

Properties of Powdered Associative Alkali-Swellable Acrylics Thickeners Synthesized by Precipitation Polymerization

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ABSTRACT: Powdered alkali-swellable acrylics thickener (ASAT) was synthesized by precipitation polymerization with acrylic acid (AA) and stearyl acrylate (SA) as monomer, allyl sucrose ether (ASE) as crosslink agent and lauroyl peroxide (LPO) as initiator in the solvent of ethyl acetate. The powders were normal distribution in the range 1–80 μm and showed sensitive to pH in water. Before pH 7, both of the viscosity and the light transmittance of the APAT emulsion increased with enhancing pH value. ASE and SA played an important role in the properties of ASAT. When the amount of ASE was increased, the crosslink degree in the ASAT molecule increased. As the result, the viscosity of its emulsion increased firstly and then decreased, but the light transmittance of the emulsion decreased monotonously. Introduction of SA led to formation of an associative ASAT. Therefore, both of the viscosity and light transmittance of ASAT emulsion increased firstly and then decrease with increasing the amount of SA. Meanwhile, the associative ASAT emulsion showed shear thinning behavior, good salt tolerate, and less sensitivity to temperature. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40512.

KEYWORDS: acrylics thickeners; colloids; crosslinking; rheology

Received 17 November 2013; accepted 22 January 2014

DOI: 10.1002/app.40512

INTRODUCTION

As an important type of rheological modifier, alkali-swellable acrylics thickener (ASAT) has been widely applied in waterborne coatings, adhesives, pharmaceuticals, person care product, and so on.^{1–5} Light crosslinked polyacrylic acid or polymethacrylic acid is a very common ASAT. The use of a crosslink agent results in formation of polymer with three-dimensional network throughout each particle and the polyacids, which exhibit expansion upon neutralization in water. At acidic pHs, the polymer remains in the formation of hydrophobic particles. However, at basic pHs, it is ionized and a swelling transition occurs in the microgel (or hydrogel) with three-dimensional structure, which increases several times the volume of the original particles emulsion. The carboxyl groups on the swelled particles repulse one another, which leads a large increase in the viscosity of its emulsions.⁶

Modification of polyacids with hydrophobe can also greatly improve its thickening properties. Such rheological modifier is known as associative ASAT which has a polyelectrolyte backbone bearing several pendant hydrophobic groups. Similar to the polyacids, the polymer thickens its emulsion at neutral pH through repulsion of carboxylate anions. Meanwhile, the hydrophobic groups in the polymer aggregate together to form microgel-like

structure in the water phase, which also enhances the viscosity of its emulsion.^{7,8} Therefore, the viscoelastic behaviors of the associative ASAT is greatly dependent on the structure and content of hydrophobic groups grafted on the microgel, crosslink density, and ionic strength.^{9–11} During the past decades, many research efforts have been directed towards the preparation of these thickeners.

The most common processes to synthesize ASAT are suspension polymerization and dispersion polymerization. These preparation processes provide some advantages such as higher polymerization rates, higher molecular weights and also as a result of an increase in the propagation rate coefficient in some cases.¹² However, it is difficult to copolymerize the hydrophobic monomer with acrylic acid because the hydrophobes are insoluble in water. At the same time, using ammable organics might cause another problem of pollution of product, which would be a more serious problem when the thickener is used in person care, food or medical product. Especially, the product from these polymerization processes is always the liquid which has some inherent disadvantages in terms of transportation, handling, and utilization. If powdered thickener is desired, an energy intensive dry process is necessary. Powdered ASAT is conventionally prepared by precipitation polymerization in

Table I. Composition of Monomers

Sample	AA (g)	ASE (wt %)	SA (wt %)
ASAT1	20	0	6
ASAT 2	20	0.2	6
ASAT3	20	0.4	6
ASAT 4	20	0.6	6
ASAT 5	20	0.8	6
ASAT 6	20	1.0	6
ASAT 7	20	0.8	0
ASAT 8	20	0.8	2
ASAT 9	20	0.8	4
ASAT 10	20	0.8	6
ASAT 11	20	0.8	8

supercritical carbon dioxide or organic solvents.^{13–15} Carbon dioxide has the advantage of nontoxic and easy separation from the product, but it is uneasy to carry out in industrial because it needs high pressure in the process. Polymerization in organic solvents has been recognized as an alternative for many aspects of polymeric synthesis, but the use of organic solvents and/or surfactants as the polymerization medium inevitably leads to chemical contamination of the environment and the product. In addition, the powder is rather difficult to disperse in water and sometimes develop an undesirable high viscosity even before neutralization because colloid particle is easily formed during preparation in organic solvent.¹⁵ Therefore, the improved solvent polymerization process is desired for the preparation of ASAT.

The aim of this work is to synthesize powdered ASAT by precipitation polymerization. With low toxicity and low boiling point, ethyl acetate was used as the solvent because it can be easy to remove and recover after reaction. To synthesize the associative ASAT, we chose the acrylic acid and stearyl acrylate as monomers, allyl sucrose ether (ASE) as the crosslink agent and lauroyl peroxide (LPO) as the initiator. Focusing on the synthetic strategy and properties of ASAT, we designed the partially neutralized macromolecule with surfactant structure and investigated the effect of usage amount of ASE and SA on the size distribution of the powder, rheological behavior, and light transmittance of its emulsion. Additionally, thermal degradation of the powder and morphology of ASAT in emulsion were also characterized to evaluate the product.

EXPERIMENTAL

Materials

Acrylic acid (AA, 99.0 wt %), stearyl acrylate (SA, 99.0 wt %), LPO (98.0 wt %), ASE (the degree of substitution was 0.6), ethyl acetate (EA, 99.5 wt %), and sodium bicarbonate (NaHCO_3 , 99.0 wt %). All chemicals were laboratory grade reagents and were used without purification. Laboratory-prepared distilled water was utilized throughout the work.

Precipitation Polymerization

According to Table I, the amount of ASE and SA was used based on the amount of AA. The mixtures of monomers and

200 mL EA were introduced into a 500 mL four-neck flask equipped with a mechanical stirrer, nitrogen purging system, thermometer, refluxing device, and drop funnel. When the solution was stirred and heated to 60°C, 0.16 g of LPO was dissolved in 20 mL EA and added into the reaction system by three times within 1 h under N_2 atmosphere. After reaction for 50 min, 0.1 g of NaHCO_3 was added to the solution. The stirring rate was adjusted to 400 rpm to prevent the sodium salt of the polymer from direct precipitation. The temperature was raised to 75–78°C and the reaction were maintained at this temperature for 4 h. After reaction, the solution was cooled to room temperature and sodium salt of macromolecule precipitated. Filtered with Bushner filter, the precipitate was washed twice with EA and dried at 40°C in vacuum for 8 h. White powdered ASAT was obtained. The yields of all the products were above 98.5%.

Preparation of ASAT Emulsion

Powdered ASAT was dissolved in water and the concentration was kept at 0.5 wt % during all the process and then added the diluted aqueous NaOH under stirring to adjust the pH to required value which was measured with a digital pH meter. The accuracy of reading was reproducible to 0.02 pH units. The emulsion was stirred at least for 24 h and left overnight to equilibrate before measurements.

Measurements

The Fourier transform infrared spectrum (FT-IR) was collected using a Bruker 88 Fourier-transform infrared spectrometer (Germany). Solid sample was mixed with KBr and ground to make pellet. Liquid sample was directly coated on the KBr pellet. FTIR spectrum was collected with a resolution of 4 cm^{-1} in the range $500\text{--}4000 \text{ cm}^{-1}$.

Thermogravimetric analysis (TGA) was carried out on a HCT-3 thermal gravimetric analyzer (China). 2–4 mg of sample was placed in a platinum sample pan and heated from 25 to 500°C at a heating rate of $10^\circ\text{C}/\text{min}$. Nitrogen was used as purge gas at flow rate of 50 mL/min.

A JEM-1011 transmission electron microscopy (TEM, Japan) was used to observe the morphology of 0.5% ASAT emulsion at different pH value. The emulsion was properly diluted, dripped onto copper grid, and dried at room temperature. The TEM observation was carried out on the TEM without being negative stained

The particle size and size distribution of powdered ASAT were analyzed by a Mastersizer 2000 Laser scattering particle size instrument (England, UK) and plotted for size distribution using the software supplied by the manufacturer. 0.1 g of powdered ASAT was dispensed uniformly in the 400 mL anhydrous ethanol by ultrasonic device for 1 min to avoid the powder swell.

For pH-dependent viscosity and light transmittance experiments, the pH value of emulsion was increased gradually using very small aliquots of concentrated NaOH solution to minimize the dilution effect. When the emulsion was reach equilibrium, the pH value of emulsion was measured using the digital pH meter, and then the viscosity of the emulsion was measured

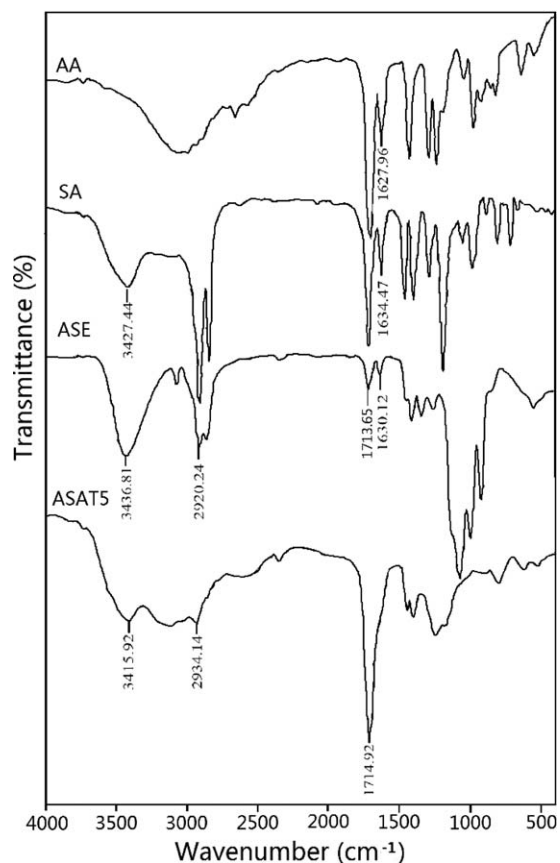


Figure 1. FTIR spectra of AA, ASE, SA, and ASAT5.

using a RehoStress RS-75 rheometer (German) with the measuring sensor system (C35/2°) at 25°C under a constant shear rate of 3 s^{-1} . The light transmittance of the emulsion was measured with a Ruli 2100 UV-visible Spectrometer (China) at a wavelength of 426 nm.

The rheological behavior of the 0.5% ASAT emulsion was investigated using the above rheometer. Steady shear rate sweep test was performed at 25°C in the range $0.1\text{--}1000 \text{ s}^{-1}$. The shear rate was swept up and then down to provide thixotropic curve.

Salt tolerance was used to evaluate the resistance efficiency of thickener to electrolyte. In this test, different concentration of NaCl solution was mixed with 0.5 wt % ASAT emulsion and then the viscosity of the emulsion was measured at 25°C under a constant shear rate of 3 s^{-1} .

Temperature resistance of ASAT emulsion was measured under the temperature from 15 to 55°C at a constant shear rate of 3 s^{-1} .

RESULTS AND DISCUSSION

Preparation and Characterization

In order to synthesize easily dispersing powdered ASAT, the synthetic processes were designed according to following strategy:

1. To synthesize the thickener with the associative character, SA was used as co-monomer to copolymerize with AA due to a long chain hydrocarbon in SA molecule.

2. To improve the dispersing property of the powder, ASE and LPO were chosen as the crosslink agent and initiator respectively. As environment-friendly material, ASE has some unsubstituted hydroxyl groups in its molecule that it can be used as an amphiphilic materials and highly efficient emulsifier.¹⁶ LPO can also be used as an initiator and as well as a surfactant in polymerization.¹⁷ Introducing the surfactant into precipitation polymerization can improve the water solubility of powdered thickener.¹⁵ Therefore, ASE and LPO were chosen as raw materials as well as surfactants in this article.
3. To precipitate ASAT easily and avoid the molecular weight too high to form colloid, NaHCO_3 was used to neutralize the carboxylic acid groups partly in macromolecule after adding initiator. The partly neutralized macromolecule was an infinitesimal particle which can polymerize with the unreacted monomers but avoid gel. Meanwhile, partly neutralized ASAT can precipitated in organic solvent easily after the stirring was stopped.
4. EA was selected as solvent because it has the properties of low toxicity and low boiling point. After polymerization, EA can be removed to reduce its residual easily by dry process at 40°C in vacuum.

In addition, we attempted to prepare the thickener under industrially relevant conditions. The monomers and crosslink agent were used without purification and the residual inhibitor (200 ppm of hydroquinone) was not removed. Although consumed a bit initiator, the inhibitor can adjust the polymerization rate to avoid colloid forming.

Figure 1 shows the FTIR spectra of the monomers, crosslink agent and ASAT5, a typical product of the samples. In the spectrum of ASE, the absorption peak at 3436.8 cm^{-1} was corresponded to $-\text{OH}$ group and it meant that the unsubstituted hydroxyl groups existed in the molecule. In the spectrum of ASAT5, a broad absorption bands in the range from 2800 to 3550 cm^{-1} was specific to $-\text{OH}$ stretching absorption of carboxylic acid and aliphatic C-H absorption due to the hydrogen bonding in the powder. Meanwhile, the strong absorption peak at 1714 cm^{-1} was associated with the C=O stretch of the ester and carboxylic acid in the polymer. Compared with the spectra of AA, ASE, and SA, the characteristic absorption peak at about 1630 cm^{-1} corresponding to C=C double bonds in acrylates

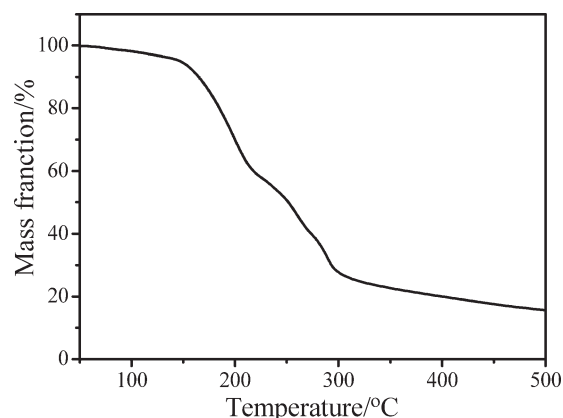


Figure 2. TGA curve of ASAT5.

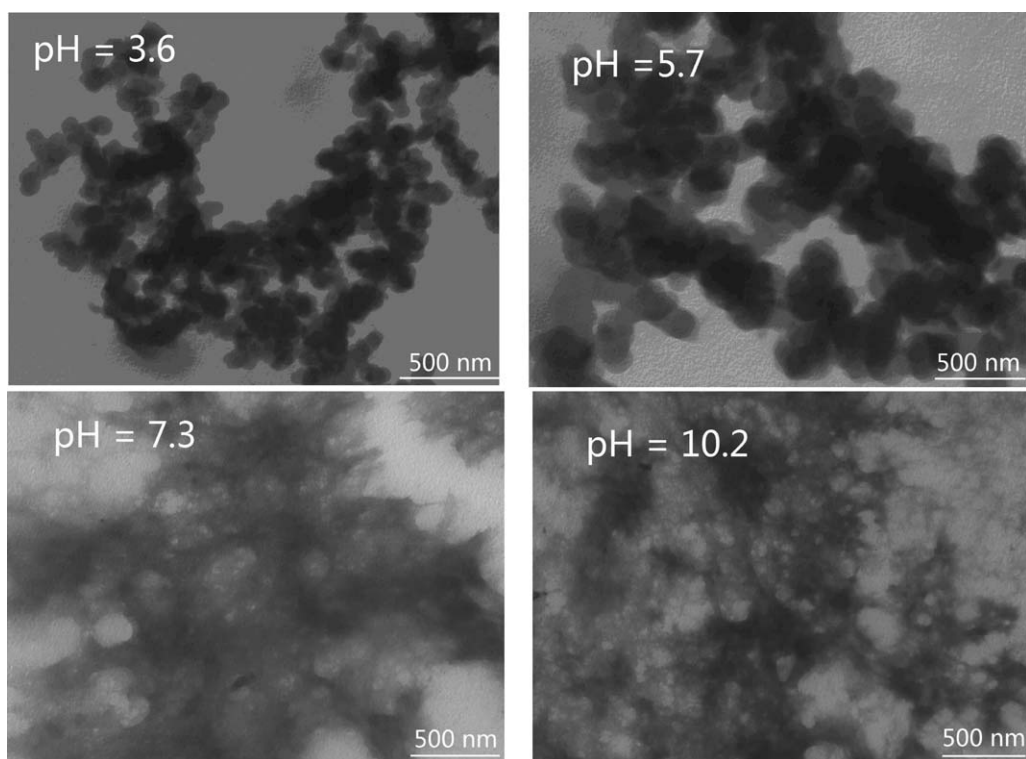


Figure 3. TEM images of ASAT5 emulsion at different pH value.

cannot be observed in the spectrum of ASAT5. It meant that the polymerization of monomers and crosslink monomer was completed.

The thermal behavior of ASAT5 was evaluated by the TGA experiment, and the result is given in Figure 2. The TGA curve showed a two-step weight loss. The first weight loss was about 40.5% occurred in the range 153–228°C, which was related to the decomposition of the chains of carboxylic acids in the macromolecule. The second weight loss was about 41.2% started from 228 to 350°C, which attributed to the decomposition of skeleton chains of ASAT.¹⁸ The TGA indicated that the powder was stable below 150°C, and the monomer or organic solvent was trace after the ASAT was washed with EA and dried.

During the dissolving process, all the powders can disperse easily in water to form emulsions due to their partially neutralized and properties of surfactant designed in preparing process. With neutralizing with NaOH solution, the opaque emulsion turned to transparent progressively. In order to understand the changes of ASAT5 particles in emulsion, their morphologies at different pH value were observed by TEM, and the pictures are

given in Figure 3. When ASAT5 was dispersed in water, the pH value of the emulsion was 3.6 and its particles were almost the hard sphere. When pH was 5.7, it was observed that the particles showed the morphology of a core-shell structure. We hypothesized that the majority of the microgel was in the nucleus of the polymer particles and formed a dense core, which was surrounded by a layer of crosslinked AA-SA chains. Above pH 7.3, the loose shell layers expanded significantly to form clusters of loose floccules. The morphology analysis provided the structural information and swelling process of ASAT in emulsion upon neutralization.

In fact, the powdered ASAT is the aggregates of macromolecules. The schematic representation of the course of dissolution and swelling in water at different pH values shows in Figure 4. After dispersed in water, the powdered particles separated into separate macromolecules. However, the particles of macromolecules exhibited in the form of hard spheres because they still remained in the hydrophobic.⁵ With neutralized by aqueous NaOH, all the carboxylic acid in the macromolecules transferred into the hydrophilic carboxylic ions, which swelled in water to form loose floccules and thickened the water.⁶

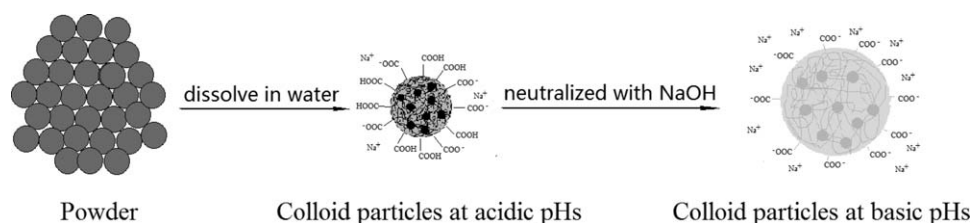


Figure 4. Schematic representation of powdered ASAT emulsion at acidic pHs and basic pHs.

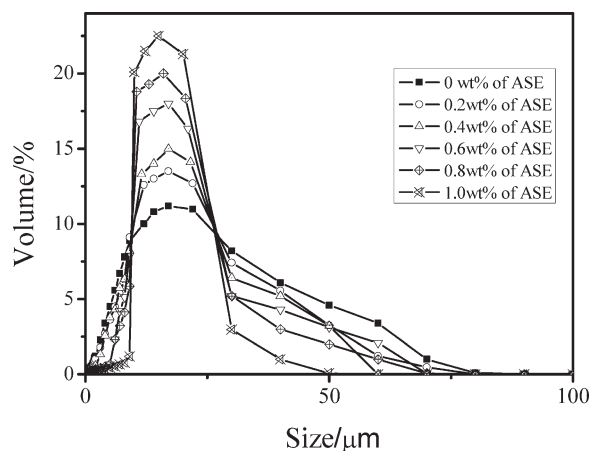


Figure 5. Particle sizes and their distribution of powdered ASATs with different amount of ASE.

Effect of the Amount of ASE on the Properties of ASAT

The properties of ASATs were studied at different amount of ASE to reveal the relationship between crosslink and the properties of ASATs for the sake of designing polymers with optimized structure.

Figure 5 shows the average particle size and its distribution of powdered ASATs with different amount of ASE in ethyl alcohol. All the powders were normal distribution in the range 1–80 μm , which were much larger than that determined by TEM. However, the average particle size and distribution of the powders were different. The particle size of ASAT1 was largest and its distribution was widest, but the particle sizes of the others became small and their distribution turned to narrow progressively with increasing in the amount of ASE. It was possible that the molecule of ASAT1 was a linear polymer which tended to wrap each other to form irregular particles.¹⁹ With increasing the amount of ASE in the mixture of monomer, the microgel with three-dimensional network formed in polymers which aggregated to yield small particle size and narrow particle size distribution. The particle sizes were larger than that tested by TEM because the powders were the aggregates of macromolecules.

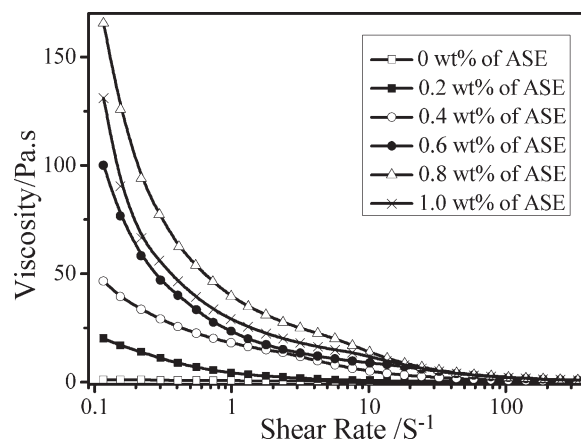


Figure 7. Effect of amount of ASE on the rheological behavior of ASAT emulsions at pH 7.

As discussed above, ASATs are always sensitive to pH. Figure 6 shows the viscosity and light transmittance of ASAT emulsions at different pH. As observed in the figure, the viscosity of all the emulsions increased from pH 3.6 to 7, and then their viscosity kept unchanged from pH 7 to 9 and a slight decrease in viscosity was observed from pH 9 to 12. Meanwhile, increasing pH value from 3.6 to 7 led to increasing in the light transmittance of their emulsions progressively, and this increase was followed by a plateau, where the light transmittance remained relatively constant when pH was in the range from 7 to 12. It is well understood that ASAT undergo abrupt changes in volume in response to pH and the concentration of mobile ions in the microgel interior relative to external solution drives the volume change.^{6,7} Therefore, the viscosity of the emulsions changed due to volume of particles changed at different pH value, the light transmittance changed because swelled particles had little light rays scattering ability.

Different amount of ASE also resulted in difference in the viscosities and light transmittance of ASAT emulsions at same pH value. The viscosity of their emulsions increased and then decreased again with an increase in the amount of ASE, but the light transmittance of the emulsion reduced monotonously with increasing in the amount of ASE. The result showed that the

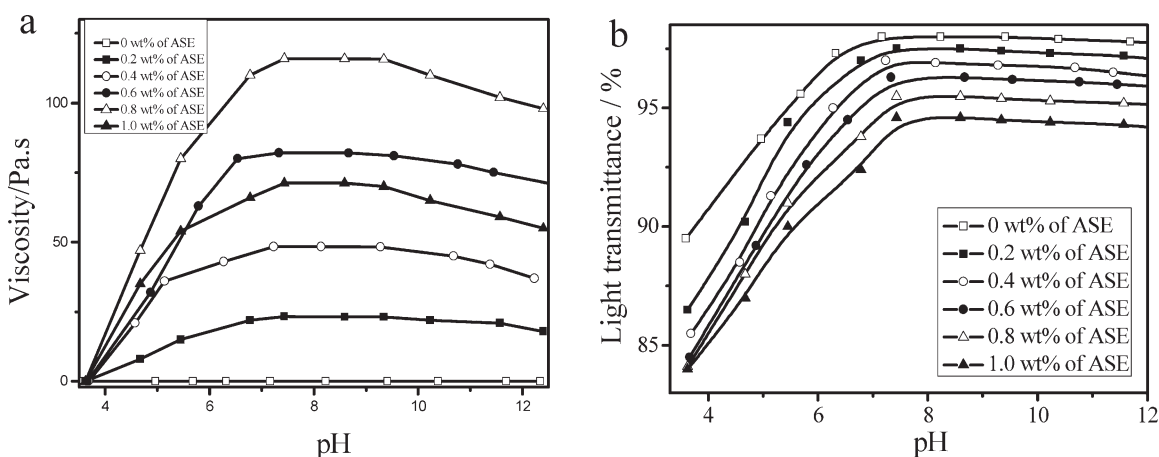


Figure 6. Effect of amount of ASE on the viscosity (a) and light transmittance (b) of ASAT emulsions at different pH.

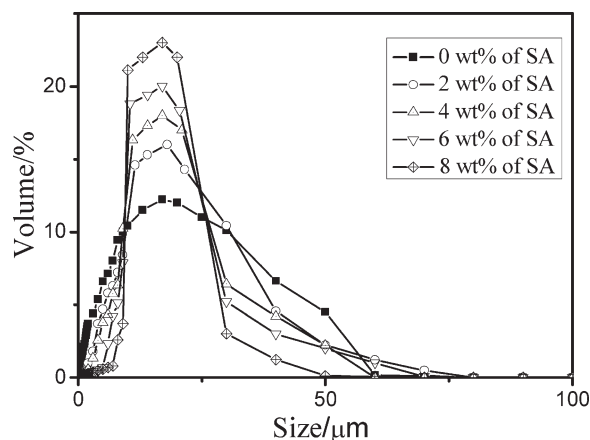


Figure 8. Particle size and distribution of powdered ASATs with different amount of SA.

crosslink density in polymers play an important role in the properties of ASAT emulsions.^{14,20,21} As a linear acrylic polymer, ASAT1 emulsion had the lowest viscosity, highest light transmittance,²⁰ whereas, the crosslink density of ASATs increased with increasing in the amount of the ASE, which resulted in high viscosity of the emulsion. When excess amount of ASE used was used, the swelling ability of microgel decreased and the viscosity of the emulsion reduced.²¹ However, The emulsion of high cross-linked polymer had poor light transmittance because microgel with high crosslink density scattered the light rays.^{21–23}

The rheological behaviors of the ASAT emulsions with different amount of ASE at pH 7 were determined and the results are showed in Figure 7. The viscosity of ASAT1 emulsion remained essentially Newtonian, but the other emulsions with ASE showed a highly shear thinning property. Meanwhile, the shear thinning behavior of the emulsions became stronger and stronger with increasing in the amount of ASE. The reason was that the shear thinning behavior increased with increasing in crosslink-density in polymer.²¹

Effect of Amount of SA on the Properties of ASAT

The hydrophilic-hydrophobic balance plays an important role in the properties of associative ASAT. Figure 8 shows the particle

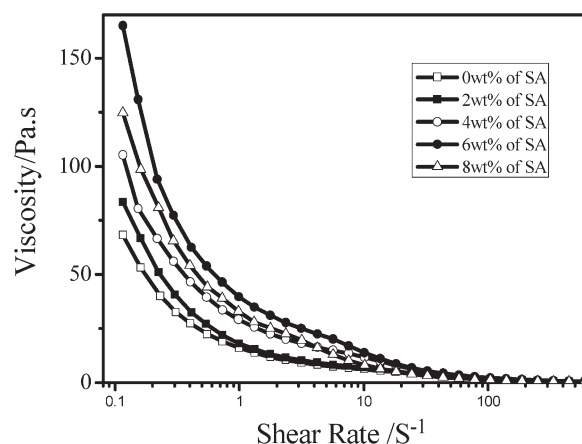


Figure 10. Effect of amount of SA on the rheological behavior of ASAT emulsions at pH 7.

size distribution of powdered ASAT with different amount of SA. The particle size of ASAT7 was biggest and its distribution was widest among all the samples. It is interesting to find that increasing the amount of SA led to decreasing in the particle sizes and narrowing in their distribution. This phenomenon was probably caused by hydrogen-bond interaction because higher content of carboxyl groups in the polymer tended to form stabilization of aggregates.²⁴ However, introducing the SA into ASAT led to decrease the content of carboxyl groups and reduce the particle aggregation.

Figure 9 shows the effect of the amount of SA on the viscosity and light transmittance of the ASAT emulsions at different pH value. The viscosity and light transmittance of the emulsions at different pH value were similar to the emulsions with different amount of ASE. However, different amount of SA led to the difference in the viscosity and light transmittance of the emulsions at same pH. The viscosity of emulsion increased to a maximum value and then decreased with increasing the amount of SA at same pH. The maximum viscosity occurred in the ASAT10 emulsion. It was surprised to be observed that the light transmittance of ASAT7 emulsion was lowest and increasing in the amount of SA led to an increase firstly and then decrease in the

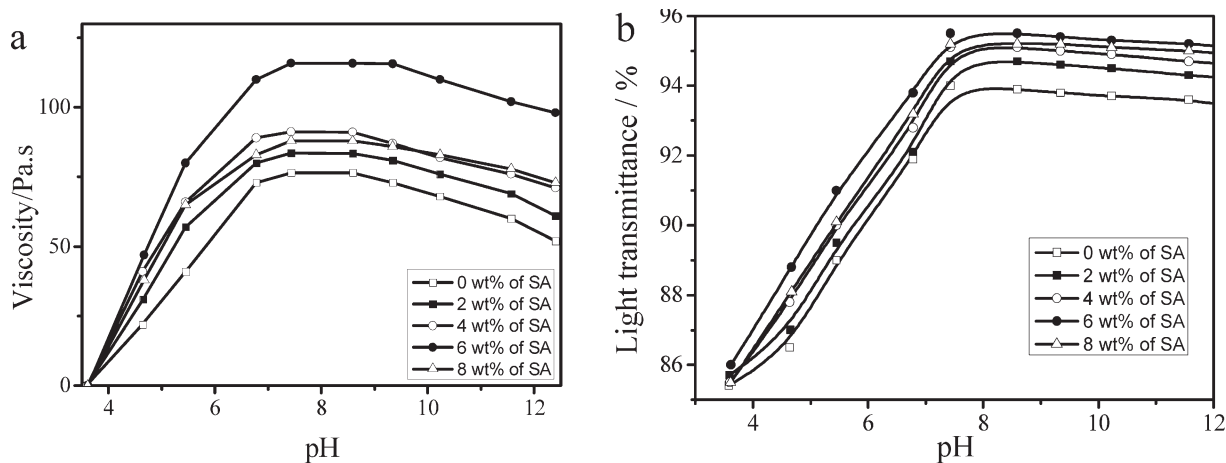


Figure 9. Effect of the amount of SA on the viscosity (a) and light transmittance (b) of the ASAT emulsions at different pH value.

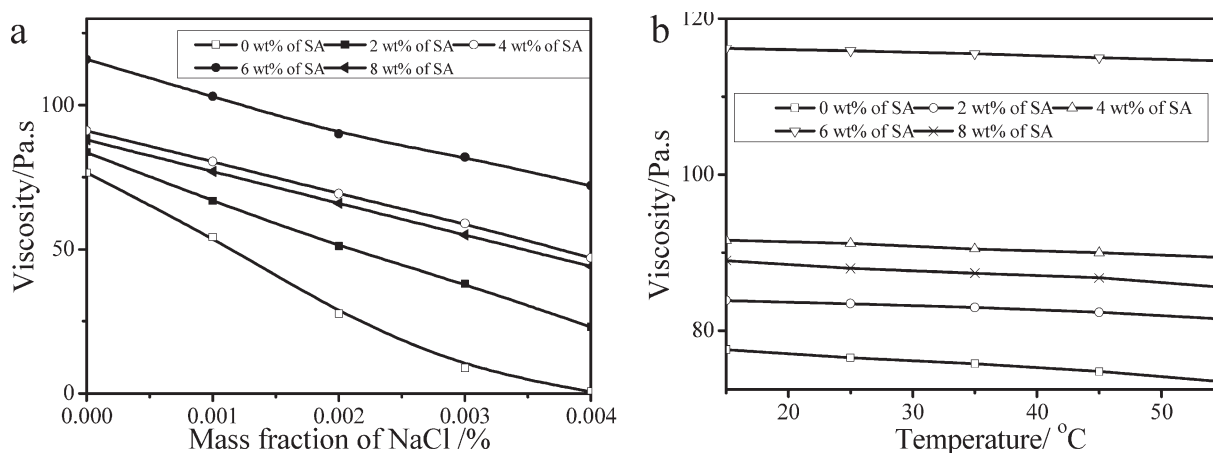


Figure 11. Effect of salt concentration (a) and temperature (b) on the viscosity of ASAT emulsions with different amount of SA at pH 7.

light transmittances of their emulsions. The effect of amount of SA on the viscosity and light transmittance of the emulsion can be attributed to intermolecular aggregation induced by hydrophobic-electrostatic interactions. In aqueous emulsions, the hydrophobes induced self assembly into aggregates comparable to surfactant micelles and the hydrophobes act as transient junctions and connect different aggregates depending on their concentration.^{10–12} With low amount of SA, the emulsions showed low level of aggregation of alkyl groups, which is assumed to cause substantial reduce in their viscosity.²⁰ Increasing in the amount of SA resulted in an increase in the aggregation of alkyl chains, which also increased in the viscosity of their emulsions. When excess of SA was used, further aggregation of alkyl chains was restricted and the viscosity of the emulsions decreased. However, It is well known that introduction of hydrophobic chains into acrylic polymers reduces the light transmittance of the emulsions because of their association interaction.^{21,22} The contrary result possible relate to the balance between the crosslinked microgel formed by ASE and the aggregation formed by hydrophobic–hydrophilic associative interaction. Increasing the amount of SA led to a decrease in the content of ASE because SA was used based on a constant concentration of AA and ASE. The low content of microgel formed from ASE compensated the effect of the associative interaction. Therefore, when exceed amount of SA was used, the association interaction produced dominant effect progressively and the light transmittance of emulsions decreased.

The rheological behavior of ASAT emulsions sufficiently attested to this result. In Figure 10, when higher amount of SA was used, the emulsions exhibited a stranger shear behavior. Under high shear stress, the associative junctions between neighboring chains were ruptured, so the inter-chain association became intra-chain association and the microgel structure was easily broken by shearing. Hence, the coil of the polymer chain and the fall of hydrodynamic volume led to the drop of the viscosity.^{11,12}

The salt tolerates and thermo-sensitive properties are important properties for associative thickener. Figure 11 shows the change of the viscosity of ASAT emulsions at pH 7 upon increasing the

NaCl concentration or temperature. Increasing NaCl concentration from 0.001 to 0.005%, all the emulsions showed a decline in their viscosity at a fixed shear rate, but the decrease range of ASAT7 emulsion was more seriously than that of the others. This phenomenon can be ascribed to the ionic shielding effects. When Na^+ ions exited ASAT emulsions, they shielded on the negative ions in ASAT chains and weakened the repulsion among these ions, which resulted in the loss of viscosity in the emulsions.⁶ Because of introduction of SA, stearyl groups in ASAT can yield association to form physical crosslink structure. Addition of Na^+ made the environment more hostile for the hydrophobic blocks and caused them to favor association each other, which enhanced the formation of the aggregates and the property of salt tolerates was greatly improved.^{6–9} For a series of ASAT emulsions with SA, slight variation in their viscosity was observed under different temperature. Increasing the temperature led to an obviously decrease in the viscosity of ASAT7 emulsion, but indistinct change for other emulsions. This result proved that the emulsion of ASAT with hydrophobic chains had less sensitivity to temperature than that with only carboxyl groups. The molecular motions and exchange rate of the transient junctions increased with a raise in the temperature, which resulted in a decrease in the viscosity of emulsion.^{25,26} ASAT with long hydrophobic chains in emulsion obviously had tight associations and less exchange due to increasing thermal motion in the temperature range, and the viscosity of the emulsion had an extremely low sensitivity to the temperature.²⁵

CONCLUSIONS

This article investigated the properties of powdered ASAT synthesized by precipitation prepolymerization with AA and SA as monomers, ASE as crosslink agent and LPO as initiator in the solvent of ethyl acetate. NaHCO_3 was used to neutralize part of carboxyl acid of the polymer to precipitate ASAT easily in the organic system. The powders were normal distribution in the range 1–80 μm and showed a thermal stability below 150°C. Powdered ASAT was a weak acid which was sensitive to pH in water. Increasing pH value led to a swelling expansion of the macromolecule. Meanwhile, the viscosity and light

transmittance of ASAT emulsion also increased before pH 7. The properties of ASAT emulsions mostly depended on the usage amount of ASE and SA. Copolymerization of acrylic monomers with ASE formed a light crosslinked polymer with three-dimensional network. Therefore, increasing the amount of ASE led to an increase firstly and then decrease in the viscosity, a decrease monotonously in the light transmittance of the ASAT emulsion. Introduction of SA endowed ASAT with the associative character. When the amount of SA increased, the viscosity and light transmittance of the emulsions increased firstly and then decreased. Especially, All the ASAT emulsions with stearyl group showed shear thinning behavior, good salt tolerate, and less sensitivity to temperature.

ACKNOWLEDGMENTS

This work was financially supported by Shanxi Natural Science Foundation of China (No. 201211046-3), Shanxi Scholarship Council of China (No. 2013-151) and National Science & Technology (Grant No 2014BAE03B03), which are gratefully acknowledged.

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