. Halloysite is similar to kaolinite in terms of structure and contains additional physisorbed-water, however halloysite presents a tubular morphology and finer primary particle sizes ($< 1 \mu\text{m}$). Palygorskite is a 2/1 type phyllosilicate (needles/tubes made of several sheets that contain alternating T–O–T layers), with a needle-like structure ($\sim 100 \text{ nm}$ of diameter, a few micrometers in length).

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