Using Chitosan as Sizing Promoter of ASA Emulsion Stabilized by Montmorillonite

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Chitosan was used as a sizing promoter to improve the sizing performance of ASA emulsion stabilized by montmorillonite. It was found that chitosan with low molecular weight significantly improved the sizing performance of ASA emulsion without inducing the flocculation of the ASA droplets when the amount was less than 0.125% based on ASA. Confocal fluorescence microscopy revealed the formation of chitosan shell around the ASA droplet. Adding ammonia into the emulsion induced desorption of chitosan from the ASA droplet surface and the ammonolysis of ASA. The former reduced the ASA emulsion stability, while the latter resulted in the secondary emulsification of ASA-water system. Meanwhile, the presence of ammonia was demonstrated to be detrimental to the sizing performance of the ASA emulsion. The hydrolysis resistance of the ASA emulsion was higher when chitosan was present.

Keywords: Chitosan; Montmorillonite; Pickering emulsion; ASA; Sizing

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INTRODUCTION

Chitosan is a linear polysaccharide consisting of β-(1-4) linked D-glucosamine with randomly located N-acetyl-glucosamine groups depending upon the degree of deacetylation of the polymer (Khor and Lim 2003). Chitosan dissolves in aqueous acidic solutions to form a cationic polymer with a high charge density (Rinaudo 2006). The physicochemical properties of chitosan are greatly dependent on its molecular weight, especially when the degree of deacetylation (DAC) is identical. The relative molecular weight of chitosan prepared from natural resources usually falls within a range of 10^5 to 10^6. Compared with high molecular weight products, low molecular weight chitosan exhibits some peculiar features, including enhanced antimicrobial activity for some bacteria due to its penetration into living cells (Zhang and Zhu 2003) and increased ease of dissolution in water. These properties give chitosan enormous potential as a natural polymer for applications in food and pharmaceutical industries, particularly in encapsulation or delivery systems for drugs (Rinaudo 2006). Low-molecular-weight chitosan can be obtained by chemical (Fedoseeva *et al*. 2006) or enzymatic hydrolysis (Nordtveit *et al.* 1996). Currently, the hydrolysis of chitosan using H_2O_2 as an oxidizing agent is widely used, and the depolymerization procedure is thought to be homogeneous and relatively simple to operate (No *et al.* 2003).

Alkenyl succinic anhydride (ASA) is a reactive sizing agent commonly used in neutral/alkaline papermaking to impart water resistance to paper (Chen *et al.* 2012; Hubbe 2006). ASA is an oily liquid at room temperature and possesses high reactivity. These properties allow it to spread conveniently on cellulose fiber surface during the drying process and to develop adequate sizing degrees for paper on a paper machine when added to paper slurry as an aqueous emulsion. As an anhydride, ASA reacts easily with water to form a product with amphiphilic nature (Wasser 1987). The hydrolyzed product (ASA-acid) may promote the spreading of ASA by lowering the interfacial tension between fiber and ASA as well as between fiber and water when a thin film of water occurs on the fiber surface (Zhmud *et al.* 2001), contributing to the quick development of ASA sizing. On the other hand, the ASA-acid may diminish the sizing performance of ASA (Wasser and Brinen 1998) since it is ineffective in paper sizing when added to paper slurry (Nishiyama *et al.* 1996) and induces uneven distribution of ASA by destabilizing ASA emulsions (Isogai 2000).

Naturally originated sizing agent prepared by reaction between maleic anhydride and esters from vegetable oils such as alkyl oleates can resist hydrolysis in the aqueous emulsion better than ASA (Isogai and Morimoto 2004). However, its sizing effect is lost completely by two days after its preparation (Isogai and Morimoto 2004). Therefore, ASA, including all products from the process of reacting maleic anhydride and esters from vegetable oils, is generally dispersed in water *in situ* with the aid of surfactant and protective colloids such as cationic starch (Isogai and Morimoto 2004; Houze and Szadecski 2005), cationic starch together with aluminum sulfate (Jaycock *et al.* 2000), hydrophobically modified and acid-hydrolyzed starches (Lee *et al.* 2004), nonionic galactomannan (Koskela *et al.* 2003), natural gum (Dostie and Nowicki 1998), grafted starch co-polymer (Farley *et al.* 2002), synthetic cationic polymers (Glover 1997; Wasser 1997) and cationic colloidal coacervate (Lauzon 2001). Of the various protective colloids, cationic starch is used most extensively. However, the cationic starch-based emulsifiers used here should be cooked (Chen *et al.* 2012) with additional cooking equipment. The obtained ASA emulsion has a fairly low concentration since a large amount of starch has to be employed to improve the sizing performance and reduce ASA emulsion hydrolysis (Lee *et al.* 2004).

It is now well established that solid particles can serve as stabilizers for emulsions which are often called Pickering emulsions (Aveyard *et al.* 2003). The solid particles anchored at the oil-water interface can develop strong lateral interactions, which results in the formation of a very rigid stabilizing film acting as a mechanical barrier to prevent the coalescence of emulsion droplets (Aveyard *et al.* 2003). Stable ASA emulsions with high ASA concentrations have been successfully prepared by using various particles as stabilizers either alone (Zhao *et al.* 2013) or together with other co-stabilizers (Ding *et al.* 2011; Li *et al.* 2012; Li *et al.* 2013; Qian *et al.* 2013; Wang *et al.* 2013; Yu *et al.* 2013). Using montmorillonite as a particle stabilizer has the advantage of being low cost, achieving suitable particle sizes with considerably low energy input (Martorana *et al.* 2008), and the obtained emulsion displays adequate sizing performance (Yu and Liu 2008). However, ASA emulsions stabilized by montmorillonite particles cannot prevent ASA from hydrolyzing due to the permeability of water through the montmorillonite particle layers.

Colloidosomes are microcapsules with a shell composed of densely packed colloidal particles (Dinsmore *et al.* 2002). Gordon *et al.* (2004) have designed and fabricated a colloidosome capsule whose shell is composed of poly-L-lysine and polystyrene beads. Poly-L-lysine molecules adsorb to and lock neighboring polystyrene beads together on the droplet surface. Originating from the idea of the colloidosome capsule, the present study aimed at preparing an ASA emulsion armored with a shell of montmorillonite and chitosan to further increase the mechanical barrier for ASA hydrolysis, and thus to improve the sizing performance and sizing stability of ASA emulsion with respect to time. An ASA emulsion stabilized by montmorillonite was first prepared as the template. Then, acetic acid protonated chitosan was added and adsorbed on the negative surface of ASA droplets, forming a stable shell together with montmorillonite particles.

It is theoretically believed that ammonia addition into the emulsion can induce chitosan deprotonation and deposition on the surface of ASA droplets, composing a rigid film protecting ASA from severe hydrolysis. Chitosan samples with different molecular weights were prepared, and the effects of chitosan molecular weight as well as addition level on the stability and sizing performance of ASA emulsions were studied. The article also reports the behavior of ammonia in the emulsion preparation and internal sizing, and the effects of chitosan/ammonia on the hydrolysis stability of ASA emulsions. The results confirm that adding low molecular weight chitosan to MMT-stabilized ASA emulsion can actually improve the sizing performance of the ASA emulsion and prevent the sizing performance of ASA emulsion from deteriorating with time. However, the introduction of ammonia induces the flocculation of chitosan/MMT stabilized ASA emulsion at low addition levels and results in secondary emulsification of the emulsion at high addition levels due to the ammonolysis of ASA. Consequently, the introduction of ammonia generally reduces the sizing performance of the ASA emulsion.

EXPERIMENTAL

Materials

Chitosan (DAC>85%, M_η=56.36×10^4) was obtained from Jinan Haidebei Marine Bioengineering Co., Ltd. ASA is a commercial product with a trade name of Hydroes AS2300 and supplied by Kemira Chemicals, Inc. Montmorillonite (MMT) was obtained by purifying and modifying bentonite with sodium fluoride (Dong and Liu 2006).

Aspen bleached chemi-mechanical pulp (BCTMP) was provided by Shandong Huatai Paper Co., Ltd and refined to 30 ^{o}SR with a valley beater before use. Cationic acrylamide copolymer (CPAM) with a product name of Percol 292 was provided by Ciba Specialty Chemicals Ltd. Hydrogen peroxide, acetic acid, ammonia, and other chemicals were all analytically pure reagents.

Degradation and Molecular Weight Determination of Chitosan

Chitosan was chemically degraded by hydrogen peroxide. In a typical process, chitosan solution containing 7.5 g chitosan and 500 mL of 1% (w/v) acetic acid was heated to 70 ^{o}C and mixed with 10 mL of 30% (w/w) hydrogen peroxide at a stirring rate of 350 rpm to start the degradation reaction. After 15 to 180 min, the reaction was terminated by cooling the resultant solution to room temperature. Chitosan that was not heavily degraded was precipitated by adjusting the pH of the resultant solution to 8 with 2 M sodium hydroxide. The precipitate was separated by filtration, thoroughly washed with distilled water, and dried in a vacuum oven at 40 ^{o}C for 3 days to obtain degraded chitosan samples (shown in Table 1).

Table 1. Characterization of Five Chitosan Samples Obtained by Degradation

Chitosan samples	Degradation reaction time (min)	Intrinsic viscosity, [η] (mL/g)	Molecular weight, M_η ($\times10^4$)
1	0	403.7	56.36
2	30	383.7	53.36
3	60	249.7	33.62
4	90	187.3	24.68
5	180	95.4	11.95

To determine chitosan average molecular weight, chitosan sample was dissolved in 100 mL aqueous solvent containing of 0.01 mol acetic acid and 0.02 mol sodium chloride. A Ubbelohde viscometer with a capillary internal diameter of 0.5 mm was used to measure the viscosity, η, of the chitosan solution with different concentrations, C, and the viscosity, η_0, of the aqueous solvent at 25 ± 0.5 °C. The intrinsic viscosity $[\eta]$ was determined by the ratio of specific viscosity η/η_0 to the concentration C that was extrapolated to zero. Average molecular weights (M_η) were calculated by the following equation: $[\eta]=1.81\times10^{-3}\ M_\eta^{0.93}$ (Maghami and Roberts 1988). The results were listed in Table 1.

Preparation of ASA Emulsions and Adsorption of Chitosan on ASA Droplets

To prepare ASA emulsions, montmorillonite (5% based on ASA) was first dispersed in deionized water and stirred for 1 min at 3000 rpm. The resultant dispersion was employed as water phase and added to ASA at a mass ratio of 2:1 (water phase to ASA), and then the mixture was stirred at 12000 rpm with FM200 high shear dispersing emulsifier (FLUKO Equipment Shanghai Co., Ltd.) for 3 min to obtain an ASA-in-water emulsion (E1) with an ASA mass fraction of 33%.

The adsorption of chitosan on ASA droplet surfaces was carried out as follows. Chitosan solution with a concentration of 0.5% (w/w) was first prepared by dissolving chitosan in 1% acetic acid. After being diluted with deionized water, the chitosan solution was mixed with the ASA emulsion (E1). The mixture was stirred at 3000 rpm for 1 min to obtain ASA emulsion (E2) adsorbed with chitosan. The mass fraction of ASA in the ASA emulsion (E2) was fixed at 24%.

As for the deprotonation of chitosan adsorbed on ASA droplets, diluted ammonia was added into the ASA emulsion (E2), and the mixture was stirred at 3000 rpm for 1 min. The ASA content of the obtained ASA emulsion (E3) was maintained at 20% by means of dilution with aqueous ammonia solution.

Characterization of ASA Emulsions

The stability of ASA emulsions was expressed by final emulsion volume fraction, the ratio of the emulsion volume to the total volume of the emulsified system measured immediately after it was prepared and centrifuged at 4000 rpm for 10 min. The hydrolytic stability of the ASA emulsion as a function of time was evaluated by the variation of the sizing performance of ASA emulsion, which was stored at room temperature (~25 °C). Higher final emulsion volume fraction and less variation of the sizing performance mean better emulsion stability and higher hydrolytic stability, respectively.

The droplet size and morphology of the ASA emulsions were analyzed using BK2000/BK3000 optical biomicroscope (Chongqing Optical & Electrical Instrument Co. Ltd). The viscosity of the ASA emulsion was determined using NDJ-8S rotation viscometer (Shanghai Precision & Scientific Instrument Co., Ltd.).

Confocal fluorescence microscope (FV300-LX71, Olympus Corporation, Japan) was used to analyze the distribution of chitosan in ASA emulsion stabilized by MMT. Chitosan was labeled with fluorescein isothiocyanate isomer I (FITC, sigma, F7250-250MG, 90+%, HPLC). For the preparation of the labeled sample, 0.15 g chitosan was first dissolved in 15 mL of 0.1 M aqueous solution of acetic acid, and then its pH was adjusted to 7.5 with 1 M sodium hydroxide. FITC ethanol solution was subsequently added to the chitosan sample, and the mixture was incubated at 25 ^{o}C for 4 h. The unreacted FITC was deactivated with 0.2 M sodium hydroxide, while the labeled chitosan was separated and washed by centrifugation at 10000 rpm using 70% (v/v) ethanol as rinsing agent until no fluorescence of the supernatant was detected at 495 nm (Son *et al.* 2003). The sediment was freeze dried to powder and kept in the dark at 4 ^{o}C.

Handsheet Making and Sizing Measurement

The ASA emulsion was diluted to 2% with deionized water just before handsheet making. BCTMP pulp was defibrated at a concentration of 1.5% (w/v) for 30000 revolutions and diluted with tap water to obtain a 1.0% (w/v) pulp suspension. Then 0.5% (w/w) of ASA and 0.02% (w/w) of CPAM based on oven-dry pulp were added in sequence. After each addition, the pulp suspension was stirred for 60 s at 500 rpm. Then, the stirring speed was adjusted to 1200 rpm letting the pulp suspension undergo 30 s of high shearing followed by the addition of 0.2% (w/w) of montmorillonite based on the oven-dry pulp at a stirring speed of 500 rpm. After the stock suspension was mixed for 30 s, handsheets with a basis weight of approximately 60 g/m^2 were prepared on a PTI Rapid-Kőthen Blattbildner-sheet Former (ISO 5269-2). Finally, the formed and wet-pressed handsheets were dried on a FI 119 cylinder dryer (Lorentzen & Wettre) at 105^{o}C for 10 min.

The sizing degrees of the sized handsheets were measured according to China National Standard GB/T5405-2002 (Liu *at al.* 2008). In a typical process, the handsheets were cut into square paper samples of 30 mm×30 mm, and conditioned at 23±1 °C and 50±2% relative humidity for over 24 h. A paper sample was folded into a square vessel with a bottom of 20 mm×20 mm. The paper vessel was floated on the surface of 2 wt% ammonium thiocyanate solution, and a drop of 1 wt% ferric chloride solution was dripped on the bottom of the vessel at the same time. The penetration time was determined until red ferric thiocyanate spots appeared. The sizing degree of the handsheets was the average permeation time of 10 paper vessels, for which half of their inner bottom are wire-side of the handsheets (Qian *et al.* 2013).

RESULTS AND DISCUSSION

Effect of Chitosan Molecular Weight on Emulsion Properties

Molecular weight plays an important role in chitosan application. Chitosan with high molecular weight may induce bridging flocculation between ASA droplets when it is added to montmorillonite (MMT) stabilized ASA emulsion (E1). To screen out the appropriate chitosan, the effects of chitosan molecular weight on ASA emulsion stability and viscosity were investigated. Figure 1 shows the schematics of chitosan interaction with ASA droplets, as well as the appearance of ASA emulsions without adding chitosan (0) or added chitosan with the molecular weight of 11.95×10^4, 24.68×10^4, 33.62×10^4,

53.36×10^4, and 56.36×10^4 for (1), (2), (3), (4), and (5) in sequence (up), as well as the corresponding ASA emulsion stability and viscosity (down) at different chitosan molecular weights, respectively. The amount of chitosan added to MMT stabilized emulsions (E1) was 0.15% (w/w) based on ASA. The photograph was taken after the chitosan was added and balanced for 30 min.

As shown in Fig. 1, the emulsion solely stabilized by MMT (E1) was a uniform creamy white emulsion.

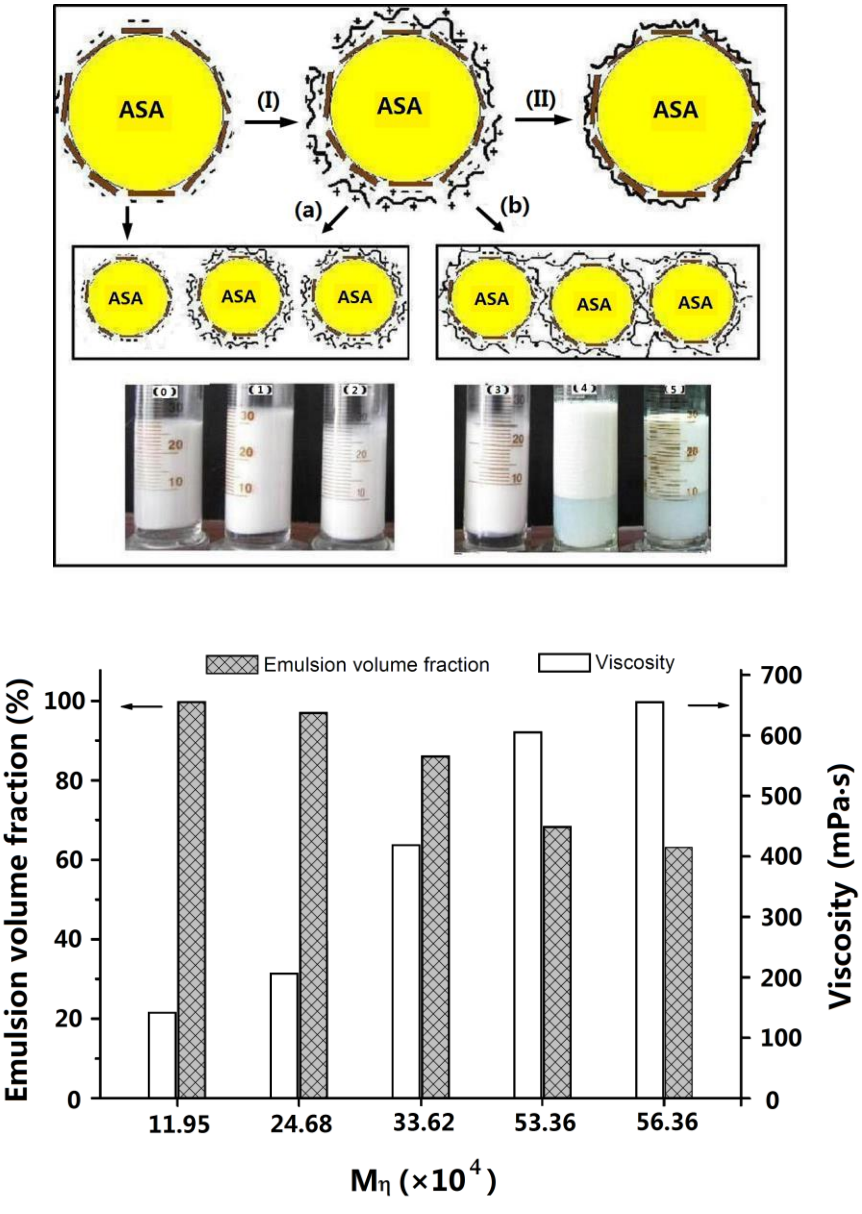

Fig. 1. Schematic interaction of chitosan with ASA droplets (top), appearance of ASA emulsions (middle), as well as the corresponding ASA emulsion stability and viscosity (bottom) at different chitosan molecular weights. (I) and (II) present addition of chitosan and ammonia, respectively. The arrows labeled by (a) and (b) stand for the added chitosan having lower and higher molecular weight, respectively. (0) corresponds to without adding chitosan; (1), (2), (3), (4), and (5) correspond to adding chitosan with the molecular weight of 11.95×10^4, 24.68×10^4, 33.62×10^4, 53.36×10^4, and 56.36×10^4, respectively.

When low molecular weight (LMW) chitosan, such as those with molecular weights of 11.95×10^4 and 24.68×10^4, were added, the emulsions (E2) were hardly changed in appearance. This implied that the chitosan molecules were not long enough to span ASA droplets, thus no flocculation occurred among ASA droplets. Also, the added amount of chitosan was not large enough to cause the coagulation of ASA droplets by charge neutralization or patch mechanism although the chitosan possesses a much higher charge density due to the protonation of its amino groups. As the molecular weight of chitosan was increased to 33.62×10^4, a water phase started to be separated at the bottom of the cylinder, suggesting the bridging effect of chitosan molecules among the droplets. Further increasing the molecular weight of chitosan induced a catastrophic coalescence of ASA droplets. This result was in accordance with the emulsion volume fraction, *i.e.*, ASA emulsions added with lower molecular weight chitosan sustained a higher emulsion volume fraction after centrifugation.

The viscosity of ASA emulsion increased with increasing molecular weight of chitosan, as also shown in Fig. 1. Chitosan with higher molecular weight should favor the improvement of emulsion stability since higher viscosity implies less free water among the ASA droplets, resulting in less water resolved. However, more water was released with increasing molecular weight of chitosan, as shown in Fig. 1 (top). This provided indirect evidence for the bridging of chitosan with higher molecular weight among ASA droplets. Therefore, within this series of samples, chitosan with $M_\eta=24.68\times10^4$ or less was optimal for adsorption onto the surface of ASA droplet as well as for maintaining a high emulsion stability.

Effect of Chitosan Concentration on Emulsion Properties and Sizing Effect

Since the yield of chitosan with $M_\eta=11.96\times10^4$ was pretty low in this study, the chitosan with $M_\eta=24.68\times10^4$ was used in the subsequent experiments. The effects of chitosan concentration on the droplet diameter, stability, and sizing performance of MMT stabilized ASA emulsions are shown in Fig. 2.

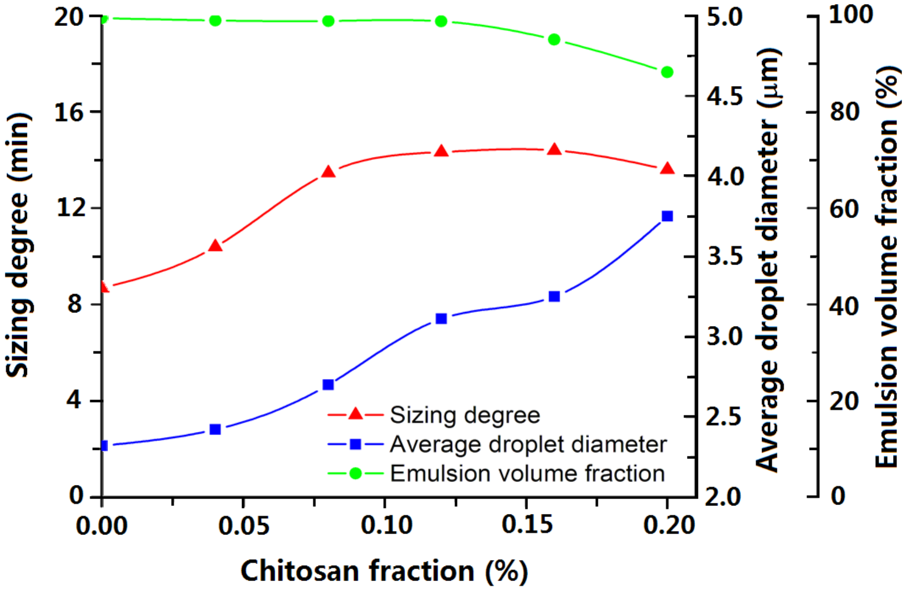

Fig. 2. Effect of chitosan (Mη=24.68×104) fraction on average droplet diameter (■), stability(●), and sizing performance (▲) of MMT stabilized ASA emulsion

The droplet diameter of the ASA emulsion increased with increasing concentration of chitosan. When the chitosan fraction was higher than 0.125% (w/w, based on ASA), *i.e.*, the average diameter of the ASA emulsion exceeded 3 μm, and the physical stability of the emulsion started to decrease. Meanwhile, the sizing performance of the ASA emulsion was enhanced by adding chitosan, as long as the chitosan fraction was lower than 0.125%. Even when the chitosan fraction was higher than 0.125%, the instability and quick increase in average diameter of the ASA emulsion did not cause a significant decrease in the sizing performance. This suggested that the enhancement of the sizing performance of the ASA emulsion did not originate from the improvement of ASA emulsion stability or the reduction of average emulsion droplet diameter.

Function of Ammonia on Emulsion Properties and Sizing Effect

Chitosan adsorption onto the surface of an ASA droplet occurs as soluble cationic polyelectrolyte in acidic solution. If ammonia is added into the emulsion, chitosan can be precipitated, which theoretically may enable the chitosan to deposit on the surface of ASA droplet, forming a new solid protective barrier around ASA as schematically shown in Fig. 1. From this point of view, the droplet diameter, stability, and sizing performance of ASA emulsion was investigated after the introduction of ammonia. The result is shown in Fig. 3, where the chitosan fraction was 0.12% (w/w, based on ASA).

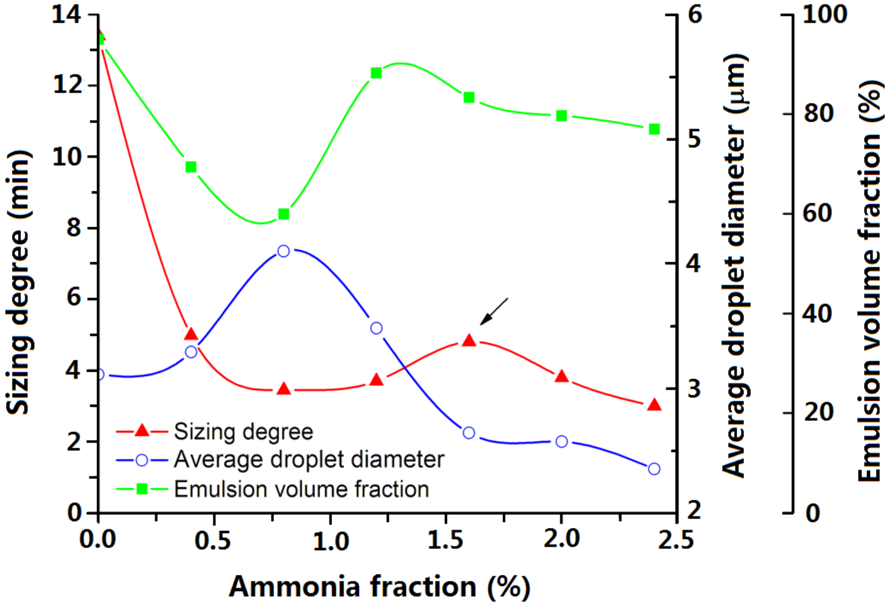

Fig. 3. Effect of ammonia fraction on average droplet diameter (○), emulsion stability (■) and sizing performance (▲) of ASA emulsion stabilized by MMT and chitosan

Figure 3 shows that the introduction of ammonia increased the average diameter of ASA droplets and decreased the emulsion stability when the added amount was less than 0.8%. When the ammonia fraction was between 0.8 and 1.2%, however, the former decreased while the latter increased with increasing amounts of ammonia. When the ammonia fraction was higher than 1.2%, both average droplet diameter and emulsion stability decreased. This indicated that ammonia at different addition levels played different roles in stabilizing the emulsions. In order to analyze the variation of ASA emulsion morphology and adsorption of chitosan with the increase of ammonia fraction, confocal fluorescence microscope images were taken and shown in Fig. 4. Apparently, the chitosan adsorbed on droplet surfaces before ammonia was added. Adding 0.5% of ammonia induced flocculation of ASA droplets, while preventing the droplet from complete coalescence due to the mechanical barrier of precipitated chitosan and MMT. By further increasing the amount of ammonia, the adsorbed chitosan desorbed from the surface of ASA droplets and transferred into the aqueous phase. Subsequently, the desorbed chitosan flocked together due to the interface tension between water and chitosan solids, resulting in the coalescence of ASA emulsion. However, when the added amount of ammonia reached 1.25%, the emulsion underwent a secondary emulsification, forming finer emulsions. This was in accordance with the result shown in Fig. 3. The secondary emulsification of ASA emulsion was probably due to the ammonolysis of ASA when extra ammonia existed under high ammonia fractions since a large amount of ammonia would significantly increase the pH of ASA emulsion and promote the hydrolysis of ASA. The formed ammonium salt of ASA-acid might act as a surfactant to reduce the interfacial tension between ASA and water.

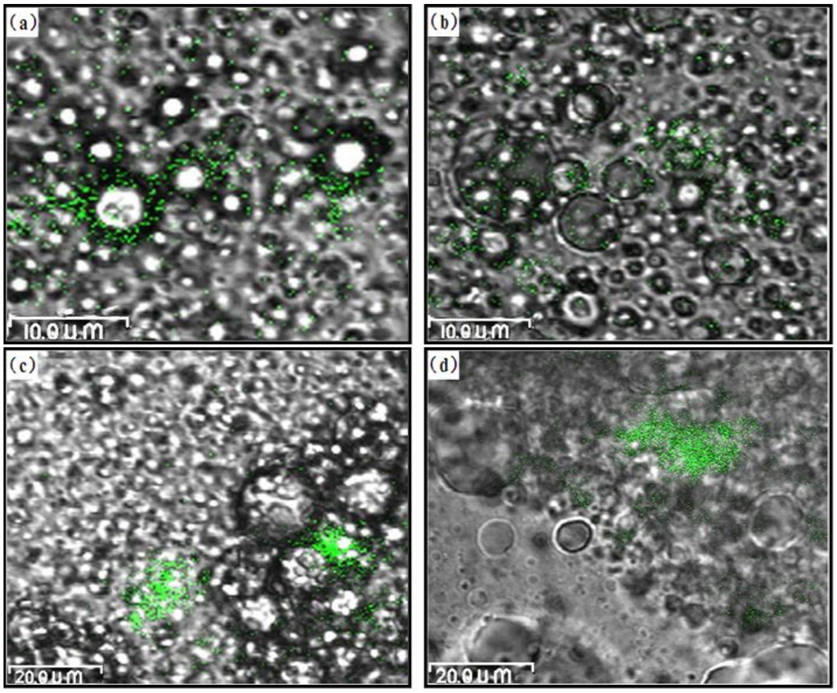

Fig. 4. Confocal fluorescence microscope images of chitosan/MMT stabilized ASA emulsions with different ammonia concentrations: (a) ammonia free (b) 0.5%; (c) 0.75%; (d) 1.25%

Figure 5 shows the droplet size distribution of ASA emulsions stabilized by MMT, MMT/chitosan, and MMT/chitosan/ammonia, respectively. As shown, the introduction of chitosan into the ASA emulsion stabilized by MMT increased the polydispersity of the emulsion, *i.e.*, considerable amounts of smaller droplets appeared even though the average droplet diameter increased. This indicated that the chitosan acted both as a coagulant and stabilizer of MMT stabilized ASA emulsion. The enhancement of the sizing performance of ASA emulsion by chitosan (as shown in Fig. 2) was partly attributed to the part of the emulsion with smaller droplet size. With the addition of ammonia, the emulsion became monodispersed and had the smallest average droplet diameter.

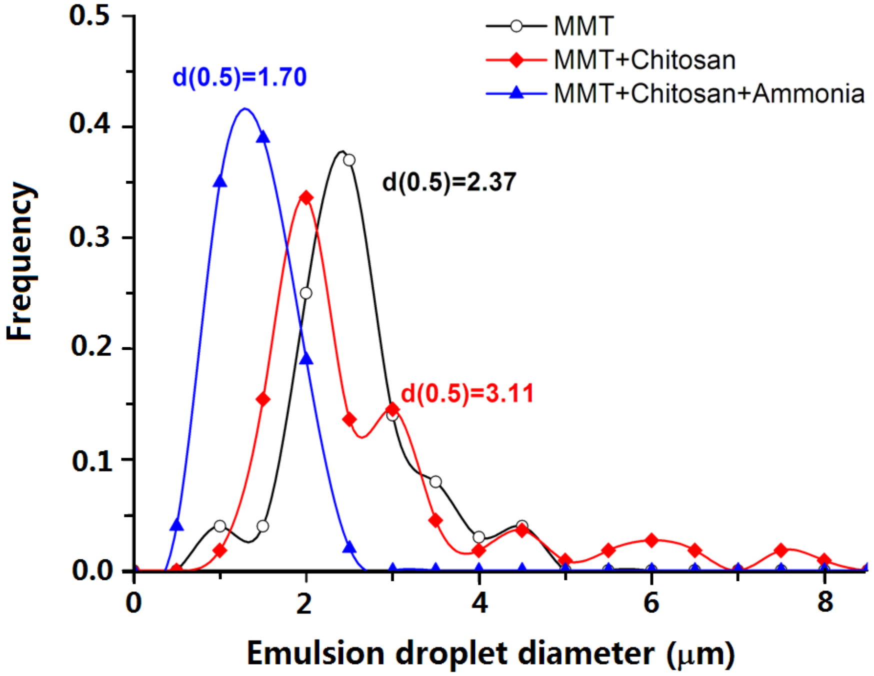

Fig. 5. Droplet size distribution of ASA emulsions stabilized by MMT, MMT/chitosan, and MMT/chitosan/ammonia, respectively. The fractions of chitosan and ammonia are 0.12% and 1.6%, respectively

The sizing performance of ASA emulsion stabilized by MMT/chitosan/ammonia was mainly dependent on the average droplet diameter when the ammonia fraction was less than 1.6%, *i.e.* the sizing degree changed oppositely with the average droplet diameter as shown in Fig. 3.

However, when the ammonia fraction exceeded 1.6%, the consumption of ASA by ammonolysis further impaired the sizing performance of ASA emulsion, resulting in its decrease with increasing ammonia fraction. Therefore, a maximum value occurred at the ammonia fraction of 1.6%. But on the whole, the introduction of ammonia was harmful for the sizing development of the ASA emulsion. From the viewpoint of ASA sizing, ammonia should not be introduced into the chitosan/ MMT stabilized ASA emulsion.

Sizing Stability of ASA Emulsions with Storage Time

The addition of chitosan either alone or together with ammonia to ASA emulsions stabilized by MMT was expected to form new barriers, which would reduce the direct contact of ASA with water. Therefore, the effect of emulsion storage time on the sizing performance of the ASA emulsion added with chitosan either alone or together with ammonia was investigated and compared with that stabilized by MMT alone (Fig. 6). The sizing performance of ASA emulsion stabilized by MMT decreased considerably after the storage time exceeded 20 min, while those added with chitosan or chitosan/ammonia were hardly changed within 40 min. This indicated that the introduction of chitosan or chitosan/ammonia increased the storage stability of ASA emulsions stabilized by MMT.

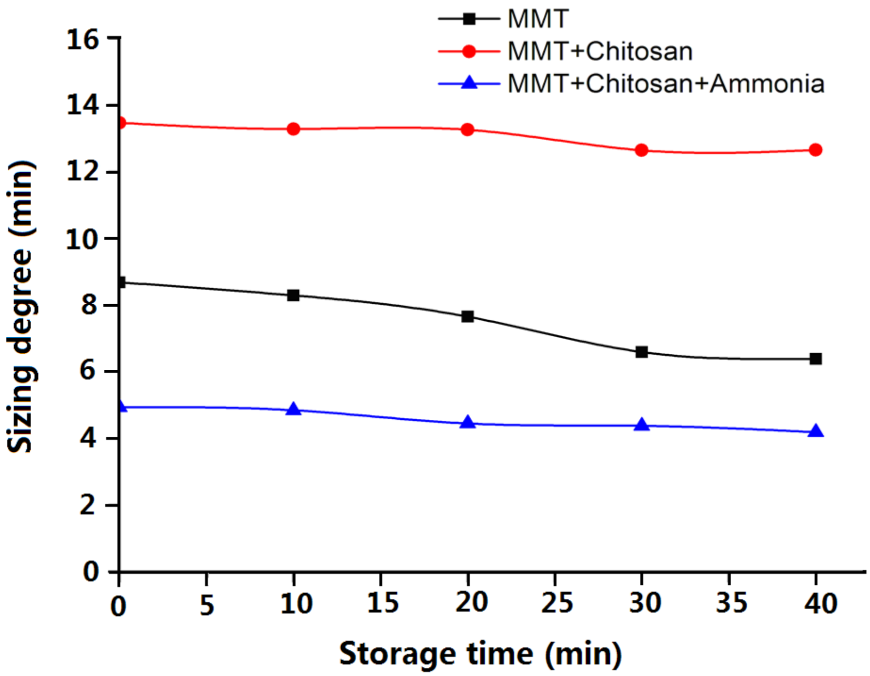

Fig. 6. Effect of storage time on sizing performances of ASA emulsions stabilized by MMT, MMT/chitosan, and MMT/chitosan/ammonia, respectively

CONCLUSIONS

1. Chitosan with low molecular weight enhances the sizing performance of montmorillonite (MMT)-stabilized alkenylsuccinic anhydride (ASA) emulsion without significantly reducing the emulsion stability when the addition level of chitosan is less than 0.125%.
2. Addition of ammonia into the emulsion induces chitosan desorption and ammonolysis of ASA, resulting in larger droplet size at lower addition levels and smaller droplet size at higher addition levels.
3. The presence of ammonia lowers the sizing performance of the ASA emulsion stabilized by MMT and chitosan.
4. The introduction of chitosan and ammonia enhances the sizing stability of ASA emulsions stabilized by MMT with time.

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