

Nanoparticle-stabilized Alkenyl Succinic Anhydride (ASA) Emulsions: A Review

WenXia Liu, HuiLi Wang, GuoDong Li, DeHai Yu, ZhaoPing Song

Kay Laboratory of Pulp & Paper Science and Technology (Ministry of Education), Qilu University of Technology, Ji'nan, Shandong Province, 250353, China

Abstract: Alkenyl succinic anhydride (ASA) is a popular paper-sizing agent that is generally added to papermaking systems as an aqueous emulsion. Herein, we reviewed the recent work focusing on ASA emulsions stabilized by solid particles. Solid particle-stabilized ASA emulsions generally possess high ASA content and exhibit good sizing performance. The particles that have been used to stabilize ASA emulsions typically include montmorillonite, laponite, alumina, TiO_2 , Fe_3O_4 , polyaluminum sulfate (PAS), and cellulose nanocrystals (CNCs). Montmorillonite is the first extensively studied particle stabilizer for ASA emulsions. Laponite is undoubtedly the most competent particle stabilizer for preparing ASA emulsions with high sizing efficiency. Montmorillonite and laponite can be used individually as stabilizers after modification or as co-stabilizers with other particles or polymers. TiO_2 , alumina, PAS, and CNCs are commonly used as stabilizers either individually or with other particles.

Keywords: alkenyl succinic anhydride; particle stabilized emulsions; montmorillonite; laponite; sizing



WenXia Liu, PhD, professor;
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E-mail: liuwenxia@qlu.edu.cn

1 Introduction

Alkenyl succinic anhydride (ASA) is one of two popular reactive sizing agents that are generally used as oil-in-water emulsions. Compared to alkyl ketene dimer (AKD), which is another commonly used reactive sizing agent, ASA is highly reactive and can develop adequate sizing degrees during papermaking over a fairly wide range of pH values^[1]. Similar to rosin, ASA allows paper sizing to be easily controlled, exhibits a high tolerance for Al salts, and results in high pulp yields^[2-4]. Thus, ASA has advantages for sizing paper and paperboard, including materials containing large amounts of mechanical pulps and secondary fibers. However, its high chemical reactivity also causes ASA to undergo rapid hydrolysis upon exposure to water^[5]. The

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hydrolysis product of ASA (i.e., alkenyl succinic acid) deteriorates paper sizing and causes machine running problems^[2,6]. To reduce the adverse effects of hydrolysis, ASA is generally emulsified *in situ* immediately before being added to paper furnishes^[2]. Cationic starch is extensively used as an emulsifier or stabilizer, but it is not an efficient emulsifier or stabilizer for the protection of ASA from water. The charge amount of cationic starch should generally be as high as four times that of ASA to ensure acceptable sizing performance^[7]. As a result, cationic starch-stabilized ASA emulsions have fairly low ASA contents because of the high viscosity of gelatinized starch, which significantly reduces the emulsification efficiency and increases the pumping energy. Adding anionic sulfosuccinate emulsifier to ASA before emulsification may reduce the charge amount of cationic starch^[8-9]. However, the presence of the surfactant negatively affects the sizing development of ASA emulsions because of its hydrophilic character and may cause foam problems in papermaking systems. Therefore, increasing attention has been paid to fine particle-stabilized ASA emulsions (i.e., Pickering ASA emulsions) in recent years. Many studies have confirmed that, when nanoparticles are used as stabilizers, ASA emulsions with high stability, high ASA content, and high sizing efficiency, can be produced^[10-15].

Similar to surfactant-stabilized emulsions, whose types are determined by the hydrophilic lipophilic balance of the surfactants, particle-stabilized emulsions are classified based on their particle wettabilities. Water-wetted particles are preferentially stabilized oil-in-water emulsions, whereas oil-wetted particles are preferentially stabilized water-in-oil emulsions in systems with equal volume fractions of oil and water^[16]. Thus, to prepare a stable ASA-in-water emulsion, water-wetted fine particles should be selected. Previously, montmorillonite^[10-12, 17], TiO_2 ^[18-19], alumina^[20], polyaluminum sulfate (PAS)^[16, 21], Fe_3O_4 ^[22], laponite^[13-15, 23], and cellulose nanocrystals (CNCs)^[24] have been investigated as particle stabilizers for ASA emulsions alone, in combination with other particles or

polymers, or after modification. Among these particles, montmorillonite is the first extensively studied particle stabilizer, and laponite is undoubtedly the most competent particle stabilizer for ASA emulsions.

2 Montmorillonite

Montmorillonite is a 2 : 1 phyllosilicate mineral with plate-shaped particles characterized as having permanent negative charges on their surfaces and positive charges at their edges, as shown in Fig.1. The particles have an average diameter of approximately 300 nm and a thickness of 9.6 nm. The negative surface charges arise from isomorphous substitutions of low valence cations for high valence cations. These negative charges are balanced by metal ions, such as Na^+ and Ca^{2+} , which can be ion-exchanged with other cations. Thus, montmorillonite particles have high water-wettabilities. Na montmorillonite (i.e., montmorillonite with interlayered Na^+) in aqueous medium with a neutral pH is generally used to stabilize ASA emulsions^[25]. Because of its high water-wettability, montmorillonite preferentially stabilizes ASA-in-water emulsions when it is used as a particle stabilizer.

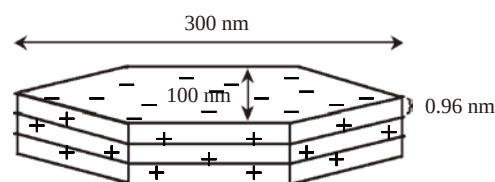


Fig. 1 Schematic of montmorillonite platelets

2.1 Use as a sole stabilizer

The plate-shaped particles of montmorillonite can be adsorbed at the ASA-water interface to form mechanical barriers against emulsion coalescence around ASA droplets^[25]. Meanwhile, free montmorillonite particles in the aqueous phase increase the emulsion stability against coalescence and creaming by increasing the viscosity and water-holding capacity of the emulsions, as schematically shown in Fig.2.

Na montmorillonite can be prepared by ion-exchanging Ca montmorillonite with NaF and used to stabilize ASA emulsions^[25-26]. Stable ASA-in-water emulsions with 100% emulsion volume fraction

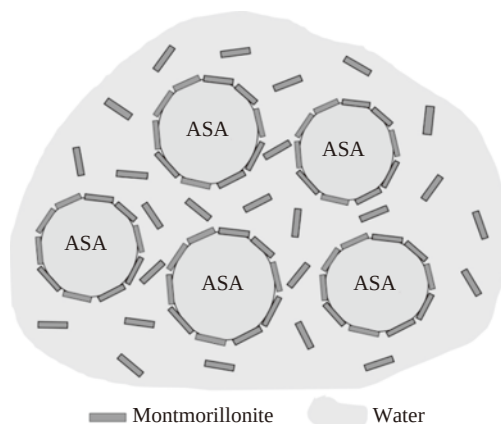


Fig. 2 Schematic of a montmorillonite-stabilized ASA-in-water emulsion

(after centrifugation at 4000 r/min for 3 min) and approximately 25% ASA have been prepared using a mass ratio of montmorillonite to ASA exceeding 4%^[26]. The as-prepared emulsion stabilized by 6% of montmorillonite exhibited the highest sizing efficiency^[26]. The sizing performance was slightly enhanced by increasing the ASA volume fraction^[26].

2.2 Use as a co-stabilizer

The high water-wettability of montmorillonite generally does not favor the adsorption of montmorillonite particles at the oil-water interface. Therefore, this material was investigated as a particle co-stabilizer.

Mg Al hydroxide (MAH), a typical hydrotalcite-like compound, consists of platelet particles characterized as having positively charged surfaces and nanoscale particle sizes^[27]. Adding a small amount of MAH to an aqueous dispersion of montmorillonite caused the aggregation of negatively charged montmorillonite particles, which promoted the absorption of montmorillonite at ASA-water interfaces, as shown in Fig.3. Consequently, the stability of montmorillonite-stabilized ASA emulsions during both centrifugation and storage is significantly improved^[10]. However, to obtain an ASA emulsion with high storage stability (i.e., an emulsion in which no ASA or water is released within 24 h after preparation), the mass ratio of montmorillonite to ASA must exceed 4%. Additionally, the aggregation of montmorillonite particles increases the apparent particle size and, thereby, the droplet size

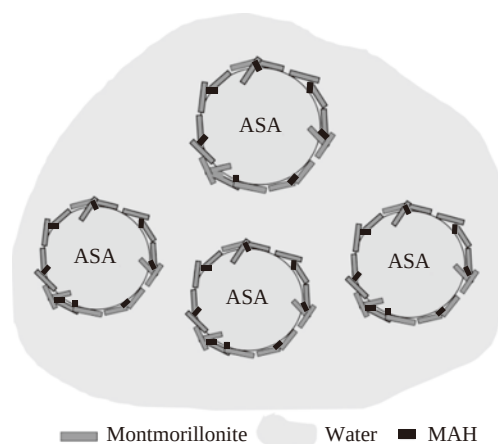


Fig. 3 Schematic of an ASA-in-water emulsion stabilized by montmorillonite and MAH

of montmorillonite-stabilized ASA emulsions^[28]; this is not favorable for the uniform distribution of ASA emulsions on paper fiber surfaces. Therefore, the mass ratio of MAH to montmorillonite should be less than 10%.

Chitosan has been used to co-stabilize ASA emulsions with montmorillonite^[29], acting as a sizing promoter to significantly improve the sizing performance of ASA emulsions. However, chitosan can induce the flocculation of montmorillonite particles, which increases the apparent particle size of montmorillonite. Thus, ASA emulsions co-stabilized by montmorillonite and chitosan commonly possess greater droplet sizes than montmorillonite-stabilized ASA emulsions^[29]. If the relative molecular mass of chitosan is higher than 24.68×10^4 or if the mass ratio of chitosan to ASA is greater than 0.12%, the creaming stability of as-prepared ASA emulsions is lowered by the introduction of chitosan because of the heavy flocculation of montmorillonite particles^[29] and the flocculation of emulsion droplets induced by positively charged chitosan, as shown in Fig.4.

2.3 Use as a stabilizer after modification

Another approach for improving the adsorption of montmorillonite at the ASA-water interface is increasing its ASA-wettability (i.e., reducing its water-wettability). The water-wettability of montmorillonite can be decreased by the adsorption of amphipathic

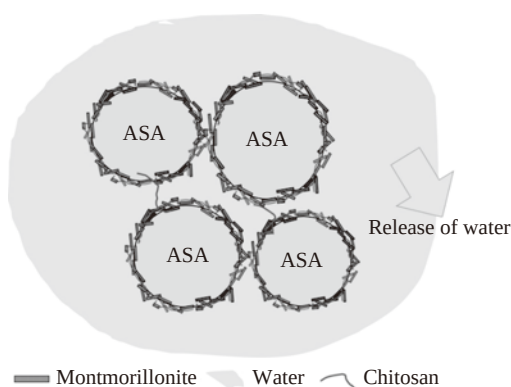


Fig. 4 Schematic of an ASA-in-water emulsion stabilized by montmorillonite and chitosan

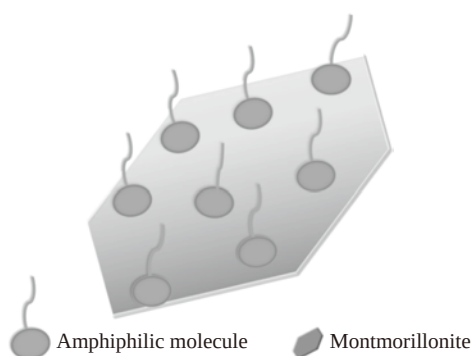


Fig. 5 Schematic illustration of a modified montmorillonite platelet

molecules via ion-exchange or electrostatic attraction^[11-12]. Fig.5 shows a schematic of a montmorillonite platelet modified with an amphiphilic substance, such as short-chain alkyl amines.

Butylamine is a short-chain amphiphilic compound that can moderately reduce the water-wettability of montmorillonite. By using butylamine-modified montmorillonite to stabilize ASA emulsions with an ASA content of 25%, the mass ratio of montmorillonite to ASA can be reduced to 1% to prepare stable emulsions that release no ASA or water within 24 h after preparation^[12]. More interestingly, the droplet size of ASA emulsions stabilized by butylamine-modified montmorillonite decreases as the charge amount of butylamine and montmorillonite increases and is minimized at a butylamine-to-montmorillonite mass ratio of 2.5% and a montmorillonite-to-ASA mass ratio of 5%.

γ -Methacryloxypropyltrimethoxysilane (γ -MPTMS),

a silylating agent, was also employed to modify montmorillonite by grafting it on montmorillonite surfaces^[11]. When the γ -MPTMS-grafted montmorillonite was used as a particle stabilizer for ASA emulsions with an ASA-to-water ratio of 1 : 2 and when the particle concentration was less than 1wt% (approximately 3 wt% relative to ASA), the clay platelets were thought to be insufficient to form particle barriers around ASA droplets. Thus, stable emulsions with primary droplet diameters of roughly 5 μm were obtained when the concentration of γ -MPTMS-grafted montmorillonite exceeded 1wt%. To further prevent emulsion coalescence over time, dense and strong particle networks should be formed in the continuous phase; i.e., the particle concentration should exceed 1.5 wt% (approximately 4.5 wt% based on ASA). The sizing performance and hydrolysis resistance of the as-prepared ASA emulsion were also improved by increasing the particle concentration, reaching desirable levels at a particle concentration of 1.5 wt%^[11].

3 Laponite

Laponite is a synthetic hectorite that is similar to montmorillonite in its structure and composition but has a much smaller particle size. Its disk-shaped crystals have diameters of approximately 25 nm and are less than 1 nm thick. Its ion-exchange capacity is even higher than that of montmorillonite. Therefore, laponite is a highly efficient oil-in-water particle stabilizer and has been extensively investigated as a particle stabilizer for ASA emulsions in combination with other stabilizers or after modification with small surfactant-like molecules.

3.1 Use as a co-stabilizer with other particles

PAS is the hydrolysis product of Al sulfate and has been widely used to reduce the adverse effects of hydrolyzed ASA on paper machine operation and promote the paper-sizing development of ASA^[3]. PAS has been employed to co-stabilize ASA emulsions with laponite^[15]. As a positively charged polyaluminum species, PAS can induce the aggregation of laponite

particles^[15] and significantly lower ASA-water interfacial tension by promoting the orientation of ASA molecules at the interface^[21]. However, the aggregation of laponite particles does not change the droplet size or droplet size distribution of laponite-stabilized ASA emulsions. Therefore, the introduction of PAS significantly improves the stability, hydrolysis resistance, and sizing performance of laponite-stabilized ASA emulsions with an ASA-to-water mass ratio of 1 : 3. The ASA emulsion with a laponite concentration of 0.5 wt% (approximately 2 wt% based on ASA) and a PAS-to-laponite mass ratio of 2% shows the highest sizing efficiency and hydrolysis stability. It should be noted that PAS with higher basicity reduces the interface tension to a greater extent than PAS with lower basicity and that when the ASA-water interfacial tension is too low, nonspherical ASA emulsions form^[21] and the sizing performance decreases^[15]. In addition, using ASA emulsions co-stabilized with PAS and laponite to investigate the reaction between ASA and cellulose fibers, as schematically shown in Fig.6, ester bond formation between ASA and cellulose fibers is confirmed under aqueous conditions in the absence of Al salts. However, removing free ASA-acid, the product of ASA hydrolysis, from sized paper via acetone extraction can significantly enhance the water resistance of the paper; that is, free ASA-acid can act as a de-sizing agent in sized paper^[30].

Alumina nanoparticles have also been used as a co-stabilizer of ASA emulsions with laponite

nanoparticles^[20]. The introduction of alumina can enhance the stability and reduce the emulsion droplet size of laponite-stabilized ASA emulsions with an ASA-to-water volume ratio of 1 : 2 and a laponite-to-ASA mass ratio of 2%. As a result, the sizing performance of these emulsions is improved by the introduction of alumina, especially when the alumina-to-ASA mass ratio is less than 0.08%^[20].

3.2 Use as a co-stabilizer with polymers

Na alginate is an excellent anionic polymer stabilizer of ASA emulsions^[31]. When used as a co-stabilizer to stabilize ASA emulsions with laponite, it can improve the emulsion stability and suppress the formation of nonspherical droplets in laponite-stabilized ASA emulsions within 24 h after preparation when the laponite-to-ASA mass ratio is higher than 1.5%^[32]. Therefore, the sizing performance of ASA emulsions co-stabilized by laponite and alginate is improved as the alginate-to-ASA mass ratio increases and is maximized at an alginate-to-ASA mass ratio of 0.4%^[32].

As observed for montmorillonite, when it is used as a particle stabilizer, chitosan can increase the droplet size and lower the stability of laponite-stabilized ASA emulsions by inducing the flocculation of laponite particles^[33]. However, chitosan can also depress ASA hydrolysis, as shown in Fig.7, and improve the sizing performance of laponite-stabilized ASA emulsions when the chitosan-to-laponite mass ratio is less than 4%^[33].

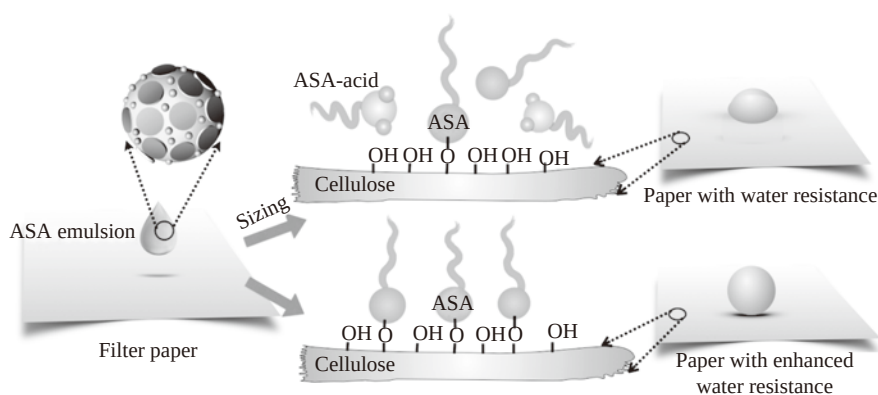


Fig. 6 Schematic illustration of an ASA emulsion co-stabilized by laponite and PAS and its sizing mechanism

Native corn starch carries weak anionic charges and hardly induces the flocculation of laponite particles. When this starch is used to co-stabilize ASA emulsions with laponite particles, stable ASA emulsions with an ASA volume fraction of 25% can be prepared at a native maize starch-to-ASA mass ratio of 3% and a laponite-to-ASA mass ratio of 0.45%^[34]. Compared to starch-stabilized ASA emulsions, the

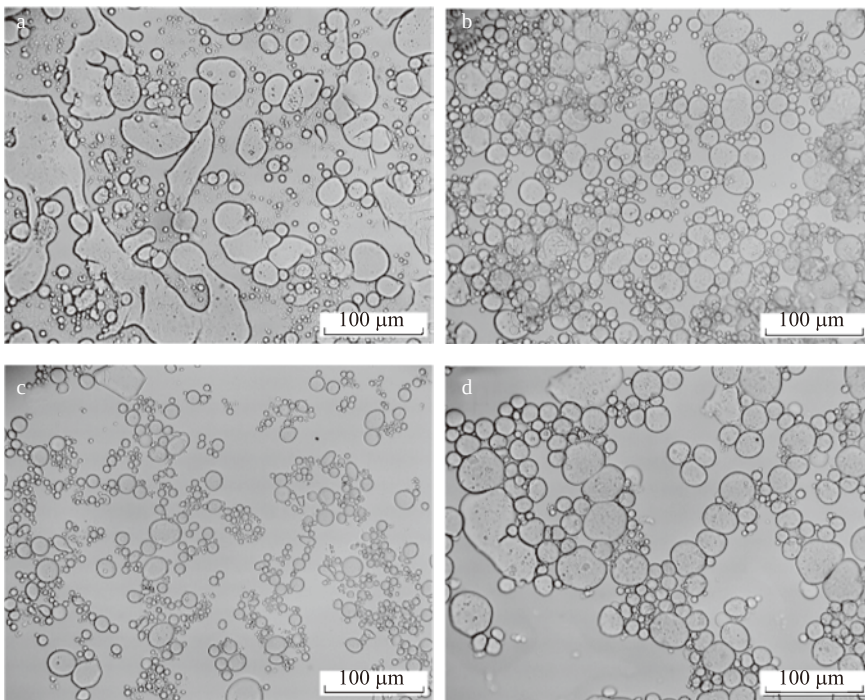


Fig. 7 Optical images of ASA emulsions stabilized by 2% laponite (a) alone and with (b) 2% chitosan, (c) 4% chitosan, and (d) 10% chitosan based on laponite

introduction of laponite significantly reduces the charge amount of starch for the preparation of stable emulsions. Increasing the laponite-to-starch mass ratio enhances the creaming stability, decreases the emulsion droplet size, and greatly improves the sizing performance of ASA emulsions because of the synergistic stabilizing effect of starch and laponite particles, as schematically shown in Fig.8. In laponite-stabilized ASA emulsions, the presence of native maize starch can reduce the deterioration of the sizing performance with increasing

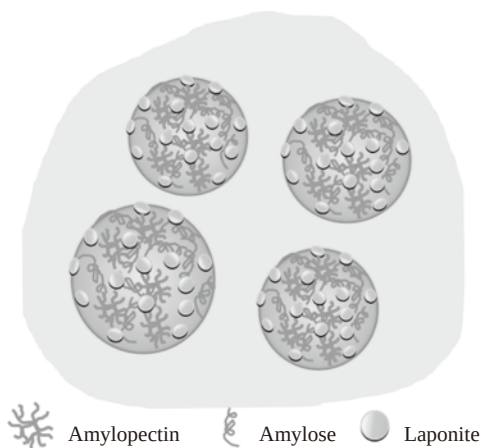


Fig. 8 Schematic of an ASA emulsion co-stabilized by corn starch and laponite

emulsion storage time^[34].

3.3 Use as a stabilizer after modification with small surfactant-like molecules

Alkylamines, such as ethylamine, propylamine, and butylamine, can moderately reduce the negative charges of laponite particles and lower the interfacial tension between ASA and laponite in aqueous dispersions^[23]. The former effect facilitates the adsorption of laponite particles at the ASA-water interface, whereas the latter effect favors the break-up of large drops during emulsion preparation. Thus, ethylamine, propylamine, and butylamine were found to substantially improve the stabilization of partly hydrolyzed

ASA (PH-ASA) emulsions and the sizing performance of laponite-stabilized PH-ASA emulsions. Of these three alkylamines, butylamine is the most efficient one in promoting the emulsification and sizing development of PH-ASA because it exerts the greatest impact on the properties of laponite^[23]; i.e., alkylamines with longer chain length modify laponite more efficiently and, consequently, improve the sizing performance of laponite-stabilized ASA emulsions to a greater extent. Comparing the effect of alkylamine-modified laponite with or without the removal of free alkylamines revealed that alkylamine molecules adsorbed on laponite stabilize PH-ASA emulsions more efficiently because of the increased affinity of laponite particles for ASA. In contrast, free alkylamines in modified laponite dispersions promote the sizing development of PH-ASA emulsions by accelerating the reaction between hydrolyzed ASA and Al sulfate^[23]. However, alkylamine-modified laponite-stabilized PH-ASA emulsions are not stable against further hydrolysis and lose most of their sizing effects within 60 min. The accelerating effect of alkylamine-modified laponite

on the sizing performance of ASA emulsions was further confirmed by the high sizing performance of ASA emulsions stabilized by butylamine-modified laponite^[35].

Alkylamines with more than one alkyl group connected to one N atom, such as diethylamine and triethylamine, can also reduce the negative charges of laponite particles, increase the turbidity of aqueous dispersions of laponite, and decrease the interfacial tension between ASA and laponite in aqueous dispersions when they are used to modify laponite. However, compared to ethylamine, the influence of diethylamine on the properties of laponite is stronger, whereas that of triethylamine is weaker^[36]. For ethylamine and diethylamine, ASA-in-water emulsions with the smallest droplet sizes and highest stability are obtained at an amine-to-laponite mass ratio of 1.5%, whereas for triethylamine, such emulsions are achieved at a mass ratio of 2.0%. Diethylamine-modified laponite-stabilized emulsions possess the smallest droplets, whereas triethylamine-modified laponite-stabilized emulsions exhibit the largest droplets, as schematically shown in Fig.9. Consequently, among amine-modified laponite-stabilized emulsions with the smallest droplet sizes, compared to ethylamine, the use

of diethylamine results in higher sizing performance, whereas the use of triethylamine results in lower sizing performance^[36].

Urea molecules contain two NH_2 groups joined by a carbonyl group. Urea causes the dehydration of laponite particles and slightly reduces their negative charges but hardly induces their aggregation^[13]. Its aqueous solution is neutral, and thus, when urea-modified laponite is used to stabilize ASA emulsions, the alkaline-catalyzed hydrolysis of ASA can be avoided. These features make urea a good modifier for laponite used to stabilize ASA emulsions. ASA emulsions with high stability and small droplet sizes can be prepared at a urea-to-laponite mass ratio of 1 : 2; at this value, the modification of the laponite particles is maximized. Using urea to modify laponite not only enhances the sizing performance of ASA emulsions but also reduces ASA hydrolysis. Even if the emulsion storage time is as long as 120 min, the sizing performance of ASA emulsions stabilized by urea-modified laponite hardly changes^[13].

Alanine is an α -amino acid with both amino and carboxyl groups. Using alanine to modify laponite reduces the aggregation of laponite by increasing its negative charge density and lowers the apparent interfacial tension between ASA and laponite in aqueous dispersion by promoting the adsorption of laponite particles at the ASA-water interface. This feature benefits the preparation of ASA emulsions with enhanced stability, reduced droplet sizes, and improved hydrolysis resistance when the charge amount of alanine is less than 1 mmol/g based on laponite. Additionally, the sizing efficiency of the as-prepared ASA emulsions is improved by the modification of laponite with alanine^[14].

Melamine is a trimer of cyanamide that is less soluble in water than alkylamine, urea, and alanine because

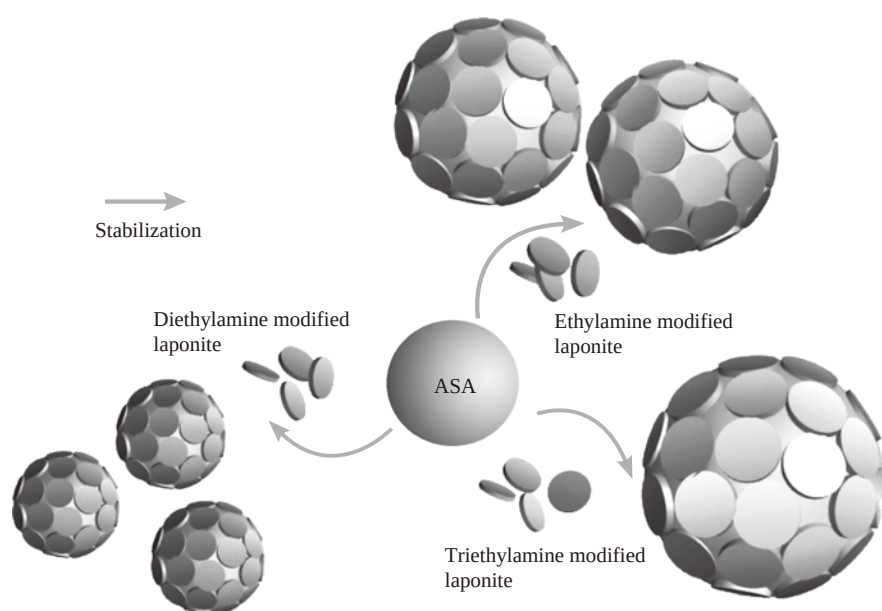


Fig. 9 Schematic illustration of ASA emulsions stabilized by laponite particles modified with ethylamine, diethylamine, and triethylamine

of its 1,3,5-triazine skeleton; however, it carries more amino groups. Modifying laponite with melamine does not cause the aggregation of laponite particles or significantly change their charge properties. However, the adsorption of melamine on laponite can significantly increase the laponite's ASA-wettability and adequately lower the apparent interfacial tension between ASA and laponite in aqueous dispersion when the melamine-to-laponite mass ratio is less than 3%. These effects enhance the adsorption of laponite particles at the ASA-water interface, improve the emulsion stability, and reduce the emulsion droplet size. Consequently, the sizing performance of ASA emulsions is improved when they are stabilized by melamine-modified laponite. The ASA emulsion with the smallest droplet size and best sizing performance is produced at a melamine-to-laponite mass ratio of 3%. Additionally, the modification of laponite with melamine can substantially limit the growth of emulsion droplets and the hydrolysis of ASA, thereby decreasing the loss in the sizing performance of the ASA emulsions with time^[37].

Tetramethylammonium chloride (TMAC) is a quaternary ammonium salt with the shortest possible hydrocarbon groups. When it is used to modify laponite, TMAC only moderately neutralizes the negative charges of laponite particles by ion-exchange and enhances the turbidity of aqueous dispersions of laponite by enhancing the hydrophobicity of the laponite particles, which favors the adsorption of laponite particles at the ASA-water interface. Additionally, TMAC significantly decreases the interfacial tension between ASA and water/aqueous laponite dispersion, thereby promoting the formation of emulsions with small droplets. When the added amount of TMAC reaches 1wt% based on laponite, the as-prepared ASA emulsions have small droplet sizes, low viscosity, and uniform droplet size distributions and exhibit good creaming/coalescence stability. Using TMAC to modify laponite nanoparticles also significantly improved the hydrolysis stability and sizing performance of ASA emulsions^[38].

4 Other particle stabilizers

4.1 TiO₂ nanoparticles

The isoelectric point of TiO₂ nanoparticles is approximately pH 6.4, whereas aqueous dispersions of TiO₂ nanoparticles are generally acidic. Therefore, when used to stabilize ASA emulsions, the aqueous-phase TiO₂ nanoparticles carry weak positive charges. This characteristic favors the adsorption of TiO₂ nanoparticles at the ASA-water interface. Consequently, ASA aqueous emulsions stabilized by 0.5%~3.5% TiO₂ nanoparticles (based on ASA) have high creaming stability^[18]. Fig.10 schematically shows an ASA-in-water emulsion stabilized by TiO₂ nanoparticles. Similar to other particle-stabilized ASA emulsions, increasing the fraction of TiO₂ nanoparticles decreases the emulsion droplet size and increases the sizing efficiency of the ASA emulsions. Nevertheless, the free TiO₂ nanoparticles in the water phase lower the sizing effects of ASA emulsions. Therefore, the emulsion with the highest sizing performance is obtained at a TiO₂ nanoparticle-to-ASA mass ratio of 2.5%^[19]. Although TiO₂-stabilized ASA emulsions have much high stabilities and relatively small droplet sizes, their sizing performances are generally lower than those of laponite-stabilized ASA emulsions, particularly when the ASA content is lower than 0.4 wt% based on paper furnishes.

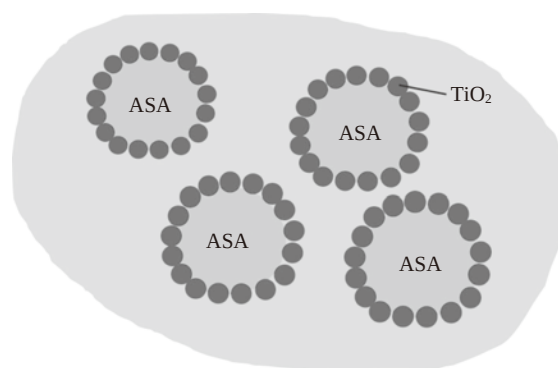


Fig. 10 Schematic of an ASA aqueous emulsion stabilized by TiO₂ nanoparticles

To improve the sizing performance of ASA emulsions stabilized by TiO₂ nanoparticles, PAS was

introduced as a co-stabilizer. However, ASA emulsions with nonspherical droplets were formed because of the lowering of the ASA-water interfacial tension by PAS^[21].

4.2 Fe₃O₄ nanoparticles

The application of Fe₃O₄ nanoparticles has attracted substantial attention in various research fields because of their ultra-fine particle sizes, biocompatibility, and superparamagnetic properties. When used to stabilize ASA emulsions, Fe₃O₄ nanoparticles protect ASA emulsions against coalescence, resulting in good sizing performance of ASA emulsions. Furthermore, they also confer magnetic properties to stabilized emulsions, making them deform readily in the presence a magnetic field^[22].

4.3 CNCs

CNCs, which are also called nanocrystalline cellulose (NCC), are nanofibers that are generally prepared by the H₂SO₄ hydrolysis of cellulose materials. After cationic modification by glycerol trimethylammonium chloride, CNCs have been used to stabilize cationic starch-stabilized ASA emulsion^[24]. The cationic CNCs adsorbed on the surfaces of ASA droplets form a multilayer structure around the droplets, thereby improving the dispersity and stability of cationic starch-stabilized ASA emulsions. Therefore, ASA emulsions co-stabilized by CNCs and cationic starch exhibit reduced ASA hydrolysis and improved sizing efficiency. The introduction of cationically modified CNCs also improves the tensile strength and burst strength of ASA emulsion-sized paper^[24].

5 Conclusions

Using nanoparticles to stabilize ASA emulsions provides a new approach for preparing ASA emulsions with high ASA content and good sizing performance. Montmorillonite, laponite, TiO₂, and Fe₃O₄ are all able to stabilize ASA emulsions when used alone, after modification, or with other nanoparticles. In terms of sizing development, laponite is currently the most competent nanoparticle stabilizer for ASA emulsions.

Acknowledgments

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