Improvement of ASA sizing efficiency using hydrophobically modified and acid-hydrolyzed starches

HAK LAE LEE, JONG SOO KIM, AND HYE JUNG YOUN

ABSTRACT: Reducing the hydrolysis and controlling the particle size and adsorption characteristics of ASA emulsion are critical to improving the emulsion stability and sizing efficiency. A new cationic corn starch has been prepared by two starch modification methods—esterification with OSA (octenyl succinic anhydride) and acid hydrolysis. These modifications were evaluated with regard to their effects on the characteristics of ASA emulsion and its sizing efficiency. Hydrophobic chains introduced to the cationic corn starch via esterification decreased the hydrolysis reaction of ASA. Acid hydrolysis of starch produced smaller particles of ASA, which increased the sizing efficiency.

Application: ASA sizing was improved by attaching hydrophobic hydrocarbon chains by esterification and controlling the molecular weight of cationic corn starches.

Alkaline and neutral processes are widely used to produce paper and board. Alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) are the two most extensively used sizing agents in alkaline papermaking. They represent two extremes. The much slower reaction rates of AKD give it a long shelf life and good stability but also increase the time required to develop sizing. On the other hand, ASA develops sizing in the sheet much faster, but its shelf life is shorter, and it is not as stable as AKD.

With ASA, 80% to 100% of the sizing is usually developed on the machine. ASA is preferred for such grades as fine papers and gypsum board because of its on-machine sizing and size press holdout [1, 2]. The high reactivity of ASA with cellulose indicates that it hydrolyzes rapidly, which means ASA suffers from extensive hydrolysis if conditions are not carefully controlled. The hydrolysis product is a dicarboxylic acid, which has been shown to be quite detrimental to sizing and machine runnability [2, 3]. The disadvantages of ASA sizing include press picking, deposits, and sheet defects such as desizing. Since these disadvantages are closely related to the hydrolysis reaction of ASA [4], a method needs to be developed that decreases the hydrolysis of ASA.

Problems associated with the hydrolysis of ASA can be minimized by controlling the temperature and pH of the emulsion [5] and by improving retention [6]. Unfortunately, however, these approaches are passive in nature, and it would be better to have ASA emulsions that are stable and resistant to hydrolysis. Furthermore, if these emulsions are retained well on fiber surfaces and if they provide good sizing, it would be possible to get more control over papermaking processes.

Cationic potato starch has been claimed to be the most effective emulsifier and stabilizer for ASA sizing [1, 7]. However, to cut costs, highly effective cationic starches can be prepared with less expensive corn starches. In this study, we prepared a hydrophobically modified corn starch by reacting corn starch with OSA (octenyl succinic anhydride) and used it along with cationic corn starch as an emulsifying agent for ASA. In addition, we carried out the acid hydrolysis of starches as a way to control the molecular weight of starch as well as the particle size of ASA emulsion. We also studied the effects of esterified starch and the acid hydrolysis of starches on the stability, sizing, and retention of ASA emulsions.

MATERIALS

A commercial ASA size with a single carbon chain of 16–18 carbon atoms was used in this experiment. Dent corn starch was cationized to DS 0.04 with a reagent containing quaternary ammonium groups. A commercial cationic potato starch and a maize starch with DS values of 0.035 and 0.036, respectively, were also used. The cationic substituents of commercial products were also quaternary ammonium groups.

Esterified starch (ES) was prepared by treating waxy maize starch with 1% OSA. A solution of 1*N* sulfuric acid was used for pH control and acid hydrolysis. Acid was added to the starch slurry before cooking (unless otherwise specified). Bleached hardwood kraft pulps were used to form handsheets for sizing tests.

EXPERIMENTAL METHODS

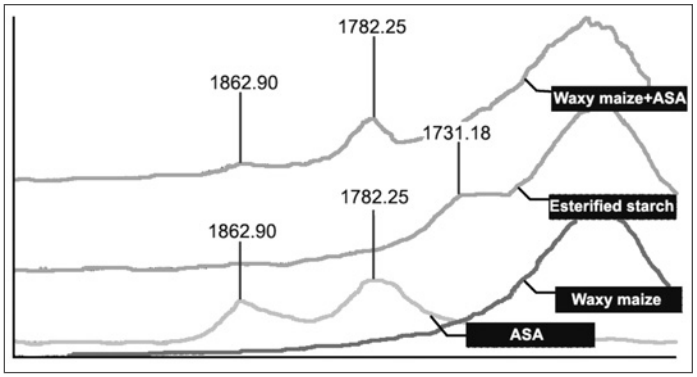
Starch cooking and emulsification

Starch slurries at 4% solids were heated to 95°C and were held at that temperature for 30 min. We carried out acid hydrolysis of starches by adding a sulfuric acid solution to the starch slurry before cooking. The cooked starch solution at 4% solids was rapidly cooled to 38°C, and then ASA was added for emulsification.

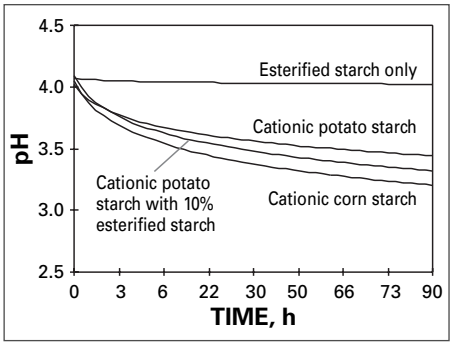
The amount of liquid ASA contained in the emulsion was 1%, and the ratio of starch to ASA was 4:1. ASA emulsions were prepared in batches of 300 g with a variable-speed, rotor-stator homogenizer (Ultra-Turrax T50). For emulsification, the rotor speed was set to 7000 rpm, and the shearing time was 120 s. Each ASA emulsion was used within 30 min after emulsification to prevent hydrolysis.

Handsheets

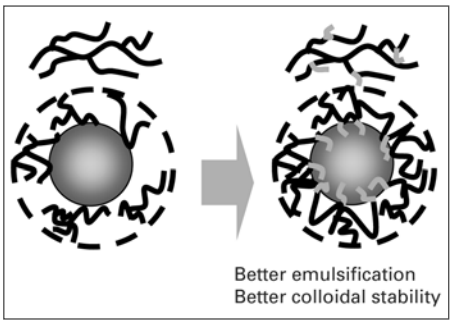
The paper furnish used for handsheet forming was bleached hardwood kraft pulp beaten to 450±10 mL CSF in a Valley beater. Handsheets at 70 g/m² were made on a laboratory sheet mold, pressed, and cylinder dried at 110°C. After conditioning the handsheets, we determined the



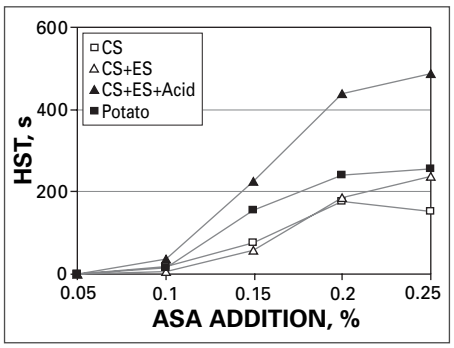
1. FT-IR spectra of ASA, esterified starch, waxy maize starch, and waxy maize starch with ASA.



2. Changes in pH for ASA emulsions prepared with various types of starches as emulsifiers.



3. Representations of size emulsions prepared with regular starch (left) and with esterified starch (right).



4. HST values of the handsheets sized with various ASA emulsions. (CS=cationic corn starch. ES=esterified cationic corn starch. Acid=acid hydrolyzed.)

degree of sizing by the Hercules Sizing Test (HST).

Adsorption characteristics of ASA emulsions

To examine the adsorption of ASA emulsions onto fibers, we determined the turbidities of ASA emulsions with concentrations ranging from 0.05% to 0.25%. We used a turbidity meter that provides a nephelometric turbidity unit (NTU) readout. We removed fines in the disintegrated bleached softwood kraft pulp by fractionating with a Dynamic Drainage Jar (DDJ) equipped with a 200-mesh screen.

A 500 mL portion of long fiber stock without fines at 0.875% consistency was placed in a DDJ that has a 400-mesh screen as a separating medium. Then we added 0.2% of ASA emulsion based on o.d. fiber. After 1 min of stirring at 500 rpm, about 100 mL of filtrate was collected, and its turbidity was determined. Zeta potentials of pulp slurries were measured with SZP 04 from Mütek.

RESULTS AND DISCUSSION

Esterified starch

To determine whether an ester was formed between OSA and starch, we obtained FT-IR spectra of ASA, waxy maize starch, and esterified starch. These spectra are shown in **Fig. 1**. ASA produces major IR peaks arising from the carbonyl of acid anhydride at approximately 1782 cm^{-1} and 1863 cm^{-1}, but it produces no IR bands in the ester range. On the other hand, starch esterified with OSA displayed a carbonyl stretching band of an ester bond at 1731 cm^{-1}. The carbonyl stretching band was rather weak because only 1% of OSA was used for esterification. When ASA was used for the esterification of starch, no change in the IR spectrum was observed from the carbonyl of acid anhydride, indicating the absence of ester bond formation.

Since dicarboxylic acid, the hydrolysis product of ASA, decreases the pH of ASA emulsion, the change in the pH of ASA size over time may be used as an indicator of the hydrolysis reaction. The pH values of ASA emulsions prepared with commercial potato and maize starches decreased with time until they stabilized at about pH 3.3 or 3.4, as shown in **Fig. 2**. The addition of 10% esterified starch to cationic corn starch decreased the reduction in pH. When the emulsion was prepared with esterified starch only, the pH remained constant, indicating the excellent protective nature of this hydrophobic starch against ASA hydrolysis.

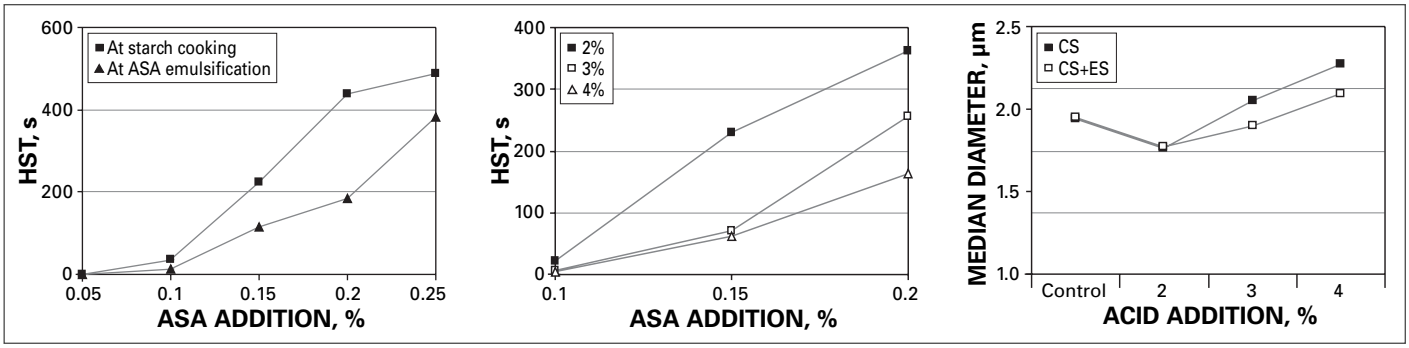
Figure 3 shows representations of size emulsions prepared with regular starch and esterified starch. Most of the hydrophobic alkenyl chains of the esterified starch appear to cover the ASA surface, providing hydrophobic encapsulation.

Sizing efficiency

As **Fig. 4** shows, the HST values of handsheets sized with ASA prepared with cationic potato starch were higher than the corresponding values of handsheets sized with ASA prepared with cationic corn starch. Cationic potato starches exhibit good emulsification properties, and they produce emulsions of small particle size and high sizing efficiency [8]. The median particle size of the ASA emulsion prepared with cationic potato starch was 1.74 μm, whereas the median particle sizes of emulsions prepared with other starches were from 1.87 μm to 1.94 μm.

Although cationic potato starch gave an ASA emulsion with a narrow particle size distribution, corn starches increased the amount of ASA emulsions with large particle sizes (>10 μm). The use of 10% esterified starch with cationic starch for ASA emulsification did not give any significant change in sizing, suggesting that even though esterified starch may decrease the hydrolysis of ASA emulsions, it would not necessarily improve sizing.

To increase the sizing efficiency of ASA, it is important to have ASA emulsion particles uniformly distributed on the fiber surfaces. To achieve a uniform distribution, we have to produce an emulsion with a small average particle size. In practice, however, producing such an emulsion can be difficult. The higher surface area of these small particles results in an increased rate of hydrolysis, particularly when the emulsion contains significant alkalinity [9].

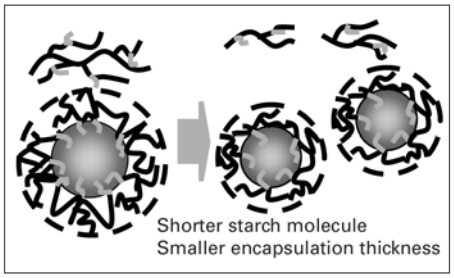


5. The effect of the acid addition point on sizing, the effect of acid dosage on HST values, and the influence of acid addition on ASA particle size.

Wasser has shown that smaller particles do hydrolyze faster, although the effect of particle size is much less than that of either temperature or pH [5]. On this basis, we examined acid hydrolysis as a way to prepare ASA emulsions with a fine particle size. The hydrolysis reaction rate has to be kept low to achieve small ASA particles, so we added 10% esterified starch to the cationic corn starch. The sizing efficiency of this ASA emulsion was far greater than that of other sizes, as Fig. 4 shows.

When the acid was added to the cooked starch just before emulsification, the improvement in sizing was relatively slight, probably because the starch molecules did not hydrolyze sufficiently (**Fig. 5**, left). Using cationic starches thinned with acid to various levels, Patton examined the effect of the initial molecular weight of starch on ASA sizing and found that the sizing response improved slightly as the initial molecular weight of starch decreased [8]. The effect of acid dosage on HST is depicted in the center graph of Fig. 5. When 2% of acid was added to the starch mixture before cooking, the HST values increased. More acid addition, however, decreased the sizing.

To see the influence of acid addition on the particle size of ASA emulsion, we determined the median particle sizes of the emulsions. Results showed that the median particle size of ASA emulsion decreased from 1.94 µm to 1.76 µm at the 2% addition rate of acid and then increased again with increasing acid addition (Fig. 5, right). When the addition of sulfuric acid was 2.3%, the particle size decreased to 1.70 µm, which is smaller than that of the emulsion prepared with cationic potato starch. Furthermore, the maximum turbidity of the ASA emulsion was obtained when 2.3% of acid was used to depolymerize starch molecules.



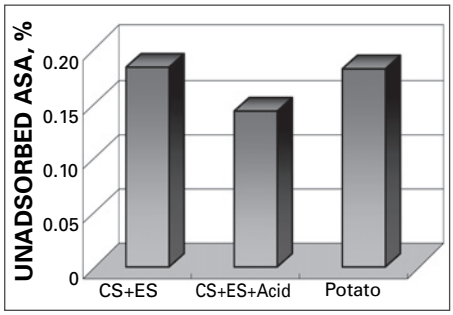
6. Acid-hydrolyzed starches can be used to prepare ASA emulsions with a smaller particle size.

Figure 6 is a sketch of the emulsion particles with acid hydrolysis employed for reducing the molecular weight of the starch emulsifier. As the particle size of the emulsion decreases, its surface area increases, which requires more starch molecules for stabilization. This finding suggests that the thickness of starch stabilizer should be reduced to generate small size emulsion particles if the ratio of starch to ASA is kept constant.

Retention of ASA emulsions

There is some evidence that an ASA emulsion of very fine particle size is not as effectively retained as emulsions of standard particle size, perhaps because of the increased number of emulsion particles or perhaps because of a reduction in the surface cationic charge. Whatever the mechanism, unretained ASA will inevitably undergo extensive hydrolysis while recirculating in an alkaline white water system. This condition will contribute to machine deposits and press picking because some hydrolyzed ASA—calcium salt is eventually returned to the headbox and retained in the sheet [9].

Size emulsion particles need to be adsorbed and retained on fiber surfaces to be effective in sizing. To evaluate the adsorption of ASA emulsion on papermaking fibers, we employed a turbidity measurement that is commonly used in estimating the weight concentrations of suspended or emulsified matter [10].



7. Amounts of unadsorbed ASA for size emulsions prepared with different starches.

The ASA emulsion adsorbed on long fiber surfaces was determined from the turbidity measurement data of the DDJ filtrate of a stock containing 0.2% ASA emulsion. For a given type of ASA, size, and additive system, we found that the turbidities of ASA emulsions depended only on the concentration of the emulsion particles, since all fines were removed by screening before the pulp slurry was prepared. Because no retention aid was used, the amount of adsorbed ASA was quite small, but acid hydrolysis appeared to increase the adsorption of ASA size (**Fig. 7**). This result indicates that the improvement of sizing with acid dosage was caused in part by the increased amount of ASA adsorption. Better retention of ASA will reduce many disadvantages of ASA sizing, including press picking, deposits, and runnability problems [11].

The adsorption of ASA emulsion onto fiber was also evaluated by measuring the zeta potential of papermaking furnishes. The zeta potential of the pulp fiber was –10 mV, and it increased to –2.4 mV when 0.15% of ASA emulsion was added. When 2% of acid was used to hydrolyze starch emulsifiers, the zeta potential increased further to –0.3 mV. Since quaternary ammonium groups gave positive charges regardless of pH, the changes in the zeta potential of a papermaking furnish after ASA sizing should reflect the amount of ASA adsorbed onto fibers.

CONCLUSIONS

ASA is an alkaline sizing agent that develops most of its sizing effect on the machine by reacting with cellulose. This rapid reactivity is desirable for on-machine sizing and size press holdout. However, rapid reactivity increases the hydrolysis reaction of ASA, which is detrimental to sizing and machine runnability. For many years, papermakers have wanted ASA emulsions that are resistant to hydrolysis.

To obtain ASA emulsions that are highly resistant to hydrolysis, we prepared a hydrophobically modified corn starch by reacting corn starch with octenyl succinic anhydride. Hydrophobic chains attached to starch molecules were expected to align onto the ASA surface and prevent water molecules from approaching and causing hydrolysis. This barrier effect of hydrophobic chains was evaluated by pH measurements. The pH of ASA emulsions prepared with the esterified starch remained constant at pH 4.1. On the other hand, the pH of ASA emulsions prepared with conventional cationic starch decreased rather rapidly to pH 3.3–3.4. Hydrophobically modified starch, however, did not show any improvement in sizing efficiency.

For better sizing efficiency, the distribution evenness of ASA on paper should be improved. As a way to improve distribution, we used acid hydrolysis of starches to prepare ASA emulsions with a small particle size. The reduction of the molecular weight of starch by acid treatment was expected to decrease the thickness of the starch layer of ASA emulsion and increase the number of emulsion particles. Results showed that the average particle size of the ASA emulsion was decreased from 1.94 μm to 1.76 μm at 2% addition rate of acid, and the sizing degree increased significantly. Furthermore, the results of turbidity and zeta potential measurements showed that the ASA emulsion prepared with esterified cationic starches and the acid hydrolysis procedure gave better retention than conventional emulsion gave.

In brief, a good combination for increasing the efficiency of ASA sizing is to reduce ASA hydrolysis with the use of hydrophobically modified starch and to improve the ASA distribution by controlling the molecular weight of the starch. **TJ**

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LITERATURE CITED

1. Farley, C.E., and Wasser, R.W., "Sizing with Alkenyl Succinic Anhydride" in *The Sizing of Paper*, 2nd edn., TAPPI PRESS, Atlanta, 1989, pp. 51–62.
2. Hodgson, K.T., *Appita J.* 47(5): 402(1994).
3. McCarthy, W.R., and Stratton, R.A., *TAPPI J.* 70(12): 117(1987).
4. Marton, J., *TAPPI 1995 Papermakers Conference Proceedings*, TAPPI PRESS, Atlanta, p. 97.
5. Wasser, R.B., *J. Pulp Paper Sci.* 13(1): 29(1987).
6. Gess, C.M., *TAPPI 1994 Papermakers Conference Proceedings*, TAPPI PRESS, Atlanta, p. 609.
7. Winters, J.C., and Best, R.W., *TAPPI 1985 Alkaline Papermaking Notes*, TAPPI PRESS, Atlanta, p. 51.
8. Patton, P.A., *TAPPI 1992 Papermakers Conference Proceedings*, TAPPI PRESS, Atlanta, p. 33.
9. Farley, C.E., *TAPPI 1985 Alkaline Papermaking*, TAPPI PRESS, Atlanta, p. 73.
10. Chen, G.C.I. and Woodward, T.W., *TAPPI 1987 Sizing Short Course Notes*, TAPPI PRESS, Atlanta, p. 93.
11. Finlayson, M.F., Hodgson, K.T., Cooper, J.L., *et al.*, *TAPPI 1996 Papermakers Conference Proceedings*, TAPPI PRESS, Atlanta, p. 309.

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INSIGHTS FROM THE AUTHORS

ASA is used in alkaline papermaking systems in many countries. This sizing agent, however, has not been widely accepted in Korea, mainly because of the runnability problems associated with its tendency to hydrolyze rapidly. To solve this problem, we have developed a hydrophobically modified starch that improves the emulsion's stability against hydrolysis.

During emulsification, hydrophobic chains attached to starch molecules are attracted to the surface of the ASA droplet. These chains prevent the ASA surface from reacting with water. We determined the emulsion's stability by measuring the changes in pH of ASA made with the modified process against the pH changes of ASA made by the conventional process. We also prepared an ASA emulsion with a small particle size to improve the distribution of ASA on paper surfaces.

Our results showed that better ASA sizing can be achieved by using hydrophobic modification and by controlling the molecular weight of the starch. This approach now needs to be tested under actual papermaking conditions.

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