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Octadecenylsuccinic anhydride pickering emulsion stabilized by γ-methacryloxy propyl trimethoxysilane grafted montmorillonite

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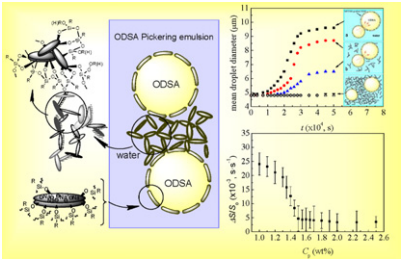
HIGHLIGHTS

- The ODSA emulsions were prepared by γ-MPTMS-grafted montmorillonite.
- The critical pH value for phase separation of the ODSA emulsions is 7.
- Effective particle films and particle network were formed at C_p 1.5 wt%.
- The lifespan and hydrolysis resistance of ODSA were improved.

GRAPHICAL ABSTRACT



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ABSTRACT

Octadecenylsuccinic anhydride (ODSA) is an internal sizing agent used to hydrophobize paper and paper board in the process of papermaking. To prepare stable ODSA Pickering emulsions, montmorillonite clay-particles modified by γ-methacryloxy propyl trimethoxysilane (γ-MPTMS) were used as particulate emulsifiers of ODSA and water at room temperature. The effects of pH value, oil-to-water ratio, and particle concentration on the stability of the Pickering emulsions were investigated. The stability of ODSA emulsions in the presence of grafted-MMT first increased and then decreased as the pH value of the aqueous phase decreased. The critical pH for the phase separation of the ODSA emulsions was ~7. Addition of ODSA oil induced phase inversion from an O/W emulsion to a W/O emulsion when the ratio of oil-to-water passed a specific threshold of 3:1 ($C_p \sim 1.5$ wt%). The particle concentration was linked to the formation of particle films at oil–water interface and of clay particle networks in water phase. The ODSA emulsions stabilized by grafted-MMT could have good sizing performance and lifespan. This study on ODSA Pickering emulsions based on MPTMS-grafted MMT particles opens up a new route to the preparation of a variety of paper sizing agents in the papermaking industry.

1. Introduction

Emulsions stabilized by solid particles instead of surfactants are often referred to as Pickering emulsions [1,2]. They have drawn increasing interest because of their extensive application in oil recovery, food preparation, and pharmaceutical formulations [3–6]. Solid particles as emulsion stabilizers are known for their irreversible adsorption, low toxicity, and low cost [3,4,7,8].

Clay is available either as a natural or a synthetic product. Natural clay is known under different names like montmorillonite and saponite. Montmorillonite (MMT) clay platelets can be exfoliated in aqueous solution to create single thin sheets that are 50–100 nm in diameter and 1 nm in thickness. MMT clay platelets are interesting compounds used in a wide range of applications [9–11]. Because of their large specific surface area of about 1000 $m^2 g^{-1}$, MMT particles can adsorb any manifold weight as their own weight and can therefore be used as adsorbers of many waste products [12–14]. However, the strong hydrophility of MMT particles causes clay to remain in the aqueous phase and makes it unstable on the interface. Surface modification is therefore necessary to obtain amphipathic clay particles to stabilize stable Pickering

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emulsions. Studies in recent years have focused on polymer–clay nanocomposites and the exchange of cations in clay galleries with long-chain aliphatic quaternary ammonium or phosphonium compounds [15–19]. Another method to form hydrophobic clay uses trialkoxysilanes as silicon source during clay synthesis [20,21]. Possible modification could occur because of the reaction of the silanol groups, which are assumed to be on the edge of the clay sheets [22]. The method uses chloro or alkoxy silanes and causes a reaction that presumably involves edge SiOH groups. Clay particles combined with surfactants can be made hydrophobic, and these hydrophobic clay particles can be dispersed in hydrocarbons [23]. When mixed with non-ionic surfactants, clay can also be used to prepare Pickering emulsions [24].

Paper sizing is a chemical and hydrophobic treatment applied to cellulose fiber surface. The process aims to reduce the penetration rate of aqueous liquid into paper. A popular alkaline paper sizing agent, octadecenylsuccinic anhydride can provide adequate sizing at different degrees by reacting with the hydroxyl groups in the polysaccharide components of the paper substrate; this reaction is facilitated by the high chemical reactivity of anhydride [25,26]. However, ODSA is introduced into the paper in the form of an aqueous emulsion, which could induce the hydrolysing between the hydrophilic group 5-membered lactone ring and water molecules. The hydrolysis reaction becomes a critical factor that determines the longevity and sizing performance of ODSA when the emulsion storage time is about 60 min at room temperature; the hydrolysates can also significantly affect papermaking [27]. Furthermore, alcohol, carboxylic compounds, and ammonia compounds are not fit for ODSA emulsions because hydrolysis, alcoholysis, and ammonolysis cause ODSA to deteriorate and lose its sizing performance. Cationic starch and cationic polyacrylamide, or a mixture of the two with a little amount of surfactant, are commonly used to emulsify ODSA. The resulting ODSA emulsions are used immediately after emulsification.Because of the gelatinization and cooling of starch as well as the negative effects caused by organic surfactants in paper sizing, ODSA emulsification is considered complex, difficult to control, costly, and harmful to the environment.

To the best of our knowledge, only a few studies have been conducted on the application of particulate emulsifiers in the preparation of paper sizing agents. Laponite clay particles modified by short amines were recently used to prepare highly stable partly hydrolyzed alkenyl succinic anhydride emulsions; these emulsions demonstrate good sizing performance but poor hydrolysis resistance so that they lose their sizing capability through hydrolysis within approximately 1 h [28]. To prepare stable ODSA emulsions, we systematically investigated MPTMS-grafted MMT particles as stabilizers of ODSA Pickering emulsions. We analyzed the effects of pH value, oil–water volume ratio, and particle concentration on the stability of ODSA emulsions. The stability of these emulsions during hydrolysis was also examined from the calculated paper sizing degree. This study aims to explore whether a stable ODSA Pickering emulsion with good sizing performance can be prepared by modified clay particles. Our research suggests a possible method to prepare a variety of paper sizing agents in the papermaking industry.

2. Materials and methods

2.1. Materials

Na-montmorillonite, a disc-shaped crystal with a thickness of 1 nm and a diameter of 50–100 nm, was provided by Zhejiang Sanding Technology Co., Ltd. The trifunctional silylating agent (γ-MPTMS, $C_{10}H_{20}O_5Si$) from Jiangsu Chenguang Coincident Dose Co., Ltd. was used without further purification. ODSA was obtained from Dixie Chemical Co., Inc., USA. It is a mixture of hexadecenyl succinic anhydride (3%), octadecenyl succinic anhydride, and their hydrolyzed products (0.5–1%). The bleached softwood pulp was provided by Dongguan Chang'an Changzhong Papermaking Co., Ltd. Cationic polyacrylamide with a molecular weight of 8 million is a commercial product of Ciba Specialty Chemicals Ltd. Ultrapure water of resistivity 18.2 M Ω cm was obtained from a Milli-Q academic water system connected to an ELGA reverse osmosis unit. All other chemicals used are analytical reagents.

2.2. Experimental methods

2.2.1. Modification and characterization of MMT

The modification reaction between raw nano-MMT clay particle and γ-MPTMS was conducted in toluene. The MMT particle (10 g) was first suspended in toluene (250 mL), and then γ-MPTMS (9 g) was mixed into the reaction flask and stirred for 8 h at 70 °C. The functionalized MMT particle was extensively washed with toluene or absolute ethyl alcohol to remove the excess silane, and then the particle was dried at 65 °C in a vacuum oven.

The infrared spectra of MMT powder were recorded with a Magna560E.S.P Nicolet FT-IR with a 4 cm^{-1} resolution ratio and a scan range of 500–4000 cm^{-1}. The static contact angle of the MMT particles was measured by an OCA40 micro contact angle measuring instrument (Dataphysics, Germany). The three-phase contact angle θ_{ow} of the MMT particle was measured with traditional particle-platelet method [29]. The solid particles were laminated onto 2 mm-thick circular chips by an HY-12 tablet machine before measurement. The morphology of the MMT particlewas observed from scanning electron microscopy (SEM) images with a Hitachi S-3700N field emission electron microscope. The particle size distribution was determined by dynamic light scattering (DLS) measurement with a Nano-ZS Zetasizer (Malvern, U.K.) at a 178° scattering angle with a He–Ne laser (λ = 633 nm) set at 298 K. The cell was washed with distilled water to prevent cross contamination before and after each measurement. The temperature of the laboratory was kept at 25 ± 2.5 °C during all the experiments.

2.2.2. Preparation of the ODSA emulsion

Aqueous suspensions of raw MMT particles and γ-MPTMS-grafted MMT particles were prepared by dispersing different particle concentrations of the corresponding MMT in deionized water and stirring for 10 min at a stirring speed of 3000 rpm. The pH value of the particle suspensions was modified with 0.1 mol L^{-1} dilute hydrochloric acid solution. The pH was monitored at room temperature with a pH meter (BS14-PH60, Midwest) equipped with a pH electrode (M307543). The resulting dispersion was used in water phase and added to the ODSA in oil phase. Then the mixture was homogenized at 6000 rpm for 5 min with an FM200 high-speed shear dispersing emulsifier (FLUKO Equipment Shanghai Co. Ltd.).

2.2.3. Stability of the emulsions

The stabilities of the ODSA emulsions during coalescence and creaming were evaluated by the volume of resolved oil, ν_o, and resolved water, ν_w, which is defined as the ratio of the resolved phase volume to the corresponding initial phase volume.

2.2.4. Types of emulsions

Generally, the conductivity of the emulsion is mainly determined by that of the continuous phase. The ODSA oil used in this study has a conductivity less than 0.1 μS cm^{-1}, and aqueous dispersions of MPTMS-grafted nanoparticles have a conductivity of 453 μS cm^{-1}. If the conductivity is above 100 μS cm^{-1}, the emulsion type is O/W, and if the conductivity is below 0.1 μS cm^{-1}, the emulsion type is W/O.