Dodecenylsuccinic Anhydride Pickering Emulsion Stabilized by Montmorillonite Nanoparticles Modified with Sodium Fluoride

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Processing convenience and paper-sizing flexibility frequently require the delivery of alkenylsuccinic anhydride oil as emulsion. The shelf life of the oil is achieved kinetically, in most cases *via* the addition of surfactants such as cationic starch or a synthetic polymer, which are the subject of increasing scrutiny with regard to their environmental impact. The modification of montmorillonite nanoparticle with sodium fluoride was found to decrease the interfacial tension between dodecenylsuccinic anhydride (DDSA) and aqueous dispersion and to change the wettability of montmorillonite, which benefits the preparation of DDSA-in-water emulsions with enhanced stability, small droplet size, and improved hydrolysis resistance. Adjusting the pH and particle concentration of aqueous solution effectively improved the stability of DDSA emulsion. Catastrophic phase inversion from w/o (water-in-oil) to o/w (oil-in-water) was investigated by monitoring the variation of emulsion conductivity with increasing oil volume fraction. Evidence of the transition from loose particle-film to compact particle shell upon introduction of salt was found, as predicted theoretically for charged particles adsorbed on interfaces. Particulate interfacial films built by SFMMT nanoparticles protected DDSA droplets from aggregation and formed a honeycomb structure. Salt in the DDSA emulsification process restrained the hydrolytic action of DDSA effectively and sustained the sizing performance of DDSA even 5 h after the emulsion preparation.

Keywords: Pickering emulsion; Montmorillonite; Dodecenylsuccinic anhydride; Interface; Paper sizing

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INTRODUCTION

Paper sizing is a hydrophobic chemical treatment applied to the cellulose fiber surface. The process aims to reduce the penetration rate of aqueous liquid into paper. Alkenylssuccinic anhydride is a reactive paper sizing agent used to hydrophobize paper and paper board in the process of papermaking with the aim to reduce the penetration rate of aqueous liquid into paper (Isogai and Morimoto 2004; Lee *et al.* 2004; Gess and Rende 2005; Hubbe 2007; Mohit *et al.* 2007). Dodecenylsuccinic anhydride contains one long hydrocarbon chain, R, which is attached to a 5-membered ring (Fig. 1). As a popular alkaline paper sizing agent, DDSA can provide adequate sizing at different degrees through the reaction of anhydride with the hydroxyl groups in the polysaccharide components of the paper substrate (Mohit *et al.* 2007). However, the high chemical reactivity of DDSA also promotes its rapid hydrolysis in aqueous system to form the hydrolyzate of DDSA (DDSA-acid; Fig. 1) which is detrimental to paper sizing and machine runnability (Hodgson 1994; Nishiyama *et al.* 1996; Isogai 2000; Ding *et al.* 2011). The common alkenylsuccinic anhydride (ASA) emulsifiers are cationic starch, cationic polyacrylamide, or a mixture of the two with a small amount of surfactant (Gess and Rende 2005; Hubbe 2007).

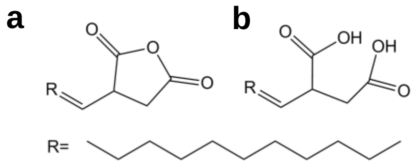

Fig. 1. Molecular structure of (a) dodecenylsuccinic anhydride and (b) dodecenylsuccinic anhydride acid

Emulsions stabilized by solid particles instead of surfactants are often referred to as Pickering emulsions (Binks 2002; Tcholakova *et al.* 2008). Their “surfactant-free” character makes them attractive for cosmetic and pharmaceutical applications because classical emulsions with surfactants often show adverse effects such as irritancy and bubbling behavior. Thus, environmental-friendly, economical, and degradable Pickering emulsions would provide an obvious benefit over the current technology (Simovic and Prestidge 2007; Frelichowska *et al.* 2009; Dickinson 2010). A variety of effective and stable ASA Pickering emulsions with a size smaller than 5 μm have been prepared by Ding and Qian (Ding *et al.* 2011; Qian *et al.* 2013). Since the hydrolysis of ASA is alkaline-catalyzed, alkaline emulsifiers would promote the hydrolysis of ASA, resulting in significant loss of sizing effect after the emulsification. Therefore, it is necessary to develop neutral particulate stabilizers in order to reduce the hydrolysis of ASA.

Clay particles as layered silicates have a thickness of 1 to 2 nm and a width in the submicrometer to micrometer range for montmorillonite (MMT). As a type of anionic clay particle, MMT nanoparticles are composed of rigid disk-shaped crystals with a well defined thickness of 1 nm and an average diameter of about 25 to 50 nm. Each platelet has a central layer made of Mg^{2+} cations in octahedral coordination to oxygen atoms or hydroxyl groups and the central layer is sandwiched between two silicate layers where the silica atoms are in tetrahedral coordination to oxygen atoms. Some of the Mg^{2+} sites of the central layer are substituted with Na^+ cations, creating a charge imbalance which is compensated by Na^+ counter ions located at the surface of the outer layers. These platelet-like nanoparticles have been extensively studied in the past years as filler materials for the formation of polymer-clay nanocomposites, which combine beneficial properties of both materials including low density, flexibility, good moldability, high strength, heat stability, and chemical resistance (Vaia *et al.* 1999; Alexandre and Dubois 2000; Hasegawa *et al.* 2005).

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. The stabilization of DDSA emulsions composed of polar liquids other than water requires quite exotic surfactants or polymers (Klapper *et al.* 2008). In the current study, we investigated whether DDSA emulsion could be stabilized by sodium fluoride modified montmorillonite (SFMMT) nanoparticles alone through systematically adjusting the pH, particle concentration, and charge of system. The goal of this study is to formulate DDSA emulsions in surfactant-free emulsion and to demonstrate their stabilities and paper sizing performances.

EXPERIMENTAL

Materials

Calcium montmorillonite, a disc-shaped crystal nanoparticle with a thickness of 1 nm and a diameter of 25 to 40 nm, was supplied by Zhejiang Sanding Technology Co., Ltd. (China) as a white powder. The oil phase was DDSA (Dixie Chemical Co., Inc., USA) with purity greater than 99%. The structure is shown in Fig. 1. Bleached softwood pulp was supplied as pulp board by Guangzhou Paper Group Ltd. (China). After being shredded and immersed in tap water overnight, the bleached softwood pulp was first disintegrated for 60 min at a concentration of 20 g/L in ultrapure water and then beaten to 43 °SR with a laboratory valley beater. The ultrapure water was purified by passing through an Elgastat Prima reverse osmosis unit (UK) followed by a Milli-Q reagent water system. Its surface tension was 71.5 mN m^{-1} at 25 °C, which was in good agreement with the accepted literature value. All other chemicals used were analytical reagents. All chemicals were used as received without further purification, and all solutions and dispersions were prepared using Milli-Q water.

Methods

Preparation and characterization of SFMMT nanoparticles

The montmorillonite nanoparticles (10 g) were first dispersed in Milli-Q water (50 mL) at 25 °C and then stored for 24 h to make the MMT completely swollen. Following this, sodium fluoride solution (50 mL, 10% w/w) was mixed with MMT dispersion into the reaction flask and stirred for 8 h at 85 °C to obtain the SFMMT nanoparticles. The SFMMT nanoparticles were extensively washed with deionized water to remove the excess sodium fluoride and then dried at 65 °C in a vacuum oven. The static contact angle of the SFMMT was measured by means of an OCA40 micro contact angle measuring instrument (Dataphysics, Germany). The three-phase contact angle, θ_{ow}, of the particle was measured with the traditional particle-platelet method (Li *et al.* 1993). The solid particles were laminated onto 2 mm-thick circular chips by use of an HY-12 tablet machine (Tianjin Xintian Potical Analytical Instruments Co., Ltd., China) before measurement. The SFMMT particles were imaged using a JEM-2100F high resolution transmission electron microscope (JEOL, Japan) to characterize their morphology. The surface and interfacial tensions of SFMMT aqueous dispersion were determined by an automatic surface/interface JWY-200 tensiometer (Chengde Dingsheng tester, China) at 25 °C.

Preparation and characterization of the DDSA emulsion

All emulsions were made by homogenizing the mixtures of aqueous nanoparticle dispersions and DDSA oil using a FM200 high shear dispersing emulsifier (FLUKO Equipment Shanghai Co. Ltd., China) with a 1.5 cm head operating at 6000 rpm for 2 to 6 min. The pH of the aqueous phase was adjusted to around 7. The pH was monitored at room temperature with a BS14-PH60pH meter (Midwest, USA). The emulsion droplet size distribution was determined by dynamic light scattering measurement with a Nano-ZS Zetasizer (Malvern, U.K.) at a 178° scattering angle using a He-Ne laser (λ= 633 nm) set at 25 °C. 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. The stabilities of the DDSA emulsions to coalescence (separate with oil phase) and cream (separate with water phase) were evaluated based on the volumes of resolved oil, v_o, and resolved water, v_w, which are used to define the ratio of the resolved phase volume to the corresponding initial phase volume. Generally, the conductivity of the emulsion was determined by that of the continuous phase. The DDSA oil used in this study had a conductivity of less than 0.2 μS cm^{-1}, and aqueous dispersions of MMT nano-platelets had a conductivity of 422 μS cm^{-1}. If the conductivity was above 10 μS cm^{-1}, the emulsion type was o/w (oil-in-water); if the conductivity was below 0.1 μS cm^{-1}, the emulsion type was w/o (water-in-oil).

The morphology of the as-prepared DDSA emulsion droplets was analyzed with an Olympus BX51 optical microscope (Olympus Corp., Japan). The emulsion samples were diluted with deionized water and were then covered with cover slips placed directly onto microscope slides. The emulsion drops appeared clear under the microscope. Microscopic image analysis software (Olympus Stream v1.0, Olympus, Japan) was used to capture the digital images and calculate the mean droplets size. The emulsions were also visualized by a FV1000 confocal fluorescence microscopy (Olympus Corp., Japan). The DDSA emulsions were labeled with Rhodamine B (Sigma-Aldrich, USA, ~10^{-5}mol/L) and excited at a wavelength of 514 nm, while the fluorescence emission was obtained in a wavelength range of 550 to 650 nm. Rheological experiments of emulsions were performed on an advanced rheometric expansion system (TA Instruments, USA) under the modes of steady shear flow and dynamic oscillatory shear at 25 °C using a plane plate with a diameter of 50 mm. The effects of salt on the stability of DDSA emulsions were evaluated by LabRAM Laser-Raman spectroscopy (LRS; HORIBA Jobin Yvon, France) with 533 nm laser excitation.

Paper making and sizing performance test of the DDSA emulsions

Bleached chemithermomechanical pulp was first distinguished at a concentration of 1.5 wt% and diluted to 1 wt%. To the pulp suspension, 0.5 wt% of aluminum sulfate was added at a stirring speed of 500 rpm for 60 s and the pH value of the pulp suspension was adjusted to a range of 7.5 to 8.5 with dilute sodium hydroxide solution. The DDSA emulsion was diluted to 0.2% with ultrapure water before sizing with 0.03 wt% of cationic polyacrylamide based on oven-dry pulp, and the emulsion was added in succession. After each addition, the paper stock was stirred for 60 s at 500 rpm. The paper stock was stirred at a high-shearing speed of 1000 rpm for 30 s and was diluted to 0.15 wt%. Then, the stirring speed was lowered to 500 rpm, and 0.2 wt% of montmorillonite obtained from oven-dry pulp was added. After mixing the stock suspension for 30 s, paper with a basis weight of 60 g m^{-2} was prepared according to TAPPI test method T205 om-88 (TAPPI T205 om-88 1988). Handsheets were conditioned at 25 °C with 50% relative humidity for more than 24 h. The sizing degrees of the paper sized by DDSA emulsions prepared with MMT were measured in accordance with GB/T5405 (2002) (Liu *et al.* 2008). The handsheets were cut into square paper samples of size 30 mm × 30 mm, conditioned at 25 °C, and exposed to 50% relative humidity for 24 h. A paper sample was folded into a square vessel with a bottom size of 20 mm × 20 mm. The paper vessel was made to float on the surface of a 2 wt% ammonium thiocyanate solution, and then a drop of 1.2 wt% ferric chloride solution was dripped onto the bottom of the vessel. The time elapsed before red ferricthiocyanate spots appeared was determined as the penetration time. The overall sizing degree of the handsheets was defined as the average permeation time of the 10 paper vessels.

RESULTS AND DISCUSSION

Characterization of SFMMT

The stability of Pickering emulsions is determined by the decrease in total free energy, size, and wettability of solid particles at an interface (Binks and Lumsdon 2001; Aveyard *et al.* 2003). A neutral Pickering emulsifier with appropriate wettability and size facilitates the stability and activity of ASA emulsion (Gess and Rende 2005). The apparent platelet structure and relatively narrow particle size distribution are illustrated by the high resolution transmission electron microscopic (HTEM) image and dynamic light scattering (DLS) distribution of SFMMT, respectively in Fig. 2a. According to the figure, the appearance of a peak at around 80 nm may correspond to the discrete and stripped SFMMT, and the peak at ~292 nm represents the agglomerated particles. Comparing with the DLS of raw MMT, modification decreases the particle size and agglomeration.

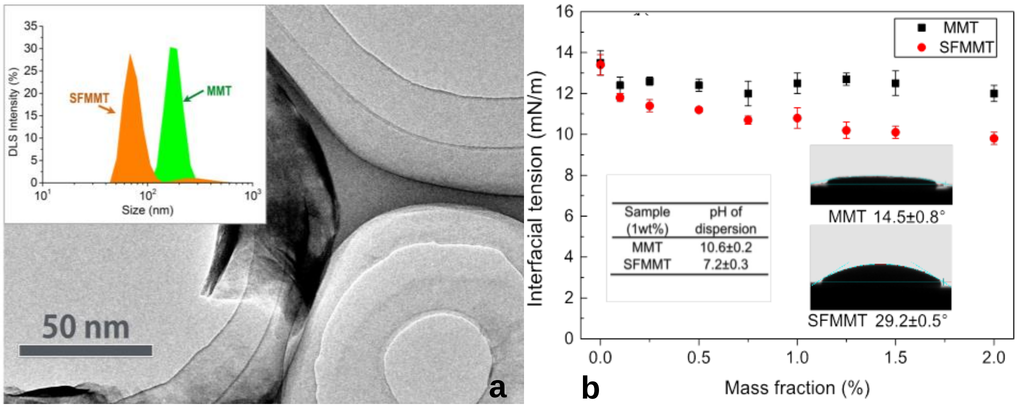

Fig. 2. (a) High-resolution transmission electron microscopic image of SFMMT nanoparticles. The inset is DLS size distribution of the SFMMT nanoparticles. (b) The interfacial tension of raw MMT (black square) and SFMMT (red cycle) aqueous at different solid particles content. The insets are pictures of contact angle and pH values of aqueous with a 1.0 wt% particle concentration.

Figure 2b shows that the interfacial tension decreased slightly with increasing of amount of SFMMT and reached around 9.8 mN/m when the mass fraction of solid particles was 2 wt%. However, no significant variation was found for MMT dispersion, indicating that SFMMT has some surfactant-like activity. In addition, the contact angle of SFMMT (29.2 ± 0.5°) was larger than that of MMT (14.5 ± 0.8°), which indicates that the wettability of SFMMT nanoparticles has been improved. Furthermore, the pH value of the SFMMT dispersion was lower than that of the MMT dispersion. The SFMMT nanoparticles exhibited better size distribution, appropriate hydrophility, and neutrality, which are proposed to benefit the preparation of stable DDSA-in-water emulsions with hydrolysis resistance and good sizing efficiency.

Effects of Particle Concentration on the Stability of DDSA Emulsions Stabilized by SFMMT Nanoparticles

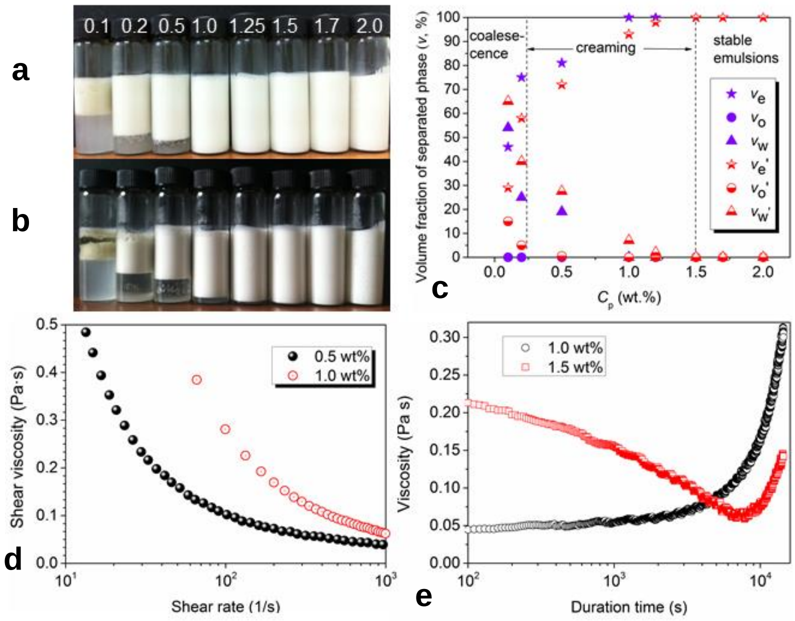

Fig. 3. Photographs of vessels containing DDSA-in-water emulsions stabilized solely by SFMMT nanoparticles at different particle concentrations (C_p) from left to right: 0.1, 0.2, 0.5, 1.0, 1.5, 1.7, and 2.0 wt%, taken (a) 0 h and (b) 1 week after preparation. (c) The volume fraction of separated phase with different C_p after 0 h (filled) and 1 week (semi-open) aging time. (d) Shear viscosity with applied shear rate for a DDSA-water emulsion stabilized by 0.5 % (w/w, solid circle) and 1.0 % (w/w, empty circle) SFMMT particle concentration in the emulsion at a water volume fraction of 0.5. (e) Time dependence of the viscosity of emulsions at different SFMMT particle concentrations being sheared at a speed of 200 rpm. The oil-water ratio is 1:2.

Paper sizing performance of DDSA depends mainly on its emulsion stability and hydrolysis resistance. A series of emulsification experiments was conducted to investigate whether a stable DDSA emulsion could be prepared from an optimized addition level of SFMMT. Agglomerated emulsion with separated water phase and stable DDSA emulsions were obtained by using SFMMT with different particle concentrations (C_p) after the preparation of emulsion (Figs. 3a and 3b). When the C_p was between 0.1 and 0.5 wt%, the water phase was separated on the bottom, and the emulsion phase gradually changed to creaming emulsion with separated oil phase on the top. The volume fraction of emulsion (v_e) increased with the increase of C_p; however, the volume of separated water and oil phase all decreased until the C_p reached 1.5 wt%, where homogeneous emulsions with no phase separation were obtained (Fig. 3c). It is proposed that when the C_p is below 1 wt%, few particles are present to form a particle network that would hinder drop flocculation. This phenomenon accounts for the significant instability observed at low particle concentrations. The poor stability of emulsions prepared at low particle concentrations indicates that the particle network structure in the continuous phase remains unformed despite the emulsion droplet size reaching the minimum level at a C_p of about 1 wt%. At high particle concentrations, where C_p is greater than or equal to 1.5 wt%, the formation of a compact particle network in the continuous phase keeps the emulsion drops well separated and thus hinders drop flocculation. Part of the water phase was separated from the emulsion phase after a week of storage time when there were no extra particles forming a network structure in the continuous phase of the separated emulsion. When the C_p exceeded 1.5 wt%, extra particles entered into the continuous phase of the emulsion to increase the emulsion viscosity, and a gelled emulsion with better coalescence stability was developed (Juárez and Whitby 2012).

As the particle concentration increases, extra particles in the water phase can be attracted to each other by van der Waals force and electrostatic force. These particles form edge-to-surface and edge-to-edge associated agglomerates and 3D structures in a fixed orientation called “house-card structure” (Van Olphen and Hsu 1978; Marinova *et al.* 1996) which could improve the coalescence stability of Pickering emulsion. With the increase of C_p, particles can fully absorb on the interface and extra particles can enter into continuous phase, forming a 3D structure that prevents droplets from coalescing. Although the coalescence stability was improved by increasing C_p, the flowability and transmission energy consumption of DDSA emulsion increased due to the increasing viscosity induced by associated agglomerates and 3D structure containing excess SFMMT nanoparticles. These effects could impact the application of DDSA emulsion as a paper sizing technology.

To ascertain whether the SFMMT nanoparticles prevent the DDSA from hydrolysis, we also studied the rheological behavior of the as-prepared DDSA emulsions at a water volume fraction of 0.5 with an applied shear rate of 200 rpm (Fig. 3d). There was a remarkable variation in the steady shear viscosity of DDSA emulsions containing different concentrations of SFMMT as time increased. The as-prepared emulsions showed non-linear, time-dependent, and transient response rheological properties when a fixed shear rate was applied. At long times, the shear viscosity of emulsion stabilized by 1.0 wt% SFMMT always increased, but the emulsion containing 1.5 wt% SFMMT decreased at first and then became boosted at about 2 h duration, indicating that the deformation of the emulsion is elastic with variation in hydrolytic stability. Adding more particles led to the transmission of excess nanoparticles into the continuous phase and gelatinization as the particle aggregates changed from loose networks to compact flocs. Thus, the DDSA emulsion stabilized by 1.5 wt% SFMMT nanoparticle exhibited a shear-thinning behavior, which is likely due to the improved hydrolysis stability of DDSA.

Pure DDSA oil shows Newtonian flow behavior and dispersing 1% (w/w) SFMMT nanoparticles into DDSA increased the viscosity only slightly (data not shown). However, with the emulsification of water into the dispersion, the viscosity increased. The effect of the particle concentration on the shear stress and viscosity of the emulsions with increasing shear rate is shown in Fig. 3e. The emulsions stabilized by 0.5 and 1.0 wt% MMT displayed a strong shear-thinning behavior, and their viscosities at zero shear rate were high. At any given shear rate, the emulsions had a higher viscosity than the particle dispersion, especially at low shear rates, and the viscosity decreased as the shear rate increased approaching a constant value at high shear rates. At low shear rates, the measured emulsion viscosity was higher than that of pure oil, particle dispersion, or their mixture described previously, indicating that house-card structures or attractive drop interactions made a significant contribution to the emulsion viscosity. At higher particle concentrations, the shear-thinning behavior was stronger, indicating that the flow behavior of the emulsions changed dramatically and exhibited the flow behavior of non-Newtonian fluid.

Effect of the Oil-Water Ratio on the DDSA Emulsions Stabilized by SFMMT Nanoparticles

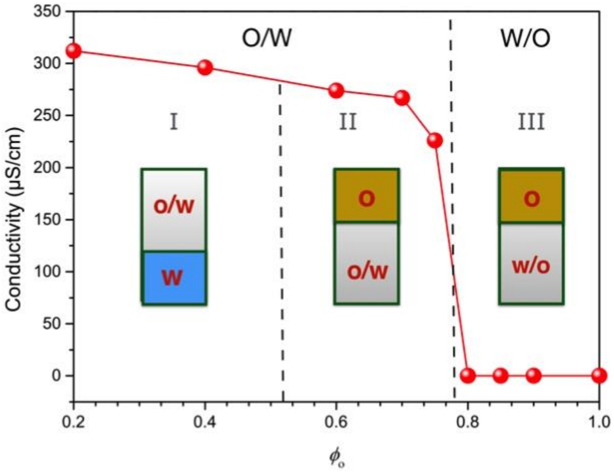

Fig. 4. Schematic illustration of the mixed states of phases with the oil volume fraction (Φ_o) of DDSA emulsion stabilized by 1 wt% SFMMT nanoparticles. The pH of aqueous phase is 7.

The volume fraction of dispersed phase has a large influence on the type of Pickering emulsion, and induced phase inversion will be accompanied by dramatic changes in the stability and size distribution of the emulsions (Binks *et al.* 2000; 2005). Figure 4 shows a schematic illustration of the mixed states of phases with the oil-water fraction of DDSA emulsion stabilized by 1 wt% SFMMT nanoparticles. For the obtained DDSA Pickering emulsions, increasing the volume fraction of oil phase (Φ_o) caused phase inversion from o/w to w/o using hydrophilic SFMMT. Three obvious emulsion states with different phase compositions can be seen. The o/w DDSA emulsions with separated water phase (W) could be prepared in region I, where the volume fraction of water phase on the bottom decreased with the increase of Φ_o. Stable o/w emulsion without separated phase could be obtained with the Φ_o at around 0.44 between regions I and II (dashed line on the left). The o/w emulsions with oil phase (O) separated on the top could be prepared in region II, where the volume fraction of separated oil phase decreased as the Φ_o increased. It is deduced that with decreasing amounts of water, the oil phase encapsulates a successively larger fraction of oil drops until there is no free layer of oil at the surface and the MMT nanoparticles are insufficient to form particle films that will coat all oil drops. The packing efficiency of the particle films is below the required efficiency rate for drop surface coverage. With increasing amounts of oil, the o/w emulsions catastrophically inverted without hysteresis to oil-water at volume fractions of oil around 0.79 between regions II and III. Due to the extreme hydrophility of MMT ($\theta_{aw} = 5°$), phase inversion did not appear until the Φ_o reached a very high value of 0.79, before which the emulsions exhibited high conductivity and maintained the o/w form of emulsion (Binks *et al.* 2000). The DDSA, referred to as “chemically reactive sizing agent”, is usually introduced into the paper pulp in the form of an aqueous emulsion where an o/w emulsion is a prerequisite for the sizing application of the DDSA. An asphalt-like complex structure with high a viscosity and Φ_o value occurs (Nonomura and Kobayashi 2009), which may affect the emulsion transport and sizing application. Thus, the oil-water ratio of the DDSA emulsion should be engineered carefully and not exceed the critical value (catastrophic phase inversion) for a given particle concentration.

Effects of pH on the DDSA Emulsions Stabilized by SFMMT Nanoparticles

The pH of a particulate emulsifier system significantly affects the wettability of particles and emulsion stability (Binks *et al.* 2006; Binks and Rodrigues 2007; Colver and Bon 2007). The effect of pH on the coalescence stability of oil-in-water DDSA emulsions stabilized by SFMMT particles was examined, and the results are shown in Fig. 5a.

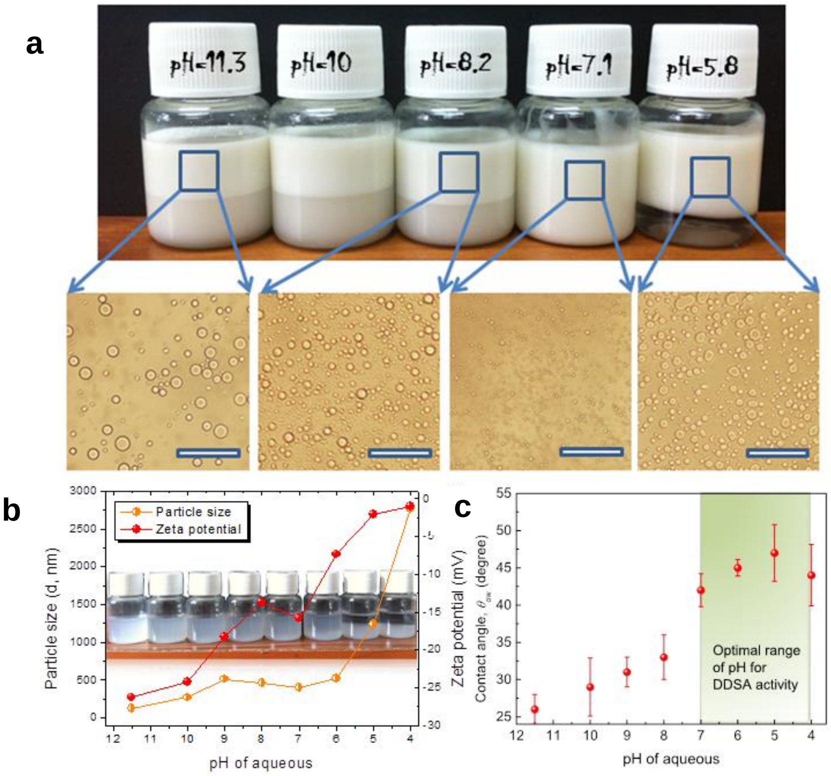

Fig. 5. (a) Digital images of DDSA emulsions stabilized by SFMMT at pH 11.5, 10, 8.2, 7.1, and 5.7 (from left to right), respectively. The volume ratio of oil to water is 1:2 and the particle concentration is 1 wt%. Scale bars in the optical microscope images equal 10 μm. (b) Effect of pH value of SFMMT dispersion on the particle size and zeta potential. The inset is an image of SFMMT aqueous dispersion. (c) Contact angle (θ_{ow}) of SFMMT nanoparticles at different pH.

It was noted that the DDSA emulsions separated with a clear aqueous phase and particle dispersion separation with the decrease of pH, but they were completely stable to coalescence with no oil phase separation. An emulsion with 100% emulsion volume fraction was obtained at a pH of 7.1, but separated with water phase at a pH of greater than 7.1, which shows poor emulsification. At a pH of about 7.1, the DDSA Pickering emulsions exhibited outstanding stability to coalescence and demulsification, which could be attributed to the irreversible adsorption of the particles at droplet interfaces. The color of the separated water phase was gray when the pH was greater than 7.1, indicating that excess non-swollen particles stayed in the separated water phase, which may be attributed to the strong repulsion between the oil–water interface and the negatively charged SFMMT particles. However, the color of the water phase was clear at a pH of about 5.8, indicating that nearly all the SFMMT nanoparticles in the dispersion were associated with the emulsification. We propose that the changes in the pH of the aqueous phase resulted in the accumulation of hydroxide ions in the interfacial water molecules and negatively charged the oil-water interfaces, inducing the adsorption of the SFMMT nanoparticles with positively charged edges. Particle flocculation induced by decreasing pH promoted the energy of detachment of single MMT nanoparticles, causing the nanoparticles to strongly adsorb on the oil-water interface.

The charge on particle surfaces in water is dependent on the pH value of the aqueous phase (Binks *et al.* 2007). A chargeable surface has maximum hydrophobicity at conditions near its point of zero charge (Binks 2002). To further confirm the effect of pH on the stability of DDSA emulsion, the zeta potential, particle size, and contact angle of SFMMT in water as a function of pH were tested, and the results are shown in Figs. 5b and 5c. Zeta potential measurements showed that the particles were highly charged at high pH such as 11.5, and they possessed little charge close to around pH 4. The uncharged surfaces of the MMT are normally more hydrophobic than charged surfaces. The SFMMT was negatively charged, and the magnitude of the zeta potential and SFMMT nanoparticle size increased as pH was decreased, with a boost at a pH of around 7. Electrostatic repulsions became the dominant interaction force of SFMMTs at a pH greater than 7, at which the ionized particles were uniformly dispersed in the water phase to form transparent sol (collosol). As the pH value was decreased, SFMMT sol gradually changed to a gel-like dispersion at around pH 7, indicating that the charge on SFMMT surfaces was shielded and reduced electrostatic repulsions led to particle flocculation and sedimentation. When the pH was greater than 5, SFMMT flocs appeared at the bottom of dispersion, which could break the stability of SFMMT hydra-gel system and Pickering emulsions. As the pH of aqueous dispersion decreased, the electrostatic repulsion between the charged SFMMT nanoparticles decreased, and SFMMT nanoparticles with abundant −OH groups on their edges became increasingly charged through dissociation (H^+). This increased the hydrophobicity and improved their wettability by oil, which is favorable for the formation of Pickering emulsions.

The adsorption and stability of particles at the oil-water interface are controlled by the wettability of the solid particles (Duan *et al.* 2004; Chevalier and Bolzinger 2013). Varying the pH changes the hydrophobicity and hence the wettability of particles that possess ionizable surface groups. Therefore, the adsorption behavior of the SFMMT at the interface and stability of the emulsion can be controlled by varying the pH. The effect of pH on the contact angle of SFMMT nanoparticles at different pH values is shown in Fig. 5c, where the θ_{ow} increases gradually as the pH value decreases, indicating that the oil wettability of SFMMT is promoted by increasing the pH of aqueous dispersion. At a pH above 5, the SFMMT nanoparticles become sufficiently ionized, strongly hydrophilic, swollen, and no longer adsorb at the oil-water interface. One thing to be noted here is that the pH is a major factor influencing the hydrolysis of DDSA and the dissociation of hydrolyzed DDSA, especially at high pH values. To maintain sizing activity of DDSA in a neutral-to-alkaline pH of between 6 and 8.5 and to retard the DDSA hydrolysis reaction in neutral-to-acidic pH less than 7, the optimal range of pH appears to lie between 6 and 7.

Effect of Salt on the DDSA Emulsions Stabilized by SFMMT Nanoparticles

Weak flocculation of solid particles can significantly improve the stability of solid stabilized emulsions by promoting the adsorption of particles on the oil–water interface (Fokkink and Ralston 1989; Binks and Rodrigues 2007). As shown in Table 1, the droplet size dependence of the emulsion volume obtained varied with the addition of salt. Emulsion destabilisation was sensitive to the salt concentration in the aqueous phase since drop flocculation is linked to particle aggregation. The salt-induced aggregation of

SFMMT nanoparticles promoted the adsorption of the nanoparticles at the DDSA–water interface, favoring the preparation of stable DDSA emulsions. It should be noted that stable DDSA emulsions with nearly 100% emulsion phase can be obtained by using NaCl and $C_8H_{20}BrN$. In contrast, the addition of $MgCl_2$ and $AlCl_3$ makes emulsions unstable and causes separation of water phase on the bottom. It can be deduced that salts compact the electrical double layer near the oil-water interface, which decreases the potential energy and weakens the repulsive force of charged particles that make the particle film denser and the emulsion more stable.

Table 1. Effect of Salt on the DDSA Pickering Emulsions Stabilized by 1 w% SFMMT Nanoparticles

Salt *****	pH of aqueous	Concentration (mol/L)	o/w ratio	Droplet size (*d*, μm)	v_e (%)	v_w (%)	v_o (%)	Type of emulsion
−	7.1±0.2	0	1:2	4.3	61	39	0	o/w
NaCl	7.0±0.3	0.02	1:2	3.8	100	0	0	o/w
$MgCl_2$	7.3±0.2	0.01	1:2	9.1	78	22	0	o/w
$AlCl_3$	6.8±0.3	0.007	1:2	15.5	67	33	0	o/w
$C_8H_{20}BrN$	7.2±0.2	0.005	1:2	3.1	99	1	0	o/w

***** All salts were initially dispersed in water and adjusted to around 0.01% (w/w) based on the aqueous phase

In general, uncharged surfaces are more hydrophobic than charged ones (Binks *et al.* 2007). The hydrophobicity of SFMMT nanoparticles with different amounts of NaCl was characterized by contact angles, and the experimental results are shown in Fig. 6a. Water droplets at a pH of about 7 containing different NaCl contents were dropped directly onto 1 mm thick SFMMT substrate immersed in DDSA oil. It was found that both contact angle θ_{ow} and θ_{aw} increased with the increase of salt, indicating an effect due entirely to the hydrophobising effect of salt that promotes the adsorption of SFMMT on the oil-water interface. Moreover, DDSA as polar oil generally increases the oil wettability of particles and tends to either form w/o emulsions when particles with intermediate hydrophilicity are used as stabilizers or improve the stability of o/w emulsions when fully hydrophilic particles are used, so the hydrophobising effect induced by salt further improves the stability of DDSA emulsion containing hydrophilic SFMMT nanoparticles (Binks and Whitby 2005).

Emulsion stability and droplet size are the most important quality parameters of DDSA emulsions for developing good sizing performance. The effects of salt on the droplet size of DDSA emulsion stabilized by SFMMT with different particle concentrations were investigated, and the results are shown in Fig. 6b. It was found that the droplet sizes of as-prepared emulsions were decreased with the addition of NaCl, suggesting that the efficiency of emulsification improved with the introduction of salt. When the C_p was below 0.5 wt%, the addition of NaCl did not improve the formation of emulsion, indicating that the excess salt would lead to agglomerated SFMMT nanoparticles with large particle size, making the emulsion unstable and even demulsified. In addition, the droplet size was affected more by the oil-water ratio than salt addition, so it can be concluded that the emulsion size has a maximum critical value and that the arrangement of SFMMT nanoparticles on the oil-water interface is fixed. Electrostatic interaction causes the formation of gaps between adjacent particles of SFMMT which induce angles that do not allow the particles to lie flat on the interfaces.

The electrostatic repulsions between the charged SFMMT nanoparticles are, in general, reduced by the addition of salt, which leads to aggregation or even flocculation of the nanoparticles. Furthermore, charged particle surfaces are shielded and combine with each other seamlessly to form compact particulate films. However, the emulsion droplet size would increase accordingly. It can be noted that when the particle concentration exceeded 2 wt%, the emulsion droplet size decreased with the addition of salt, indicating that the droplet size could be regulated not only by employing salt but also by adjusting particle concentration or oil-water ratio (Pardhy and Budhlall 2010).

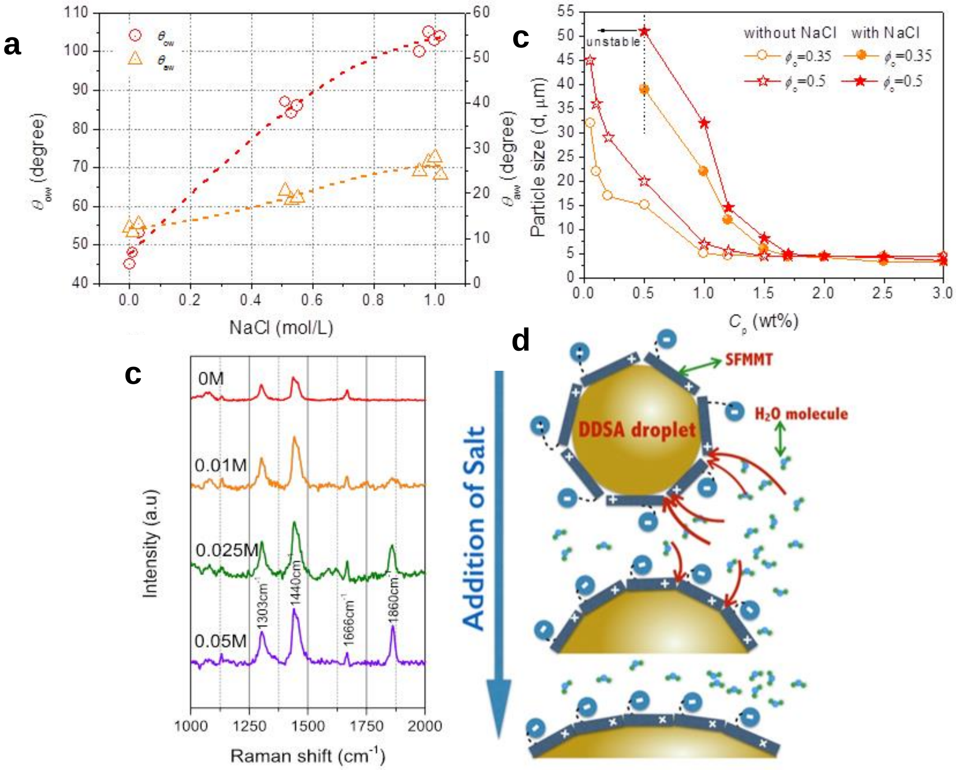

Fig. 6. (a) Contact angles of water drops, measured through water, in air on SFMMT sheets as a function of NaCl concentration at pH 11.2 and 25 °C. (b) Particle concentration (C_p) dependence of the droplet size (*d*) in emulsions prepared with or without 0.01 M NaCl at Φ_o (oil volume fraction)~0.35 and Φ_o~0.5, respectively. The pH of aqueous was fixed at around 7.2. (c) Laser-Raman spectra of DDSA emulsions with the presence of NaCl at different concentrations after 2 h aging time. (d) Schematic representation of SFMMT particles arrangement on the interfaces with the addition of NaCl.

The effect of salt concentration on the emulsion stability was determined by the hydrolysis stability of DDSA through LRS testing. Figure 6c shows the Laser-Raman spectra of DDSA emulsions stabilized by SFMMT with the presence of NaCl at different concentrations after different storage times. In a Raman spectrum, the carbonyl stretching frequencies of DDSA are usually located at approximately 1860 cm^{-1}, and the characteristic absorption peak of the DDSA-acid occurs at approximately 1666 and 1303 cm^{-1} and is assigned to the stretching vibration of carboxyl groups form the hydrolysed product of DDSA (Colver and Bon 2007; Yu *et al.* 2013). As the salt concentration was increased, an enhancement of the peak at 1860 cm^{-1} was observed, where the vibration was mainly generated by the lactonic ring of DDSA. Additionally, the stretching frequency of the COOH at 1302 cm^{-1}, C=O at 1666 cm^{-1}, and -OH at 1078 cm^{-1} was weakened gradually with the increase of NaCl, indicating an accelerated hydrolysis reaction of the DDSA. This is in agreement with the study of droplet size induced by salt (see Fig. 6b). These observations led us to conclude that the DDSA hydrolysis reaction could be retarded by addition of salt but accelerated in alkaline conditions (pH > 7) and that the lifespan and stability of the emulsions appear to be favored with a moderate salt concentration.

Figure 6d schematically shows the representation of SFMMT nanoparticle arrangement on the interfaces with the addition of NaCl. According to this scheme, it can be inferred that the addition of salt facilitates the formation of compact particulate film and that the electrostatic interactions between the particles are sufficiently screened for the anisotropy of the charge distribution around each particle to control their interactions, allowing hydrolysis-resistance at much lower particle concentration. This phenomenon could be explained by the possible stabilization mechanism proposed above.

Stability Mechanism of SFMMT Nanoparticles on the DDSA-Water Interface

Pickering emulsion stability mainly depends on particle coating film at the oil/water interface or a 3D network building up in the aqueous phase (Binks 2002). To investigate the particle adsorption and coating at the DDSA-in-water emulsions droplets, laser-induced confocal scanning microscopy was conducted. Confocal microscopy images show evidence of particle shield formation and protection in the emulsions (Fig. 7a). The nanoparticles were stained with Rhodamine B (the fluorescent dye appears bright in the images) and were clearly visible on the edge of DDSA emulsion droplets. Homogenous droplets without deformation and coalescence were obtained after the preparation of emulsion. However, as the storage time increased, the emulsion droplets collided with each other, and compressional deformation occurred until the emulsion droplets reached a maximum compressional deformation with a "honeycomb-like structure". Transfer of oil from the smaller drops to the larger ones must be enhanced by permeation of DDSA molecules across the SFMMT nanoparticle layers that stabilize the thin liquid films between neighboring drops in direct contact. The trapped emulsion droplets under protection and aggregation formed honeycomb structures, indicating the presence of particle film shield formation and its stabilization effect. Coagulation of the SFMMT nanoparticles would lead to complex structures in the emulsions as the interactions between the particles cause rapid growth of large particle clusters or films. The DDSA droplets were trapped within these aggregate particulate structures and stabilized. The resulting structure is a wall-like particulate film of interconnected drops and particles that spans the whole storage time (Fig. 7b). The SFMMT particles with high zeta potential contribute to the stability of DDSA emulsion and the particles are mutually exclusive through electrostatic interactions that prevent aggregation between droplets (Binks *et al.* 2007).

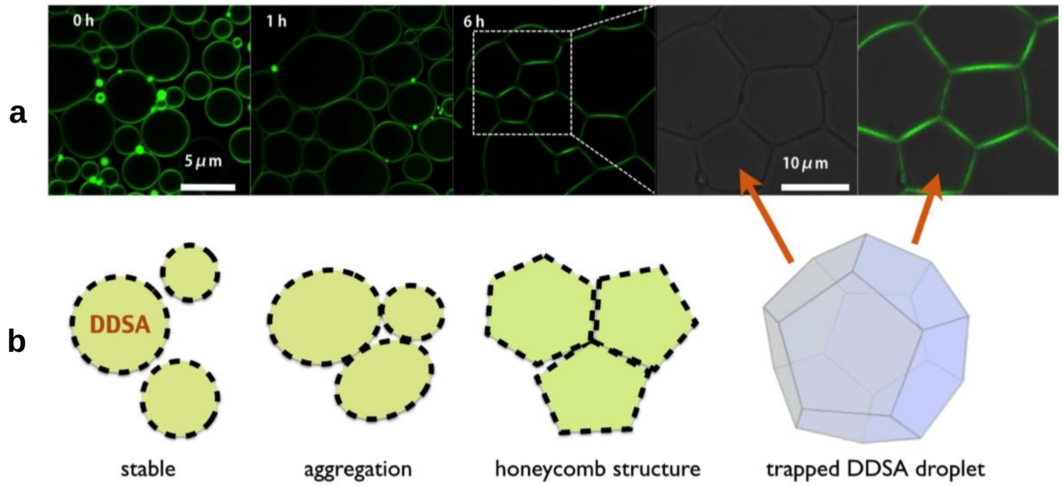

Fig. 7. (a) Confocal fluorescence images of DDSA Pickering-emulsion stabilized by 1 wt% MMT contaminated with 5 mmol/mL Rhodamine B (green fluorescence) after 0, 1, and 6 h emulsion formulation, respectively. (b) Schematic representation of the morphology revolution of DDSA droplets coated by SFMMT nanoparticles after different storage times. The pH of aqueous phase is set to 7.4 and the oil-water ratio is set to 0.5. The DDSA droplets with honeycomb structure are marked by white, dashed box.

Sizing Performance of the DDSA Emulsion Stabilized by SFMMT Nanoparticles

Sizing performance and hydrolysis resistance are important properties of DDSA sizing agent emulsions utilized in the papermaking process. During the sizing reaction between DDSA and the hydroxyl groups of cellulose, the 5-member ring of DDSA opens and a *β*-ketoester linkage is formed between the DDSA molecule and cellulose. The DDSA is chemically bound to the cellulose substrate through outward-pointing hydrophobic hydrocarbon chains, producing a water-repellent surface (Carter 1997). It is anticipated that the DDSA emulsions stabilized solely by SFMMT nanoparticles will show improved and stable sizing performances. The sizing degree and hydrolysis extent of the DDSA from emulsion stabilized by SFMMT with salt was obviously higher than that from the emulsion stabilized by MMT at the same storage time (Fig. 8).

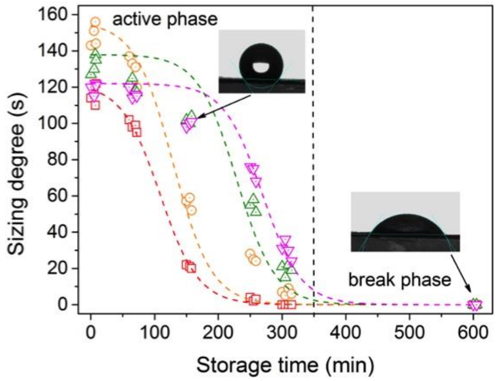

Fig. 8. Effect of emulsion storage time on the sizing degree of DDSA emulsions stabilized by 1 wt% of SFMMT nanoparticles with (▽) or without (△) NaCl and 1 wt% MMT nanoparticles with (○) or without (□) NaCl. The insets show the water contact angle image of sized paper at the active phase and break phase of DDSA, respectively.

Addition of salt reduced the hydrolysis of DDSA stabilized by SFMMT or MMT nanoparticles but it did not stop the hydrolysis. Compared with the conventional ASA emulsions prepared by acidified starch or other particulate emulsifiers which lose their sizing performance within about 1 to 3 h (Ding *et al.* 2011), the DDSA emulsions we prepared using SFMMT nanoparticles showed relatively improved hydrolysis resistance and better sizing performance within an active phase of 5.5 h. Sizing activity of as-prepared DDSA emulsion would be lost after about 5.5 h and the paper sized by hydrolyzed DDSA in the broken phase would fail to achieve its water-resistance. It is anticipated that the neutral SFMMT nanoparticle will become an excellent Pickering stabilizer for many kinds of oil-water emulsions with an optimum emulsification condition being required depending on the application.

CONCLUSIONS

1. Stable Pickering-type dodecylsuccinic anhydride (DDSA) emulsions with good sizing activity and lifespan can be prepared by the use of sodium fluoride modified montmorillonite (SFMMT) nanoparticles at the moderate pH and salt concentration. Catastrophic inversion of DDSA emulsion from o/w to w/o occurs when the oil volume fraction is increased.
2. Varying the pH changes the hydrophobicity and enhances the oil wettability of the SFMMT nanoparticles. Introduction of salt not only enhances the stability of DDSA emulsion stabilized by SFMMT nanoparticles, but also reduces the hydrolysis of DDSA and improves the water-resistance of paper sized by the as-prepared DDSA emulsion.
3. Particulate interfacial films built by SFMMT nanoparticles protected DDSA droplets from aggregation and formed a honeycomb structure. The DDSA emulsions containing 1 wt% SFMMT nanoparticles show relatively improved hydrolysis resistance and better sizing performance within an active phase of 5.5 h. The SFMMT nanoparticle facilitates the design of new particulate emulsifiers for the preparation of paper sizing agents.

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