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Laponite and PAS Costabilized ASA Emulsion with High Hydrolysis Resistance and Sizing Efficiency

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ABSTRACT: ASA emulsions costabilized by Laponite and polyaluminum sulfate (PAS) were prepared by homogenizing the mixture of ASA and aqueous dispersion of Laponite and PAS. The properties, sizing performance and hydrolysis resistance of the prepared ASA emulsions, were investigated in this article. The results show that the introduction of PAS significantly improves the stability, hydrolysis resistance, and sizing performance of ASA emulsions. The ASA emulsion stabilized by 0.5% of Laponite (based on total mass of emulsion) and 2% of PAS (based on the mass of Laponite) shows high hydrolysis stability and high sizing efficiency on bleached chemi-thermomechanical pulp. At the addition level of 0.3% based on bleached chemi-thermomechanical pulp, the sizing degree of ASA-sized paper can be as high as 120 s. Even when the storage time of the ASA emulsion exceeds 3 h, its sizing performance is hardly changed. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

INTRODUCTION

In paper and paper board manufacture, internal sizing is used for making the end products more resistant to liquid penetration.[1–3] Alkenyl succinic anhydride (ASA), the product of internal olefins reacting with maleic anhydride, is one of the typical internal sizing agents in paper industry. It imparts water resistance to paper efficiently and introduced into papermaking system as an ASA-in-water emulsion.[4–12] However, ASA emulsion is unstable because of its high reactivity towards water. Its hydrolysis product, alkenyl succinic acid (ASA-acid), is ineffective in paper sizing[6,10] and causes deposit problem by forming sticky calcium salt during circulation with white water.[6,13] Therefore, it has to be converted into the emulsion form just before introducing into papermaking system. Once prepared, the aqueous emulsion must be used as soon as possible.[13,14]

For traditional ASA emulsions, the most commonly used stabilizers are surface active agents and polymers,[4,15–17] e.g., cationic starches in conjunction with lignosulfonates /naphthalene sulfonic acids. Unfortunately, using surfactants to disperse ASA usually leads to a series of disadvantages, such as interfering with sizing, causing foam problem, and complicating white water system, while using polymers to protect the ASA droplets leads to form a ASA aqueous emulsion with rather low concentration because a large quantity of polymers have to be employed in order to resist the hydrolysis of ASA.[17] Recently, much attention has been focused on particle stabilized emul-

sions i.e., Pickering emulsions,[18–23] because solid particles offer many advantages over the conventional surfactants for emulsion preparation, such as enhancing emulsion stability to coalescence, preparing emulsion with high internal phase fractions and eliminating or reducing of the adverse effects of surfactants.[24]. Particle stabilized emulsions also provide templates for preparing a variety of new materials and model systems for the investigation of particle mobility, aggregation, and assembly at the curved oil–water interface.[25,26] It is well established that solid particles adsorb to oil–water interface and develop strong lateral interactions, which results in the formation of a rigid film acting as a physical barrier to droplet coalescence.[19,23,27–29] Therefore, the solid particles adsorbed on the ASA–water interface prevent the water and ASA from directly osculating, reducing the hydrolysis reaction of ASA. Laponite is a synthetic hectorite with disk-shaped particles that have a diameter of about 25 nm. It has been extensively used as a particle stabilizer for preparing oil-in-water emulsions.[18,30–33] Our previous research has also demonstrated that Laponite is a competent particle stabilizer for aqueous emulsion of both ASA and partially hydrolyzed ASA after being modified by short amines.[34,35] However, the short-amine-modified Laponite-stabilized ASA emulsion significantly loses its sizing performance within 60 min as a result of the hydrolysis of ASA.[34] Aluminum sulfate is often used to reduce the adverse effect of hydrolyzed ASA on paper machine runnability and promote the development of water resistance in ASA-sized paper.[6] It hydrolyzes in papermaking system to form

polymeric aluminum species, i.e., polyaluminum sulfate (PAS). PAS can also be directly synthesized by peptizing the aqueous dispersion of aluminum sulfate and fresh aluminium hydroxide and employed as a particle stabilizer to stabilize aqueous ASA emulsion together with TiO_2 nanoparticle.[36] The PAS significantly reduces ASA–water interfacial tension and the hydrolysis of ASA. However, PAS with high basicity, a molar ratio of OH^-/Al^{3+}, makes the ASA–water interfacial tension too low to form spherical ASA emulsions even at low charge levels. Meanwhile, ASA emulsions stabilized by TiO_2 nanoparticle do not perform as well as those stabilized by Laponite and short amine.[37] In this article, aqueous ASA emulsion was prepared by using Laponite and PAS with low basicity as particle stabilizers. The PAS was expected to interact with either ASA or hydrolyzed ASA at water–ASA interface to resist the ASA from further hydrolysis. The sizing performance of the as-prepared ASA emulsion on aspen chemi-thermomechanical pulp (BCTMP) was also investigated.

EXPERIMENTAL

Materials

Aspen bleached BCTMP was supplied by a paper mill from Shandong province, China. It was refined for 11,000 revolutions with PFI mill (KRK Company, Japan) to about $40°SR$ (QB/T1463-2010) before use. Laponite was supplied by Rockwood Additives with a trade name of Laponite RD. It is a white powder composed of disk-shaped crystals with a thickness of about 1 nm and a diameter of 25–30 nm according to the supplier. High-resolution transmission electron microscopic image, which was taken with a JOEL JEM 2100 microscope, was used to verify the Laponite morphology. ASA was a commercial product from Dixie Chemical Company. It is a light-amber liquid at room temperature, being composed of more than 70 wt % of hexadecenylsuccinic anhydride ($C_{20}H_{34}O_3$,), less than 25 wt % of octadecenylsuccinic anhydride ($C_{22}H_{38}O_3$) and less than 2.5 wt % of mixed C_{15-20} olefins, according to the supplier's specification. The ASA has a density of 0.955 g/cm^3 at 25°C. Aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$, >99.0%), ammonia ($NH_3 \cdot H_2O$, 25–30 wt %), and other chemicals were analytical grades. Deionized water was thoroughly used in dissolving chemicals, dispersing particles and preparing emulsions.

Methods

Preparation of PAS and Laponite Water Dispersion. The PAS was prepared by peptizing the aqueous mixture of freshly synthesized aluminum hydroxide and aluminum sulfate. In a typical experiment, 80 mL of aluminum sulfate solution containing 0.1 mol aluminum and 60 mL of ammonia solution containing 0.31 mol of $NH_3 \cdot H_2O$ were simultaneously added dropwise into a three-necked flask under rapid stirring. The resulting slurry was further stirred for 30 min and repeatedly washed with deionized water, and centrifuged until its filtrate tested to be pH 7, thus obtained aluminum hydroxide. It was then mixed with aluminum sulfate solution containing 0.9 mol of aluminum, adjusted with deionized water to a concentration of 5 wt % (based on Al_2O_3), and then peptized for 2 h at 40°C and 4 h at 80°C consecutively under gentle stirring. The obtained PAS

had a basicity, which is defined as the molar ratio of OH^-/Al^{3+} of PAS,[38] of 0.3.

Aqueous dispersion of Laponite was prepared by dispersing the Laponite powder in deionized water and the dispersions were thermostatted at 25°C and stored for 72 h after preparation when changes in turbidity and phase separation had ceased.[18] PAS dispersion was prepared by diluting the PAS motherstock with deionized water. The surface and interfacial tension were determined by an automatic surface/interface tensiometer (JWY-200, Chengde Dingsheng tester) at 25°C.

Preparation and Characterization of Emulsions. Aqueous dispersions with various mass ratios of Laponite and PAS were prepared by dispersing a known mass of the latter into diluted Laponite aqueous dispersion under stirring. After thermostatted at 25°C, 45-mL particle dispersion was added into 15-mL ASA and homogenized using a FM200 high-shear dispersing emulsifier (FLUKO Equipment Shanghai) with a 10-mm head operating at 6000 rpm for 3 min to obtain ASA emulsion. Immediately after the homogenization, the emulsion was transferred into 100 mL measuring cylinder for emulsion stability evaluation or 100 mL breaker for conductivity and viscosity measurements. The conductivity and viscosity of the emulsion were determined using a DDS-11 digital conductivity meter (Shanghai Pengshun Scientific Instrument) with Pt/Pt black electrodes and a NDJ-8S Digital Display viscometer (Shanghai Precision & Scientific Instrument), respectively. The morphology of the emulsion was recorded on an OLYMPUS CX21 optical biomicroscope. The drop size and distribution of the emulsion were obtained by applying microscopic image analytical software supplied by manufacturer. The chemical variation of the ASA after being emulsified was characterized by infrared spectrum, which was recorded on Nexus 670 Fourier Transformation Infrared-Raman spectrometer (Thermo Fisher Scientific). The ASA was separated from ASA emulsion by dissolving 1-mL ASA emulsion in 10-mL acetone, which contains 2 g of anhydrous sodium sulfate and 2 g of anhydrous magnesium sulfate. After a period of more than 4 h reaction, the sulfate solids were removed by centrifugation, and the obtained solution of ASA in acetone was directly used for infrared analysis.

Handsheets Making and Sizing Degree Measurement. Handsheets with a basis weight of approximately 60 g/m^2 were prepared on a PTI Rapid-Kőthen Blattbildner-sheet Former (ISO 5269-2) and the preparation method can be found elsewhere.[35,39,40] The formed and wet-pressed handsheets were dried with a speed dryer at 105°C. The sizing degree of the handsheets was measured according to China National Standard GB/T460-2008. 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 ferricthiocyanate 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.

RESULTS AND DISCUSSION

Laponite particles are too hydrophilic to completely resist the release of ASA from ASA emulsion. Ding et al.[35] suitably reduced the hydrophilicity of the Laponite by using butylamine as a modifier and obtained stable partly hydrolyzed ASA emulsion. However, the butylamine-modified Laponite cannot resist the hydrolysis of ASA, resulting in the loss of sizing performance of the partly hydrolyzed ASA emulsion within 60 min. In addition, Binks et al.[41] inferred that particle aggregation could decrease OH group content because of interaggregate hydrogen bonding, making such particles more hydrophobic. Moreover, electrolyte could lead to coagulation of the particles[19] and increase particle–particle adhesion and effective hydrophobicity.[42] When weak coagulation/flocculation of particles was induced, emulsion stability could be significantly enhanced.[19] Therefore, the introduction of PAS into Laponite dispersion was expected to enhance the emulsion stability of ASA by either inducing weak coagulation of Laponite particles or reducing the hydrophilicity of the Laponite particles, so as to obtain stable emulsion with high hydrolysis resistance of ASA.

Effects of PAS Charge Amount on Properties of Laponite Aqueous Dispersion

Laponite particles are synthetic disc-shaped magnesium silicate crystals, typically 25 nm in diameter by 0.92 nm thick. The crystal faces have negative charge from isomorphic substitutions of Mg^{2+} ions with Li^+ ions, whereas the edges have pH-dependent charges from Mg–OH groups positive below a pH of 9, and Si–OH groups negatively charged.[43] The charge is balanced by predominantly Na^+ ions. When dispersed in deionized water, Laponite hydrates and swells to form a clear colloidal dispersion of nanoparticles (as shown in Figure 1) with the Na^+ ions forming double layers on the faces.[44]
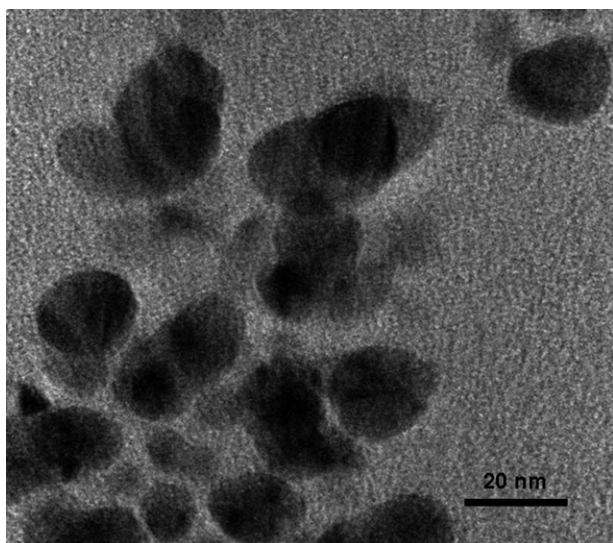

Figure 1. High-resolution transmission electron microscopic image of Laponite particles.
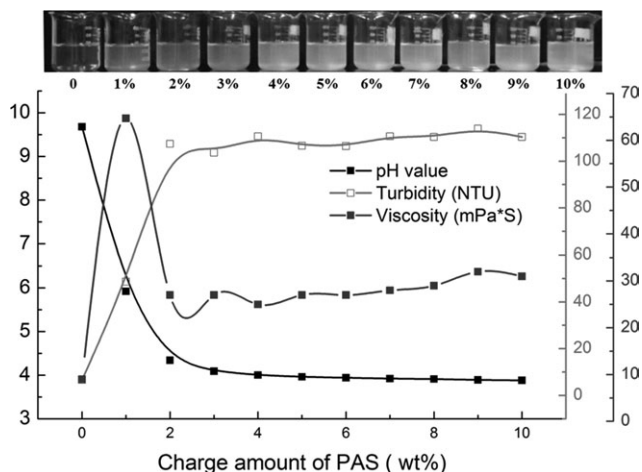

Figure 2. Appearances, pH, turbidity, and viscosity of Laponite aqueous dispersions as a function of PAS charge amount based on Laponite. Laponite concentration is 5 g/L.

Figure 2 shows the appearance, pH, turbidity, and viscosity of Laponite aqueous dispersions as a function of PAS, where the Laponite concentration was fixed at 5 g/L, the charge amount of PAS was based on Laponite. As shown in Figure 2, the Laponite aqueous dispersion is almost transparent in the absence of PAS. With the introduction of 1 wt % of PAS, which consists of polynuclear aluminum species with positive charges and act as a coagulant,[45] the dispersion becomes cloudy and its turbidity is increased sharply, indicating that the Laponite particles are coagulated by PAS to form particle clusters or flocs. Meanwhile the apparent viscosity is drastically increased to its maximum value 64.7 mP·s, suggesting the formation of flocs with uniform and open structure holding considerable amount of water. As the charge amount of PAS further increases, the viscosity is decreased remarkably while turbidity is increased, quickly indicating that the open particle clusters or flocs turn into clusters or flocs with denser structure. When the charge amount of PAS exceeds 2 wt %, both the viscosity and turbidity are hardly changed with PAS. This illustrates that the PAS cannot re-disperse the Laponite clusters or flocs into smaller flocs or single particles by reversing the face charge of Laponite particles. The natural pH value of the Laponite dispersions is 9.68 and the pH of the aqueous dispersion decreases systematically with increasing the charge amount of PAS. It plunges from 9.68 to 4.34 between 0 and 2 wt % of PAS charge amount, then, decreases slightly and levels off at 3.9 finally. The most noticeable reduction corresponds to the initiation of Laponite coagulation. This implies that edge charges also contribute to the coagulation of Laponite particles.

Although the reduction of interface tension is not the operative stabilization mechanism of particle-stabilized emulsion,[46] it plays a very important role in determining the emulsion's stability.[35,47] PAS is an inorganic polymer with high hydrolysis inclination[48] when in contact with water, rendering colloidal particles to stabilize emulsion. As an aluminum species with positive charge, PAS may also act with ASA by either Coulomb force or coordination. Therefore, the variations of surface
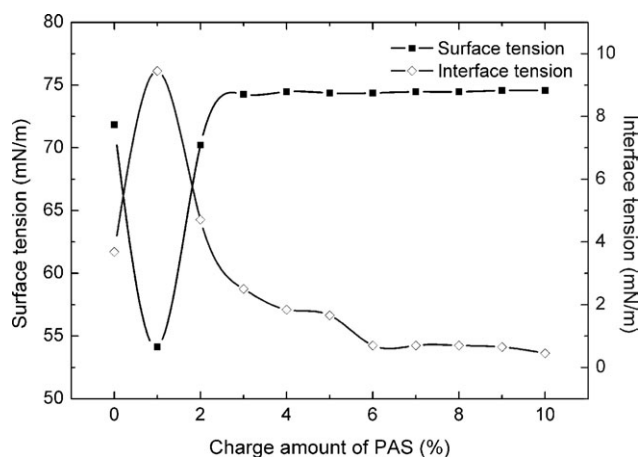
Figure 3. Effect of PAS charge amount on surface tension of Laponite aqueous dispersion and aqueous dispersion–ASA interface tension, where the Laponite concentration was corresponding to the emulsifying condition (0.5% based on the total mass of ASA and water, the mass ratio of ASA to water is 1:3).

tension of Laponite particle dispersion and interface tension between the aqueous dispersion and ASA with the charge amount of the PAS based on Laponite were investigated. The interface tension between ASA and water is 9.66 mN/m. As can be seen from Figure 3, the surface tension of Laponite dispersion without PAS is 71.83 mN/m, whereas the interface tension between the Laponite dispersion and ASA is 3.68 mN/m. The Laponite significantly lowers the interface tension because of its alkaline feature that promotes the hydrolysis of ASA, and the hydrolysis product acts as surface active substance to lower the interface tension. With the introduction of 1 wt % of PAS, the surface tension decreases remarkably to 54.43 mN/m, whereas the interface tension increases to 9.45 mN/m. The reduction of the surface tension is attributed to the spontaneous adsorption of PAS-induced Laponite clusters or flocs to the water surface, which decrease the internal energy and increase the entropy of the system, resulting in the lowering of the surface tension.[49] This may be evidenced by the maximum viscosity of the disper-

sion because the lowering of surface tension is only substantial for crystal-like particle suspensions.[50] The enhancement of the interface tension is because of the alteration from alkalinity to acidity of the Laponite dispersion, as shown in Figure 2. This alteration reduces the hydrolysis of ASA. Further increasing the charge level of PAS, the surface tension starts to increase as the structure of the Laponite clusters/flocs becomes denser and free PAS starts to play a role in enhancing the surface tension, whereas the interface tension starts to decrease rapidly because of the bonding of PAS with ASA by either hydrogen or coordination. The changes slow down as the charge level of PAS exceeds 3 wt %, which corresponds well with the viscosity variation of the Laponite dispersion, as shown in Figure 2. However, the interface tension can be decreased to as low as about 0.7 mN/m when the mass fraction of PAS exceeds 6%. This indicates that the interactions of aluminum species with carboxyl groups of ASA, either hydrolyzed or anhydride, promote ASA molecules to be orientated with their hydrophilic groups toward the water.

Effect of PAS Charge Amount on Properties of ASA Emulsion
ASA emulsions with ASA to water mass ratio of 1 : 3 have been prepared by homogenizing the mixture of ASA and Laponite aqueous dispersion containing various amounts of PAS. Figure 4 shows the appearance, apparent viscosity and conductivity of ASA emulsions measured immediately after preparation, where the charge amount of PAS is based on Laponite. As can be seen from Figure 4, all the as-prepared emulsions are milk-white and uniform emulsions without either water or ASA released. The conductivity of the ASA emulsion stabilized by Laponite alone is 150 μS/cm, whereas with the introduction of PAS, the conductivity is further enhanced because of the high conductivity of aluminum species in water. Therefore, all the as-prepared ASA emulsions are oil-in-water type.

According to the figure, the viscosity of the ASA emulsion shoots up from 12 to 200 mPa s initially, then decreases slowly and levels off at 100 mPa·s as the charge amount of PAS exceeds 2%. This variation trend is similar to that of Laponite aqueous dispersion, suggesting that the structure of particle cluster or
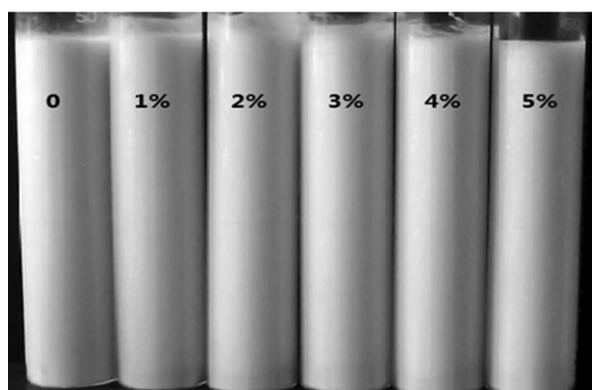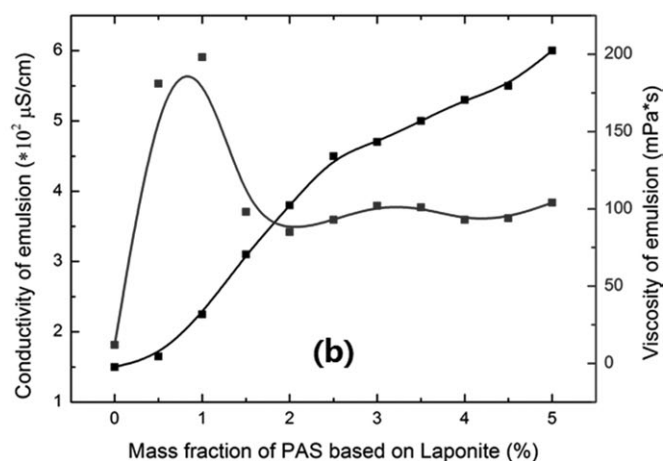
Figure 4. (a) Appearance, (b) viscosity and conductivity of ASA emulsion as a function of PAS charge amount based on the mass of Laponite. The concentration of Laponite in ASA emulsion is 0.5% (w/w). The mass ratio of ASA to water is 1 : 3.
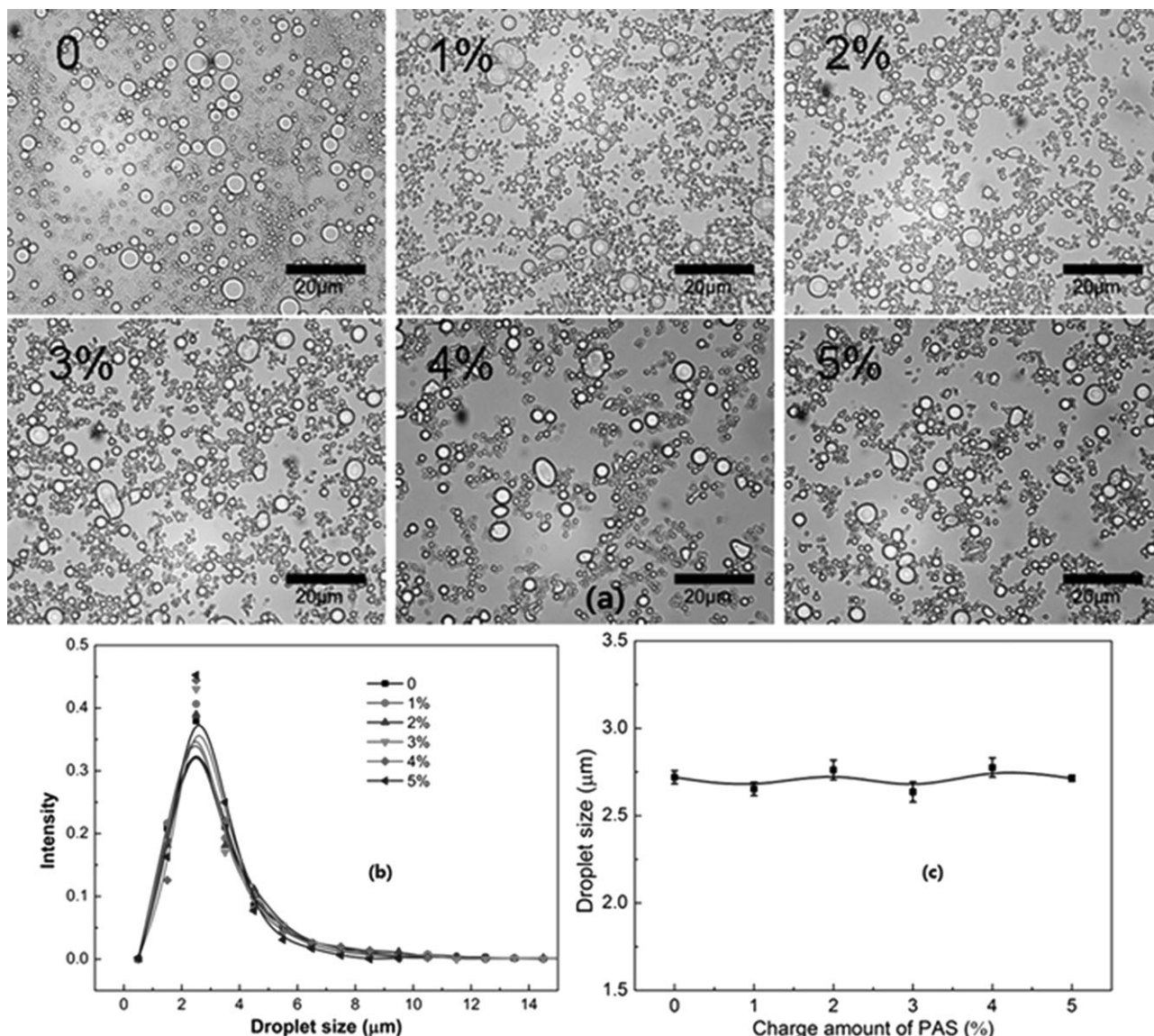
Figure 5. (a) Optical microscope images, (b) droplet diameter distributions, and (c) average droplet size of fresh ASA emulsions costabilized by Laponite and PAS as a function of PAS charge amount based on the mass of Laponite. The charge amount of PAS were 0, 1%, 2%, 3%, 4% and 5% based on the mass of Laponite.

flocs plays an important role in determining the fluidity property of ASA emulsion.

Figure 5 shows the morphology, droplet size distributions and average droplet size of the ASA emulsions corresponding to those of Figure 4. As shown, the droplet size and droplet size distribution are not changed significantly, but the ASA droplets aggregate considerably with the introduction of PAS. This indicates that the repulsion force among ASA droplets is lowered because of the coagulation of Laponite particles by PAS, i.e., charge neutralization occurs among the interactions of PAS and Laponite particles. In addition, a few nonspherical droplets appear probably as a result of fusing between droplets. Nevertheless, the stability of the emulsion is improved after the emulsion is slightly shaken, favoring the pumping of ASA emulsion.

Sizing Performance of ASA Emulsion

The sizing performance of the ASA emulsions costabilized by Laponite and different charge amount of PAS is investigated. Figure 6(a) shows the sizing degree of ASA emulsion sized paper as a function of charge amount of PAS based on Laponite. In emulsion preparation, the concentration of Laponite is fixed at 0.5% (w/w) based on the total mass of ASA and water. The charge level of ASA based on the mass of aspen BCTMP is 0.3% and 0.4%. Clearly, for the ASA emulsion sized paper, adding 0.5% of PAS (based Laponite) in emulsion preparation results in the reduction of the sizing degree. However, further increasing the charge level of PAS remarkably enhances the sizing performance of ASA emulsion as the charge level of PAS is less than 2%. When the charge amount of PAS exceeds 2%, the sizing degree is not enhanced significantly for the paper sized
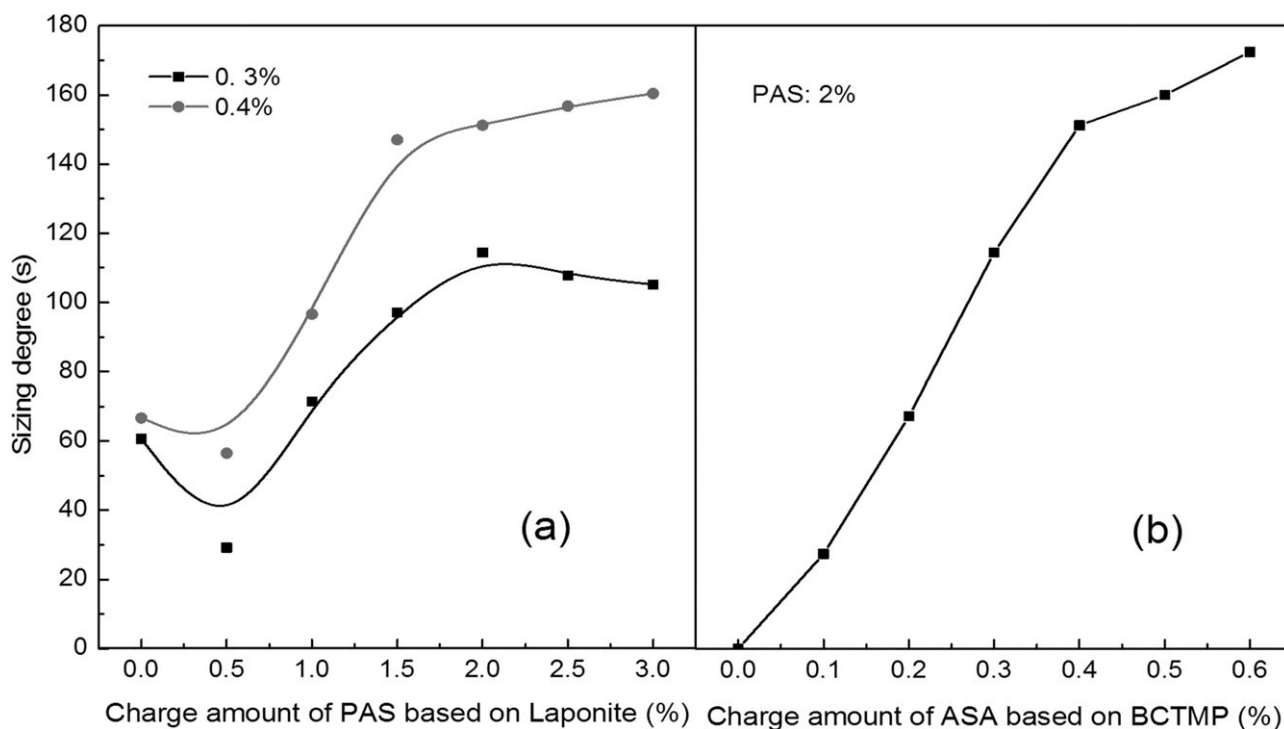
Figure 6. Sizing performance of ASA emulsion costabilized by Laponite and PAS as a function of (a) charge level of PAS based on mass of Laponite; (b) charge amount of ASA based on oven dry pulp. The concentration of Laponite in emulsion is fixed at 0.5% (w/w). The charge level of ASA based on the mass of BCTMP is 0.3% and 0.4% in (a). The charge level of PAS in (b) is 2% based on Laponite.

with 0.4% of ASA while even starts to decrease for that sized with 0.3% of ASA. This indicates that introducing suitable amount of PAS can greatly enhance the sizing performance of ASA emulsion stabilized by Laponite because of the interaction of PAS with ASA. Figure 6(b) shows the sizing degree of ASA emulsion sized paper as a function of ASA charge amount based on oven dry pulp, where the charge level of PAS is 2% based on Laponite in emulsion preparation. As can be seen from the figure, the sizing degree increases gradually as the dosage of ASA increases and the ASA emulsions have much high sizing efficiency. Paper made by BCTMP can obtain a sizing degree of approximately 28 and 152 s by adding 0.1% and 0.4% of ASA based on oven dry BCTMP, respectively. However, the increase of sizing degree slows down as the charge level of ASA exceeds 0.4%. Therefore, the charge level of ASA emulsion stabilized by Laponite and PAS should be less than 0.4% if its sizing efficiency is considered.

The hydrolysis of ASA impairs the sizing performance of ASA emulsion and the runnability of paper machine because of the loss of ASA and formation of sticky deposits by the hydrolyzed ASA and calcium ion or other substances in paper making system.[15] Developing stabilizers for ASA emulsion with high hydrolysis resistance is necessary. Therefore, the sizing performance of the Laponite and PAS costabilized ASA emulsion with storage time was investigated, and compared with that of Laponite stabilized one. The results are shown in Figure 7, where the Laponite concentration of the emulsion is 0.5%; the PAS charge level is 2% based on the mass of Laponite; the

charge level of ASA based on oven dry pulp is 0.3%. As shown in Figure 7, the sizing degree of the Laponite stabilized ASA emulsion sized paper increases gradually with the increasing storage time and reaches a maximum value at 110 min, after that, the sizing degree decreases sharply. This indicates that proper hydrolysis of ASA may favor the sizing development of ASA sized paper because of the presence of aluminum species, but the bulkily hydrolyzed ASA can even act as a desizing agent
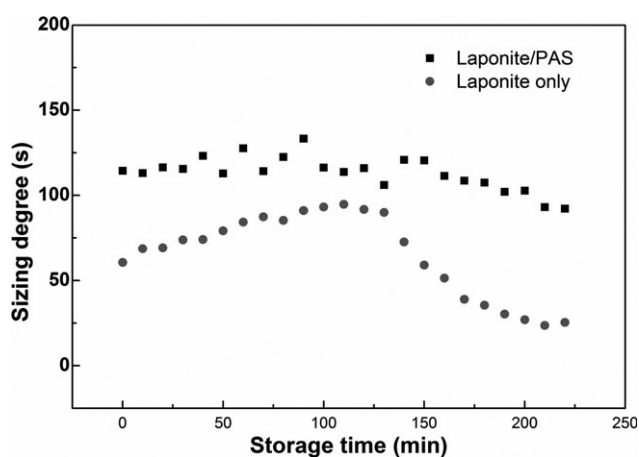

Figure 7. Sizing performance of ASA emulsion stabilized by Laponite and PAS as a function of emulsion storage time. The Laponite concentration of emulsion is 0.5%. The PAS charge level is 2% based on the mass of Laponite. The charge level of ASA based on oven dry pulp is 0.3%.
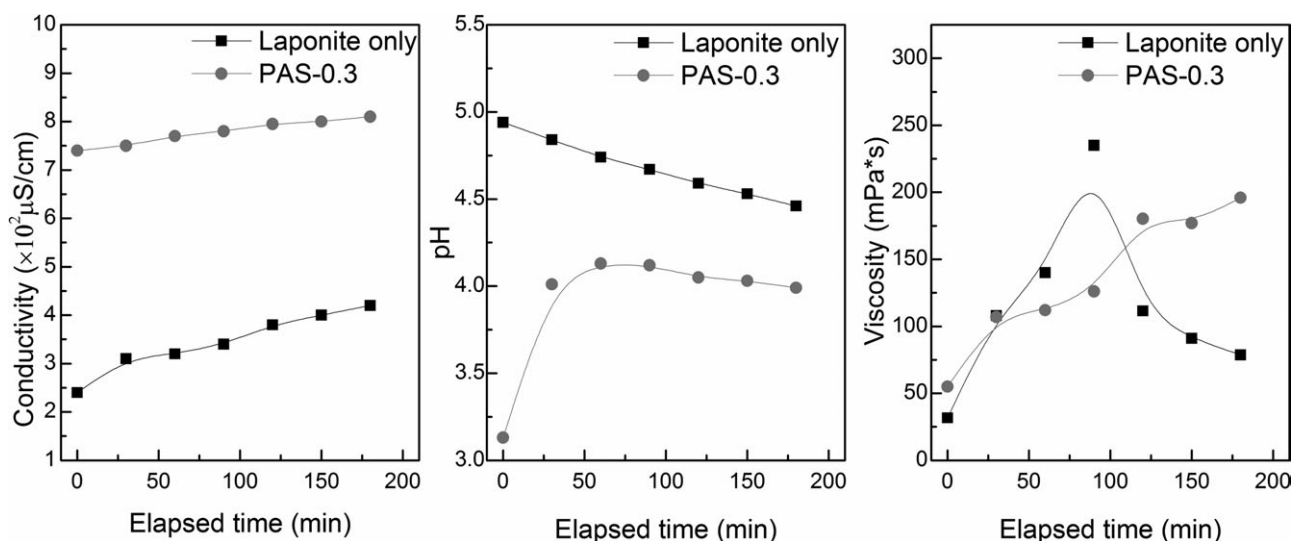
Figure 8. Conductivity, pH, and viscosity of ASA emulsion stabilized by Laponite either alone or together with PAS as a function of elapsed time. The Laponite concentration of emulsion is 0.5%. The PAS charge level is 2% based on the mass of Laponite.

and induce the coalescence of ASA emulsion, which results in the formation of large flocks of ASA substances and consequently inefficient distribution on paper web.[51] Meanwhile, as a result of its amphiphilic nature, the hydrolyzed ASA can lower the surface tension of polar liquids, such as water, thus interfere with the sizing development of paper. However, the sizing degree of paper sized by the Laponite and PAS costabilized ASA emulsion is hardly changed within the 3 h of storage time. This indicates the emulsion has high hydrolysis stability with the presence of PAS.

Variation of ASA Emulsion Properties and Hydrolysis of ASA with Storage Time

The variation of sizing performance of ASA emulsion with storage time is related to either the variation of the emulsion properties or the hydrolysis of ASA. Therefore, variation of ASA emulsion properties with storage time was first investigated.

The conductivity, pH, and apparent viscosity of the ASA emulsion as a function of elapsed time are shown in Figure 8. The reduction of pH and enhancement of conductivity generally indicate the hydrolysis of ASA because the hydrolyzed product of ASA is ASA-acid, which contributes hydrogen ions because of dissociation. The pH enhancement of Laponite and PAS costabilized ASA emulsion with the storage time from 0 to 60 min is probably because of the reaction of PAS with Laponite. Apparently, the variations of conductivity and pH of ASA emulsion stabilized by Laponite alone are greater than that of ASA emulsion stabilized by Laponite together with PAS after the storage time is longer than 60 min although the latter has higher conductivity and lower pH because of the presence of PAS. Therefore, the hydrolysis resistance of Laponite and PAS costabilized ASA emulsion is higher than the Laponite-stabilized emulsion. The variation of emulsion viscosity may be attributed either to the hydrolysis of ASA or to the variation of emulsion morphology with storage time.

Figure 9 shows the morphology, droplet size distribution, and average droplet size of ASA emulsion stabilized by Laponite either alone or together with PAS as a function of emulsion storage time. The emulsion preparation conditions are same with those in Figure 8. As shown in Figure 9, spherical drops with diameters of 1–50 μm are visible and have no tendency to coalescence but aggregate slightly for either Laponite alone or Laponite and PAS costabilized ASA emulsions. With extending the emulsion storage time, the droplets of ASA emulsion stabilized by Laponite alone starts to coalesce and fuse into bigger droplets. At the storage time of 180 min, the bigger drops break down to form irregular emulsion with some of "smaller" droplets. This indicates that the Laponite particles cannot protect the ASA emulsion droplets from coalescence completely. The formation of irregular greater ASA drops may also explain why the emulsion viscosity starts to reduce as shown in Figure 8. For the emulsion costabilized by Laponite and PAS, however, the coalescence process is much slower and the emulsion maintains spherical droplets and uniformity at all the tested storage time, indicating that addition of PAS reduces the electrostatic repulsion between negatively charged Laponite particles and allows denser film to form around oil drops thus increasing their stability to coalescence.

Through fitting the droplet size distribution data with lognormal distribution equation, it is found that all the emulsion droplet size distribution can be described by the following lognormal distribution equation:

$$y = \frac{1}{\sqrt{2\pi}wx} e^{\frac{-[\ln\frac{x}{x_c}]^2}{2w^2}} \qquad (1)$$

where y is the intensity of the droplet size distribution, the parameter x_c and w are average droplet size and standard deviation, respectively. Table I lists those parameters of the two ASA emulsions at different storage times. R is correlation coefficient.

According to Table I, the standard deviation of the fitting curve for ASA emulsion stabilized by Laponite alone is lower than
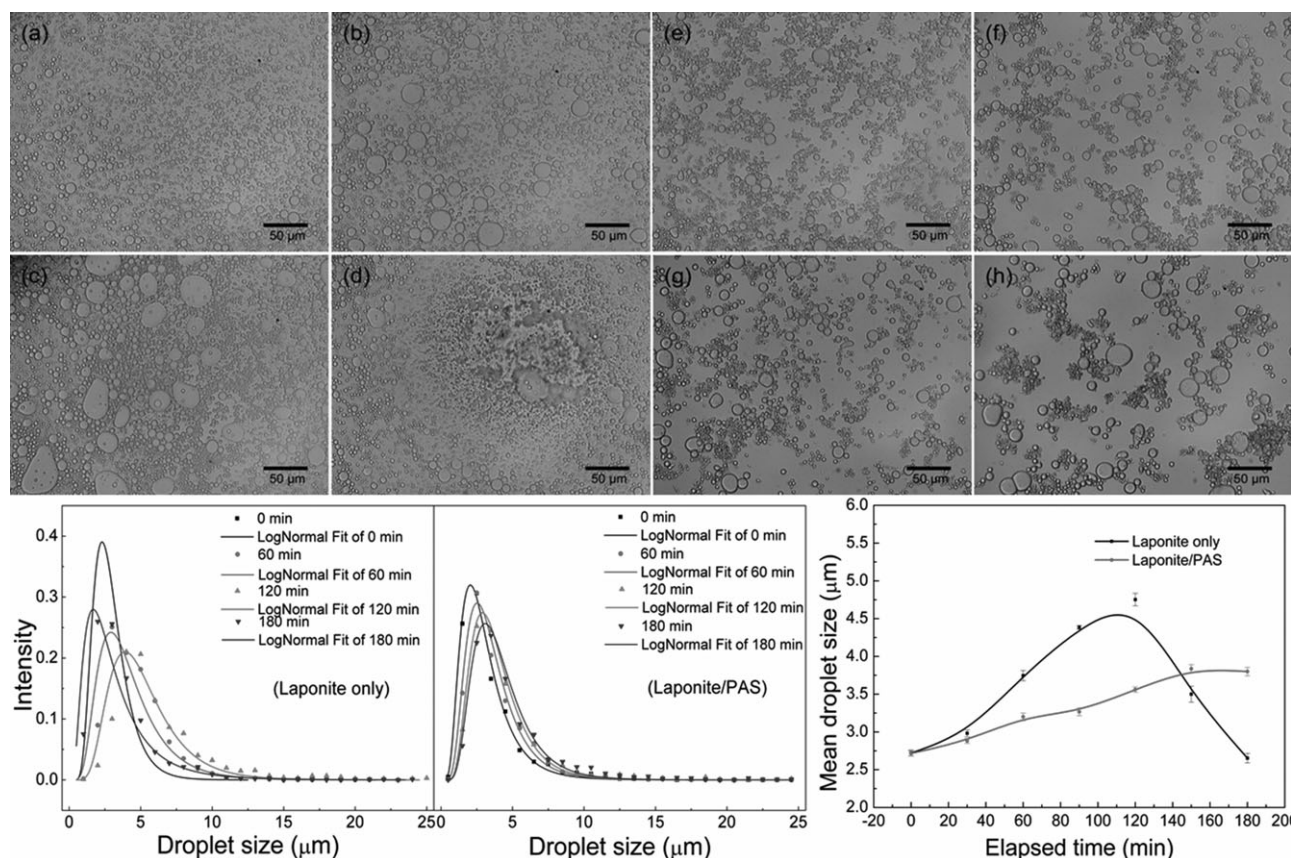
Figure 9. Optical microscope image (a–h), droplet size distribution and average droplet size of ASA emulsions stabilized by either Laponite alone (a–d) or together with PAS (e–h) as a function of emulsion storage time: (a, e) 0 min, (b, f) 60 min, (c, g) 120 min, (d, h) 180 min. Emulsion preparation conditions are same with those in Figure 8.

that for ASA emulsion stabilized by Laponite together with PAS, indicating the wider droplet distribution of the ASA emulsion stabilized by Laponite and PAS because of the presence of PAS. However, with extending the storage time, the polydispersity of ASA emulsion stabilized by Laponite alone increases, whereas that stabilized by Laponite and PAS decreases. This indicates that the coalescence happens among bigger ASA drops for the former, whereas among smaller ASA drops for the latter. After standing for 60 min, the former has already had a wider droplet distribution than the latter. The reduction of the standard deviation for ASA emulsion stabilized by Laponite alone at 120 min of storage time is probably because of the large scale of droplet fusion that reduces the numbers of greater droplets, as shown in Figure 9(c). It can also be found from Figure 9 that the two

emulsions have droplets with similar average diameters initially; however, with increasing the storage time, the average droplet size of emulsion stabilized by Laponite alone increases much faster than that stabilized by Laponite and PAS. The reduction of average droplet size of emulsion without PAS at storage time longer than 120 min corresponds to the broken of emulsion as shown in Figure 9(d). In brief, the properties of Laponite and PAS costabilized ASA emulsion undergoes much smaller variation and has more uniform droplet size distribution than that of Laponite stabilized one with elapsed time.

To determine the hydrolysis resistance of the ASA in emulsion stabilized by Laponite either alone or together with PAS, ASA/ hydrolyzed ASA was separated from the ASA emulsions stored, respectively, for 0, 60, 120, and 180 min, and employed to

Table I. Parameters Obtained by Fitting Droplet Size Distribution of ASA Emulsions Using Lognormal Distribution Equation

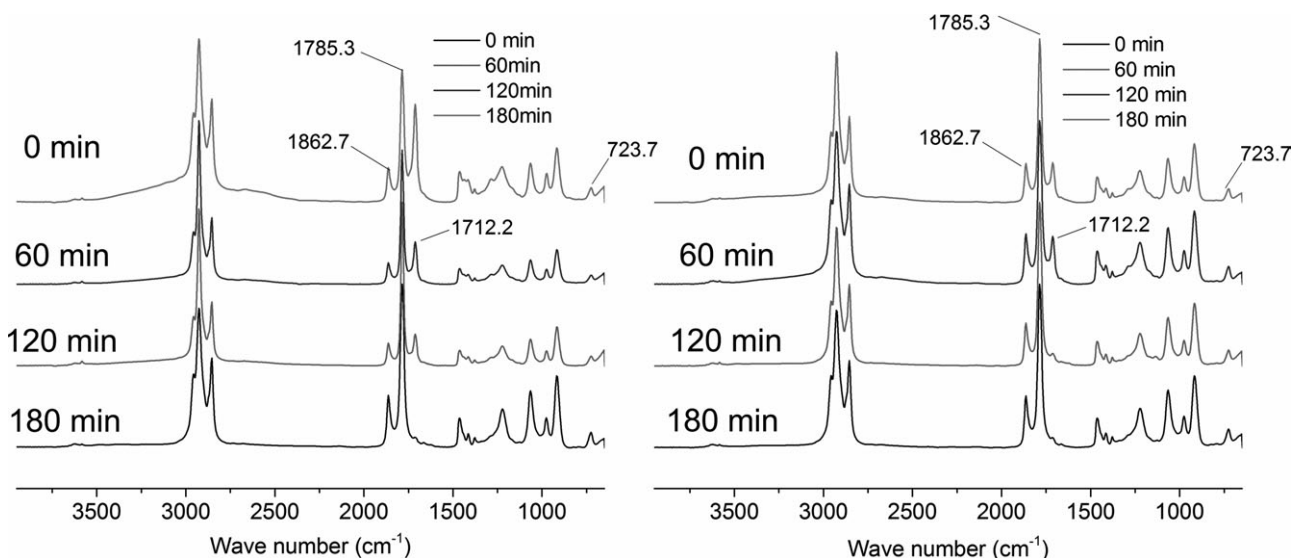| Time (min)	Laponite only			Laponite/PAS		
	x_c	w	R^2	x_c	w	R^2
0	2.720	0.408	0.99096	2.716	0.528	0.99214
60	3.745	0.498	0.98596	3.200	0.482	0.98625
120	4.752	0.440	0.97550	3.561	0.453	0.99306
180	2.653	0.675	0.98822	3.800	0.454	0.98433

Figure 10. Infrared spectra of ASA/hydrolyzed ASA separated from (a) Laponite stabilized and (b) Laponite and PAS costabilized ASA emulsions with various storage times. The preparation conditions of the emulsions are same with those in Figure 9.

record their infrared spectra, which are shown in Figure 10. In infrared spectrum, the carbonyl stretching frequencies of ASA are located at 1785.3 and 1862.7 cm^{-1}, whereas the absorption frequency of carboxyl group from the hydrolyzed product (ASA-acid) appears at 1712.2 cm^{-1}.[52] The absorption band located at 723.7 cm^{-1} corresponds to the CH$_2$ rocking vibration of long-chain methylene, which is not changed by the hydrolysis of ASA. Therefore, by calculating the absorbance ratio of the absorption bands at 1712.2 and 723.7 cm^{-1}, which belong to carboxyl group from ASA-acid and the methylene groups from both ASA and ASA-acid, respectively, the hydrolysis extent of ASA can be approximately evaluated. Table II lists the absorbance ratio, $A_{1712.2}/A_{723.7}$, where the $A_{1712.2}$ and $A_{723.7}$ are absorbance at 1712.2 and 723.7 cm^{-1} in Figure 10, respectively.

As can be seen from Table II, the infrared absorbance ratios from the two emulsions increase with extending the emulsion storage time, indicating that the ASA hydrolysis extent is correspondingly increased. However, the hydrolysis extent of the ASA from emulsion costabilized by Laponite and PAS is obviously much lower than that from the emulsion stabilized by Laponite alone at the same storage time. This confirms that the addition of PAS significantly reduces the hydrolysis of ASA but does not stop the hydrolysis.

Table II. Infrared Absorption Ratios of ASA/Hydrolyzed ASA Separated from ASA Emulsions with Various Storage Times

Time (min)	$A_{1712.2}/A_{723.7}$	
	Laponite only	Laponite/PAS
0	0.679986	0.534655
60	3.242712	0.786211
120	4.665968	2.672510
180	6.681508	2.873062

CONCLUSIONS

ASA emulsions with high stability were prepared by using Laponite and PAS as particle stabilizers. The Laponite and PAS costabilized ASA emulsions show a high sizing efficiency on aspen BCTMP. The sizing performance of the ASA emulsion stabilized by 0.5% of Laponite (based on the total mass of ASA and water) and 2% of PAS (based the mass of Laponite) is not changed within 3 h. The introduction of PAS into Laponite aqueous dispersion remarkably reduces the hydrolysis of ASA in emulsion and enhances the stability of ASA emulsions.

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