Preparation and Characterization of Styrene Acrylate Emulsion Surface Sizing Agent Modified with Rosin

Jianfeng Xu, Huiren Hu

Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology, Tianjin, 300457, China

Received 24 January 2011; accepted 17 March 2011
DOI 10.1002/app.34495
Published online 28 July 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A series of core-shell type cationic soap-free latex were prepared by using styrene(St), butyl acrylate(BA), and methyl methacrylate(MMA) as main materials and introducing rosin as the functional monomer. Cationic starch (CS-8), which has low relative viscosity, was used as the emulsifier and dispersant. The influencing factors of the reaction were studied and the optimal conditions were achieved. Then the products were characterized by scanning electron microscope (SEM), FT-IR, laser particle sizer, and particle charge detector (PCD). The results showed that the excellent performance and good sizing effects of SAE were achieved when the reaction conditions were as follows: the starch amount was 8 wt %, the charge of the initiator (APS) was 0.5%, and the amount of rosin was 2 wt %. Under these conditions, the particle size of the latex was around 100 nm and had a narrow distribution, and the charge density of latex was 0.61 mmol L^{-1}. The water-resistant performance of paper was improved significantly when SAE was modified with rosin, and the Cobb value decreased by 46.8% compared to that of the paper sized by SAE without rosin. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 611–616, 2012

Key words: SAE; cationic soap-free latex; rosin; functional monomer; surface sizing

INTRODUCTION

With the development of papermaking, printing, and the related fields, more and more attention has been paid to the properties and advantages of surface sizing. Moreover, surface sizing is indispensable to obtain good printability, shape stability, water-resistant, and oil-resistant ability of paper. So there is a huge demand for the surface sizing agent with good characteristics.[1,2] The commonly used polymer surface sizing agents are as follows: alkyl ketene dimmer (AKD), styrene-maleic anhydride (SMA), styrene acrylic acid (SAA), styrene acrylate emulsion (SAE), and polyurethane (PU). Compared with AKD, the hydrolysis of SAE is more difficult, therefore the fugitive sizing phenomenon is almost eliminated and there is no more curing problem. Meanwhile, the application cost of SAE is much lower than that of polyurethane, its film-forming property is superior to SMAs, and its water resistance is better than SAAs.[3–5]

Rosin, which is mainly composed of alkyl-perhydrophenanthrene, is a kind of resin acid. Because of the nonpolar tricyclic structure of its molecule, the rosin has excellent water-resistance performance, which is advisable and critical for rosin to be used in surface sizing.[6] Furthermore, traditional SAE has excellent film-forming property, but limitation on weatherability and water-resistance performance.[7,8] In this study, a series of core-shell type cationic soap-free latex, combining the advantages of rosin and traditional SAE, had been synthesized by using rosin as the functional monomer. And the cationic starch, which has low cost and excellent electrochemical performance, was used as the protective colloid and stabilizer. In the process of emulsifying, the surface of the monomers is covered by cationic starch emulsifier. Because of the cationic charge of cationic starch, the electrostatic repulsion between the monomers is formed, which keeps a stable emulsion system. Subsequently, the effect of rosin on the characteristics of SAE and its surface sizing behavior were determined.

EXPERIMENTAL

Materials

The main materials were styrene (St), butyl acrylate (BA), methyl methacrylate (MMA), acetic acid, and ammonium persulfate (APS): analytically pure. The starch used in modifying SAE was CS-8. Dimethylaminoethyl methacrylate (DM), starch (CS-8), and rosin were industrial products. The starch used in sizing process was cationic cassava starch. Corrugated medium with basis weight of 110 g m^{-2} was

Correspondence to: J. Xu (xujianfeng198218@yahoo.com.cn) or H. Hu (huiren@tust.edu.cn).

supplied by Tianjin Guangjuyuan Paper. Aluminum sulfate was chemically pure, SAE was synthesized in laboratory.

Preparation of cationic SAE

First, an amount of distilled water was used in a four-port flask with stirring device, condensing device, and thermometer. Then, a certain quantity of CS-8 and APS were added into the flask under stirring. The flask was heated till 90°C, and it was kept for 30 min. Then, a certain quantity of acetic acid was added into the reactor, followed by 20% of the mixed monomers and 20% of the initiator (APS, wt % = 10%). The residual monomers including St, BA, MMA, DM, and rosin were continuously added drop wise within 70 min while the residual initiator was added within 90 min. After all the chemicals were added, the temperature was cooled down to 86–88°C and maintained for 3 h. Finally, the cationic SAE emulsion was obtained by removing the latex out of the reactor, cooling and filtering.

Characterization

The polymer structure was determined by FT-IR(BRUKER VECTOR22); the morphology and size of particles were observed by SEM (JEOL JSM-5310) and laser particle sizer (Brookhaven 90Plus), respectively. And the particle size was measured at the concentration of 0.01%. The charge density of emulsion was measured by particle charge detector (BTG, PCD03) at the concentration of 10^{-4} g L^{-1}. The emulsion stability, including mechanical stability, storage stability, pH stability, calcium ion stability, and dilution stability were investigated.[9]

Surface sizing of cationic SAE

Certain amount of cassava starch was cooked with addition of ammonium persulfate, and then the concentration was regulated to 10% by adding water. The gelatinized starch, aluminum sulfate, and self-made SAE were mixed at a certain weight ratio. The surface sizing was made under concentration of 10% and temperature of 50–70°C. According to the literature,[4] the sizing films were prepared by drawdown using wire-wound bars, and dried on the glazer at a temperature of 105°C.

Physical properties of paper sheets

The physical properties and sizing degree of sized paper sheets were measured according to ISO standard methods, respectively: ISO/DIS 12192 and ISO 535.

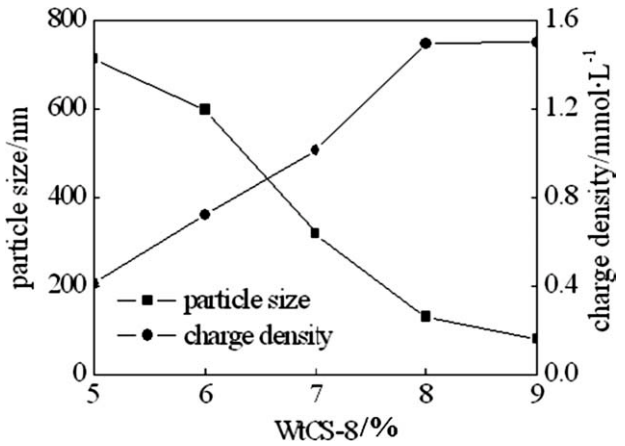

Figure 1 Effect of the dosage of CS-8 on the particle size and charge density of SAE.

RESULTS AND DISCUSSION

Effect of the dosage of CS-8 on the particle size and charge density of SAE and its surface sizing behavior

Effect of the dosage of CS-8 on the particle size and charge density of SAE

In this study, CS-8 has dual functions. It not only provides the location for polymerization, but also stabilizes the polymer particles.

The particle size affects the emulsion performance and its application performance. In general, narrow distribution and small dimension of particle size contribute to excellent emulsion performance. In addition, because of the electro-negativity of the papermaking raw material-fiber, the paper chemicals should be electro-positive and the charge density of the emulsion is certainly a key index. In this study, the particle size and the charge density of emulsion are of particular interest.

Figure 1 showed that with the increase of the dosage of CS-8, the particle size of latex decreased and the charge density of latex increased.

When the dosage of CS-8, used as the emulsifier and dispersant, is small, it is hard to generate lots of latex particles in system, leading to poor dispersion of the polymer particles. Moreover, because of the inadequate emulsification, starch (CS-8) couldn't cover the whole latex particle completely and the emulsion system is less stable. In addition, low surface charge density of polymer particles and thin hydrated layer can result in the coagulation due to more frequent collision of the particles, thus leading to larger particle size of the SAE. Oppositely, the increase in the dosage of CS-8 led to the increase in the number of micelles and increase in the rate of initiation reaction and the rate of whole reaction. So the polymer particles disperse much better and the diameter becomes smaller.

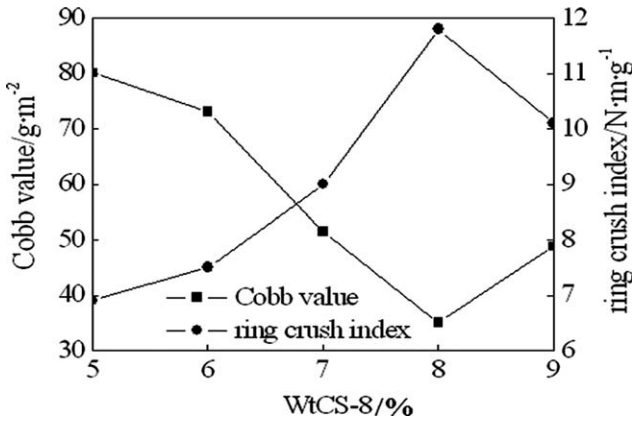

Figure 2 Effect of the dosage of CS-8 on the surface sizing behavior of SAE.

On the other hand, when the dosage of CS-8 is small, the conversion of the cationic monomer (DM) is low, leading to low charge density of emulsion. With the increase of the CS-8 dosage, the amount of the micelles becomes larger and the rate of polymerization becomes faster. As a result, the conversion of DM becomes gradually higher. Because of the more cationic groups provided by DM on the polymer molecular chain, the higher charge density of latex is obtained. When the dosage of CS-8 was higher than 8%, the conversion of DM changed little and the charge density of latex almost unchanged.

Effect of the dosage of CS-8 on the surface sizing behavior of SAE

As shown in Figure 2, it was obvious that an increase in the dosage of CS-8 led to an increase in the ring crush index of paper sheets. When the dosage of CS-8 was larger than 8%, the ring crush index of paper decreased. This is because with the increase of the CS-8 dosage, the amount of the solubilization micelles increases at the initial reaction stage, which leads to the increase of the amount of emulsion particles, and the particle size becomes smaller (Fig. 1). Owing to the small particle size, the permeation and film formation of polymer on the paper surface is easy, which is helpful for the improvement of the mechanical strength of polymer film. As a result, the ring crush index increases. When the dosage of CS-8 is higher than 8%, the hydrophilicity of polymer increases, leading to more absorption of water by paper and the decrease of the ring crush index of paper.

Figure 2 showed that with the increase of the dosage of CS-8, the Cobb value of paper decreased at first then increased. It indicates that the sizing degree of paper increases at first then decreases. It is because when the dosage of CS-8 is small, the massive generation of emulsion particles is restricted at the initiation reaction stage, leading to larger particle size (Fig. 1). So it is difficult for the permeation and film formation of polymer on the paper surface and low sizing degree of paper is obtained. With the increase of the dosage of CS-8, the particle size becomes smaller and more emulsion particles are got. So it is easy for the permeation and film formation of polymer on the paper surface and the high sizing degree of paper is obtained. But when the dosage of CS-8 is larger than 8%, the hydrophilicity of polymer increases, leading to lower sizing degree of paper. Finally, the optimized dosage was obtained with 8% (wt %).

Effect of the dosage of the initiator (APS) on the particle size and charge density of SAE and its surface sizing behavior

Effect of the dosage of APS on the particle size and charge density of SAE

The type and dosage of initiator have critical affect on the performance of latex. In this study, APS is chosen as the initiator.

From Figure 3, it was shown that with the increase of the dosage of APS, the particle size decreased at first then increased and the opposite trend of charge density of emulsion was observed. When the dosage of APS was larger than 0.6%, the charge density changed little.

With the increase of the dosage of APS, the formation rate of free radicals and the chain termination rate increase, leading to lower average molecular weight of polymer and larger amount of emulsion particles. As a result, small particle size is got. When the dosage of APS is larger than 0.5%, the termination rate of polymerization increases, leading to a decrease of average life of the free radicals. And the dosage of initiator, which participates in the initiation reaction, is small. With the increase of the dosage of APS, the reaction rate relatively decreases and the amount of latex particles, which participate in

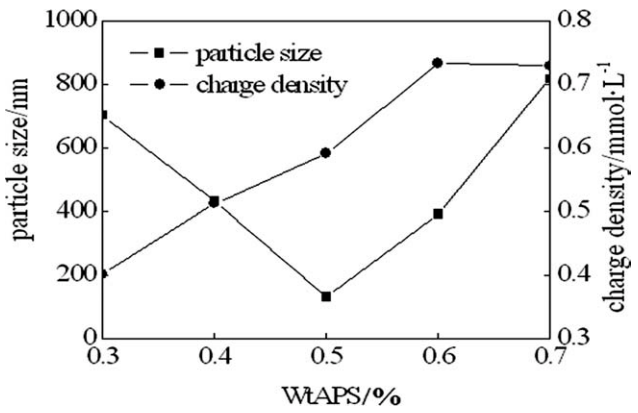

Figure 3 Effect of the dosage of APS on the particle size and charge density of SAE.

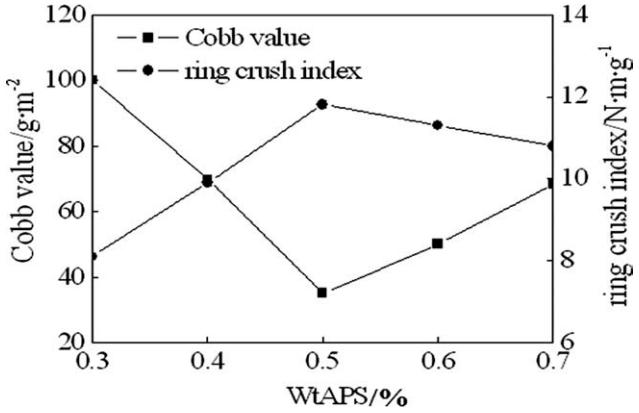

Figure 4 Effect of the dosage of APS on the surface sizing behavior of SAE.

the reaction, becomes small. As a result, the particle size of latex becomes bigger.[10]

On the other hand, when the dosage of APS is small, the reaction rate is low, resulting in the residual of some of the monomers. Because of the presence of residual monomers, the conversion of the cationic monomer (DM) is low, leading to lower charge density of emulsion. And with the increase of the dosage of APS, the amount of the free radicals becomes larger and the rate of polymerization becomes faster. So the conversion of cationic monomer gradually enlarges. Because of more cationic groups provided by DM on the polymer molecular chain, the higher charge density of emulsion is obtained. When the dosage of APS is higher than 0.6%, the conversion of DM increases little and the charge density of latex is almost unchanged.

Effect of the dosage of APS on the surface sizing behavior of SAE

The ring crush index of paper, sized by SAE, increased at first then decreased (Fig. 4). This is because with the increase of the dosage of initiator

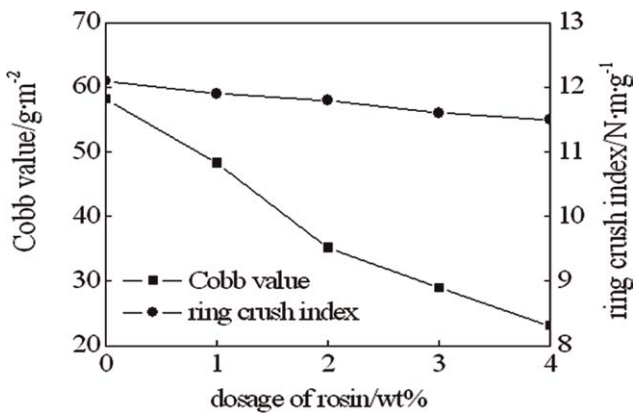

Figure 5 Effect of the dosage of rosin on the sizing performance of SAE.

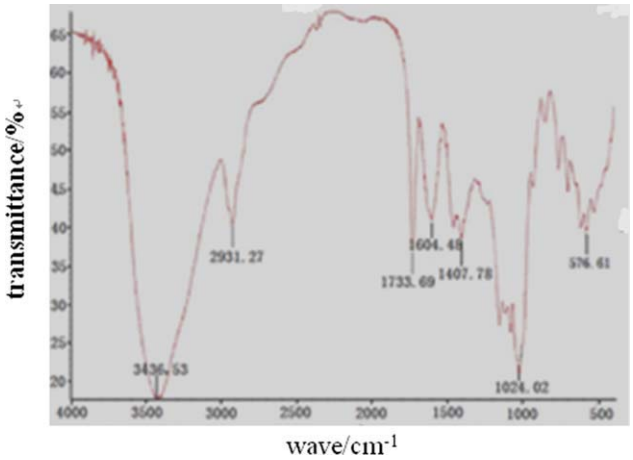

Figure 6 FT-IR spectra of SAE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(from 0.3 to 0.5%), the particle size of SAE becomes smaller (Fig. 3). So the permeation and film formation of polymer on the paper surface is easy, which is helpful for the improvement of the mechanical strength of polymer film. But when the dosage of APS is larger than 0.5%, the particle size of SAE becomes bigger (Fig. 3) and it isn't close for the stacking of the particles when the polymer film forms, leading to the forming of poor film on the paper. So the ring crush index of paper decreases.

In addition, with the increase of the dosage of APS, the particle size of SAE decreased at first then increased (Fig. 3). When the particle size is small, it's close for the stacking of the particles when the polymer film forms, so it is difficult for the water's permeation into the film. As a result, excellent water resistance of paper is obtained, which is presented as low Cobb value. Oppositely, when the particle size becomes large, poor film on the paper is got and it is easy for the permeation of water into the film. So the water resistance of paper is poor, which

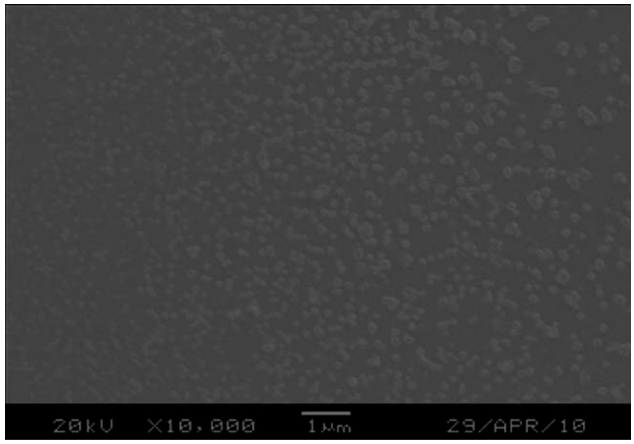

Figure 7 SEM photograph of copolymer emulsion particles.

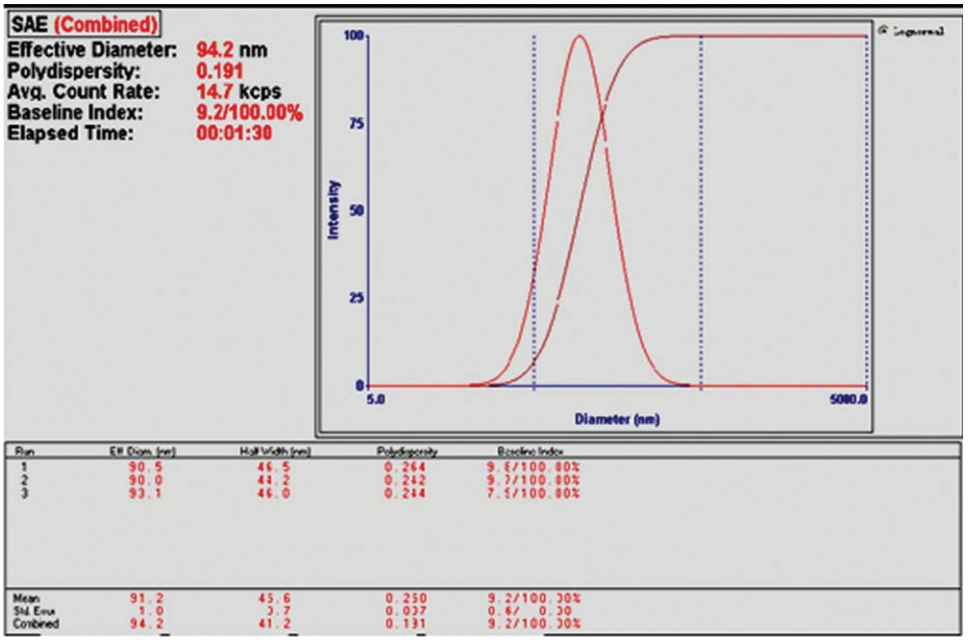

Figure 8 Particle size distribution of copolymer emulsion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is presented as high Cobb value. Finally, the optimized dosage was obtained with 0.5% (wt %).

Effect of the dosage of rosin on the surface sizing behavior of SAE

The water-resistant performance of paper, sized by SAE, is critical for the evaluation of SAE. So rosin is chosen as the functional monomer to improve the sizing performance of SAE. In the reaction, rosin was dissolved into the mixed monomers and charged in drops continuously. And because rosin doesn't participate in the propagating reaction, the dosage of rosin has little effect on the particle size and the charge density of emulsion. So the effect of the dosage of rosin on the surface sizing behavior of SAE was investigated only.

As shown in Figure 5, with the increase of the dosage of rosin, the Cobb value of paper, sized by SAE, decreased significantly, this indicated that the water-resistance of paper increased significantly. And with the increase, the ring crush index of paper changed slightly.

It was shown in Figure 5 that the SAE, modified with rosin, had an excellent sizing performance, compared to the SAE without rosin. The Cobb value of paper, sized by the emulsion with rosin, decreased significantly. When the dosage was 2%, the good sizing effect had been got. This is because there are masses of hydrophobic-groups, provided by rosin; masses of hydrophobic-groups on the paper surface after latex's film forming on paper surface are obtained. As a result, the water resistance of paper is improved and the more rosin is used; the lower Cobb value is got.

Figure 5 also showed that with the increase of the dosage of rosin, the ring crush index of paper decreased slightly. The reason is that after the drying and forming-film of SAE, the fragile film is got, due to the presence of rosin in emulsion. So the ring crush index of paper decreases slightly. But in general, there is just a very small decrease in the ring crush index.

TABLE I
Performance of SAE Prepared in Lab

	Property
Particle size (nm)	94.2
Charge density (mmol L^{-1})	0.61
Appearance	Transparent, blue light
Mechanical stability	Stable
Storage stability stability	Stable during 90 days
pH stability	9–1
Calcium ion stability	Stable, has no layer
Dilution stability	Stable

TABLE II
Physical Properties of Corrugating Medium After SAE Surface Sizing

	Unsized paper sheets	Paper sheets sized by SAE	
Cobb value (g m^{-2})	119.8	60.3 (rosin 0)	32.1 (rosin 2%)
Ring crush index (N m^{-1} g^{-1})	5.0	9.9 (rosin 0)	9.8 (rosin 2%)

Note: the dosage of SAE is 2 kg ton^{-1} paper.

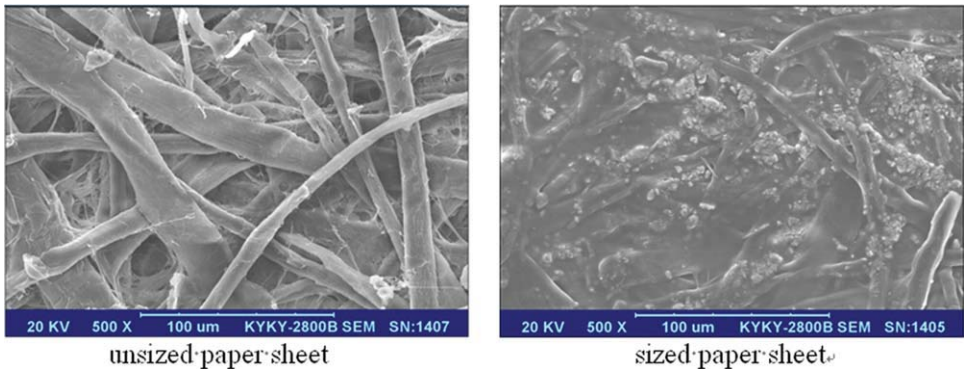

Figure 9 SEM of paper sheets. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Considering the effect of rosin on the sizing performance of SAE and the production cost, the optimized dosage was obtained with 2% (wt %).

Characterization

The polymer was characterized by FT-IR, SEM, laser particle sizer, and PCD. Figure 6 showed that there were specific adsorption peaks of main functional groups for SAE. The stretching vibration adsorption peak of hydroxyl (—OH) is 3436.53 cm^{-1}, 2931.27 cm^{-1} is stretching vibration adsorption peak of C—H in methyl and methylene, 1733.69 cm^{-1} is adsorption peak of carbonyl (C=O) in ester group, 1604.48 cm^{-1} is stretching vibration adsorption peak of C=C in olefin. FT-IR indicates that the polymer product contained molecular chain of St, BA, MMA, and DM.

From Figures 7 and 8, we observed that the particle of SAE was fine and with spherical shape. The particles were well distributed, with the average diameter around 100 nm. The performance of SAE, which was prepared under the optimum conditions, was studied, the results were shown in Table I. From Table I, it is observed that the excellent performance of emulsion is got in the lab. The small particle size, moderate charge density, and good stability are obtained.

Sizing properties of SAE

Under the optimum conditions, SAE soap-free emulsions, modified with rosin, were prepared. The sizing behavior of SAE was studied, as shown in Table II. As shown in Table II, after sizing with SAE, Cobb value of corrugated medium decreased significantly and the ring crush index increased remarkably, compared to those of unsized paper. Moreover, the SAE, with the rosin as the functional monomer, had an excellent sizing performance (46.8% decrease of Cobb value), compared to the SAE without rosin. It indicated that the water resistance of paper, sized by SAE with rosin, was improved significantly. Figure 9 showed that compared to the unsized paper, there was a compact film on the paper surface, which was sized by SAE. It indicated that the film-forming property of SAE was excellent.

CONCLUSIONS

1. The core-shell type cationic soap-free latex with excellent performance were obtained under the conditions as follows: when the dosage of CS-8 was 8%, APS was 0.5%, rosin was 2%, the particle size of the latex was around 100 nm and had a narrow distribution. Under these conditions, the charge density of latex was moderate and excellent sizing effect was obtained.
2. The water resistance of paper, sized by SAE with rosin, was improved significantly. When the dosage of SAE was 2 kg ton^{-1} paper sheets, the Cobb value of paper sheets decreased by 46.8%.

References

1. Brine, W. R. Pulp Pap 2004, 63, 50.
2. Hu, H.; Xu, L.; Dong, R., Eds. Papermaking Chemicals; Chem Industry Press: Beijing, 2008.
3. Koji, I. Paper preventing curl and method for producing 2002, Japanese patent: 2002307927.
4. Li, J. Preparation, Properties, and Application of a Soap-Free Latex Based on Styrene Acrylate Copolymer as a Surface Sizing Agent; South China University of Technology: Guangzhou, 2007.
5. Exner, R. Pap Technol 2002, 30, 45.
6. Wang, F.; Wu, Z. H.; Tanaka, H. Wood Sci 1999, 45, 475.
7. Donnelly, S.; Stockwell, J. R.; Plonka, J. Aqueous polymeric latex compositions and their use for the sizing of paper 2004, American patent: 6802939B1.
8. Carlos, F.; Luz, C.; Luis, J. J Appl Polym Sci 2007, 103, 3964.
9. Warson, H.; Finch, C. A., Eds. Applications of Synthetic Resin Latices; Wiley: Chichester, 2001.
10. Liu, B.; Shen, Y. Fine Chem 2010, 6, 604.