

Use of Cationic PAM as a Surface Sizing Additive to Improve Paper Properties

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ABSTRACT

This study was focused on the use of cationic PAM (Polyacrylamide) as a surface sizing additive to improve the surface sizing properties of paper. Effects of the ionic property, viscosity and charge density of PAM on bending stiffness of surface sized papers were investigated. Use of cationic PAM as a surface sizing additive improved bending stiffness while addition of anionic PAM did not show any effect. Increase of starch holdout with the addition of cationic PAM was attributed as a prime reason of stiffness increase. Viscosity of PAM was one of the most important factors affecting surface sizing due to its influence on the interaction between cationic PAM and oxidized starch solution. Greater improvement of bending stiffness of paper was obtained when high charged PAM was used as an additive. The order of addition was found to have significant influence on the effect of additives since it influences the formation of network structure among starch, cationic PAM, and SA (styrene acrylic acid copolymer). Investigation on the penetration of starch solution was carried out with CLSM (Confocal Laser Scanning Microscopy), and it was shown that the addition of cationic PAM to oxidized starch solution made starch molecules stay on the paper surface rather than penetrating into the paper structure because of the electrostatic interaction between negatively charged fibers and positively charged cationic PAM.

INTRODUCTION

Increasing the filler content in printing paper is one approach to achieve cost savings in papermaking since expensive fibers can be substituted with cheap fillers. Increasing filler content also provides opportunities to improve many paper properties such as opacity, brightness, smoothness and printability. Conventional ways of increasing filler loading often results in decreases of mechanical properties, which limits the filler level in paper products [1]. Stiffness is most seriously affected with an increase of filler content in paper. To alleviate these problems of strength reduction associated with an increase in filler content, papermakers has developed a method called preflocculation of filler materials [2, 3, 4].

Preflocculation of fillers has been claimed to decrease the loss of many strength properties of paper compared with conventional filler loading system [5, 6, 7]. It is unavoidable, however, to lose strength properties of papers with an increase in filler contents even though preflocculated fillers are used. In other words, preflocculation of fillers just reduces the negative effect of filler loading on paper strength. This indicates that new methods or technologies should be found to solve the problem of strength reduction associated with increases in filler contents of paper. Surface sizing of paper can compensate the detrimental effects of fillers on

paper strength. In surface sizing, starch is applied to paper surface where it cements fibers to the body of paper and deposits a more or less continuous film on the paper surface. Oxidized starches are the major type of modified starches used for surface sizing since they show excellent resistance against retrogradation and good fiber bonding capability [7]. Oxidized starch solution, however, tends to penetrate deeply into the paper structure and remains less starch film on the paper surface. Thus it has marginal effect on improving the bending stiffness [7, 8]. Layer structure is the most effective way to obtain high bending stiffness. A layered structure is possible by surface sizing when the size does not penetrate into the sheet [9]. To reduce the penetration of starch solution into paper, it is necessary to promote interaction between starch and fiber. Since the fiber is negatively charged, use of cationic starch or additives will increase the interaction of the sizing agents with fiber. Application of cationic additives to increase the holdout of coating colors has been studied by Kogler *et al* [10]. They showed that cationic coating color improved coating holdout, fiber coverage and printability. Recently, Lee *et al* [8] showed that use of cationic starch instead of oxidized starch in surface sizing improved bending stiffness, optical properties and printability. Anionic trash load during broke recycling was also reduced. Total change of anionic surface sizing system to cationic one, however, increases the cost of paper

production due to the high price of cationic starches. It is required, therefore, to develop a method to improve the holdout of surface sizing agent on paper surface without using cationic starch system that requires complete substitution of cheap oxidized starches with expensive cationic starches. In other words, it is required to develop a method to improve the surface sizing efficiency with the use of cationic additives.

In this study, various cationic polyacrylamides (PAMs) have been prepared and tested for their effect on the properties of surface sized papers. Also the penetration phenomena of the surface sizing agents into paper have been investigated.

Experimental

Materials

Oxidized corn starches with different viscosities were used for surface sizing. Brookfield viscosities of 0.5% solutions of oxidized starch at 20°C were 7.0 cPs. Styrene acrylic acid copolymer (SA) was used as an additive for surface sizing. Diverse PAMs with different charge densities, molecular weights and ionic properties were prepared and utilized as surface sizing additives. The PAMs used are shown in Table 1. Low shear viscosity and charge density of the polymers used are summarized in the Table 1. Brookfield viscosity shown in Table 1 was measured at 20°C using 0.5% polymer solution. To examine the effect of molecular weight of PAM two cationic PAMs with high and low Brookfield viscosities were prepared. They were HV.C-PAM (high viscosity PAM) and LV.C-PAM (low viscosity PAM). These two PAMs showed similar charge densities while their viscosity values were quite different. Cationic and anionic PAMs were also prepared to evaluate the influence of charge types. And two cationic PAMs with high charge density (HC.C-PAM) and low charge density (LC.C-PAM) were prepared to investigate the effect of cationic charge density of PAMs as surface sizing additives. The difference of their viscosities was around 12%, while the difference in their charge density was 300%. LV.C-PAM is the same polymer as HC.C-PAM. Acridine orange was used as a fluorescent dye for staining the starch and PAM [8]. Sodium hydroxide solution (1 N) was used to control pH of starch solution. In most of experiments, handsheets made with hardwood BKP (bleached kraft pulp) was used. Properties of BKP are listed in Table 2.

Methods

Forming handsheets

Handsheets at a basis weight of 100 g/m² was prepared according to TAPPI Test Method T205 sp-02. Hardwood bleached kraft pulp was beaten to 450 mL CSF in a Valley beater. Sheets with a basis weight of 100 g/m² were formed on a square sheet former and pressed under the pressure of 345 kPa for 5 minutes. Handsheets were cylinder dried at 120°C and conditioned at 50% RH, 23±2°C for over 48 hours.

Table 1. Properties of polymers used for surface sizing

Polymers	Charge density (meq/g)	Viscosity (cPs) (0.5%, 20°C)	Molecular weight (Dalton)
OS	-0.16	7.0	
SA	-3.23	5.0	
High viscosity PAM (HV.C-PAM)	1.42	7.6	500,000
Low viscosity PAM (LV.C-PAM)	1.19	2.5	200,000
High charge density PAM (HC.C-PAM)	1.19	2.5	200,000
Low charge density PAM (LC.C-PAM)	0.41	2.8	200,000
Anionic PAM (HV.A-PAM)	-2.34	7.0	500,000

Table 2. Properties of hardwood BKP used for surface sizing

Ash content (%)	ISO brightness (%)	Initial freeness (mL CSF)
0.05	86.0	670

Preparation of surface sizing agents and surface sizing

Oxidized corn starch was cooked for 30 minutes at 95°C at 10% consistency. Starch solution pH was controlled to 8.5 using sodium hydroxide solution (1 N). Solution of PAMs that different in charge density, molecular weight, ionic property were added to the cooked starch solution with mechanical stirring, and then addition of styrene acrylic acid copolymer (SA) was made. Solids content and temperature of the final starch solution were kept constant at 10% and 50°C, respectively. The sequence of addition was as follows; starch, PAM, and styrene acrylic acid. The addition sequence was followed in all experiments. The amounts of addition of PAM and SA were 5 parts of starch solids. 5 pph of cationic PAM, and SA was added into starch solution based on starch solids content, respectively.

During surface sizing process, the temperature of 10% starch solution was kept constant at 50°C using a constant temperature heating system. Starch solution was applied to paper using an automatic rod coater (PI-1210 Film coater, Tester Sangyo Co. Ltd.). Starch pickup was controlled at 4.5 g/m² for the handsheet made from beaten stock to 450 mL CSF. Only one side of the handsheet was surface sized. After surface sizing with starch solutions with an automatic rod coater, it was air dried at 105°C and cylinder dried at 120°C. Conditioning of surface sized papers was carried out at 50% RH, 23±2°C for over 48 hours. Bending resistance of the samples was measured using a bending resistance tester.

Then bending stiffness was calculated from bending resistance. The results of all measurements were reported with error bars of 95% confidence intervals.

Evaluation of interaction between starch and PAM

Thermal titrations were carried out using an ultra-sensitive isothermal titration calorimeter (VP-ITC, Microcal Inc.) [12]. Before the titration, all samples were degassed using a Microcal Thermo-Vac for 5 min. The differential power (baseline) between the sample cell and the reference cell was $5 \mu\text{cal s}^{-1}$. Titration data were processed by MicroCal Origin version 5.0 and background titration heat was subtracted. In the isothermal titration calorimetry experiments, 0.5% cationic PAM solution was gradually added, drop-by-drop ($5 \mu\text{L}$ per drop) into 1.6 mL of 0.5% oxidized solution at 50°C , and the resulting heat effect of each injection was measured. The time interval between drops was 180 s and the temperature remained constant at 50°C . The results are expressed as heat flow into the calorimeter, so a positive heat reading indicates an endothermic reaction, and a negative reading an exothermic reaction.

Analysis of starch penetration into paper

Acridine orange solution 10 mL at a concentration of 0.05% was added to the starch solution 300 mL with 10% solids content and stirred for dyeing the solution at 50°C [13]. Acridine orange absorbs the visible light with wavelengths around 480 nm and emits fluorescence at wavelengths around 530 nm. Surface sizing with starch solutions containing acridine orange was carried out with an automatic rod coater. Then the surface sized handsheet was air dried at 105°C , and cylinder dried at 120°C , respectively. Conditioning of surface sized papers was carried out at 50% RH, $23 \pm 2^\circ\text{C}$ for over 48 hours.

CLSM images of the cross section of surface sized papers were obtained. Since the green color image in Fig. 1 indicates the presence of acridine orange contained in starch solution, the distribution of starch solution in z-direction can be evaluated by measuring the intensity of the green color. After acquiring images from z section of paper, profiling of fluorescence intensity was performed through the whole thickness of paper structure. Fig. 1 shows the profiling of fluorescence intensity, which was shown with a white bar. The length of the white bar was $204 \mu\text{m}$. The length from the starting point of white to paper surface was $58.12 \mu\text{m}$. The intensity of green color measured through the whole range of the white bar is shown in Fig. 2. As seen here the intensity was very low when the measurement was made outside of the paper. At the paper surface it increased abruptly and decreased again to reach the low level. The highest intensity of green color was 250, and its length of green color was $4.74 \mu\text{m}$. The thickness of handsheet was $148.3 \mu\text{m}$. The starch content was very high on paper surface. The highest intensity of green color of the

CLSM image should be obtained at the surface of the paper since some of the surface sizing agents remained on paper surface, and it would decrease as the distance from the paper surface increased. The intensity profile curve was moved to the left to make the maximum coincide with the Y axis and shown in Fig. 2 as a black profile curve. This shows that the starch content was quite high in the vicinity of the surface where surface sizing was made, and decreased abruptly inside of the paper [3, 11]. Almost no starch was detected on the opposite side of surface application.

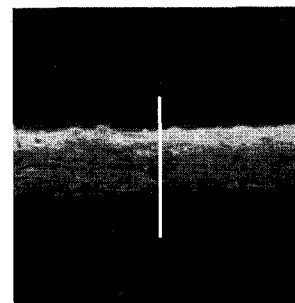


Fig. 1. Profiling method of fluorescence intensity to evaluate penetration of starch solution ($\times 200$).

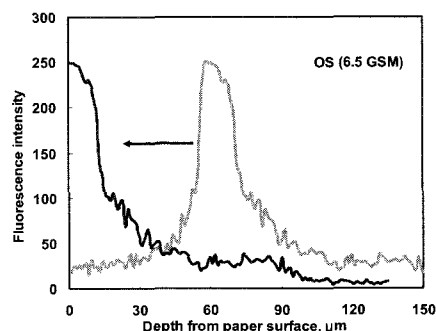


Fig. 2. Effect of surface application of oxidized starch on penetration of starch solution.

Results and discussion

Effects of PAM on the physical properties of handsheets

Effect of the addition of PAM into starch solution on pickup weight was evaluated and shown in Fig. 3. Pickup weight remained constant at 4.6 g/m^2 irrespective of the additives used. Addition of SA into starch solution gave no significant change in pickup weight. Effects of ionic properties of PAM were also evaluated and shown in Fig. 3. Viscosities of cationic and anionic PAMs were 7.6 cPs and 7.0 cPs, respectively. Pickup weight of starch was 4.5 g/m^2 , and the type of PAM did not cause any differences in pickup weight. The addition of PAM and SA gave no significant changes in pickup weight.

Effect of the addition of different PAMs into starch solutions on bending stiffness of paper was examined and shown in Figs. 4–6. The bending stiffness

of base paper and surface sized paper with oxidized starch was 0.77 mNm and 0.81 mNm, respectively (Fig. 4). Surface sizing with oxidized starch improved bending stiffness by 4.7%. Addition of SA did not contribute to the improvement of bending stiffness. The SA did not make starch remain on paper surface because the solution of SA penetrated easily into paper structure due to its anionic nature. Effects of the ionicity of PAM on bending stiffness were evaluated and depicted in Fig. 4. The use of high viscosity PAM as a surface sizing additive improved bending stiffness, but the application of anionic PAM did not increase the bending stiffness. The increase of bending stiffness with the addition of cationic PAM can be attributed to the fixation of oxidized starch on paper surface. It has been shown that starch solution with cationic PAM tends to stay on the paper surface rather than penetrating into the paper surface because of the electrostatic interaction between negatively charged fibers and positively charged cationic PAM molecules [8].

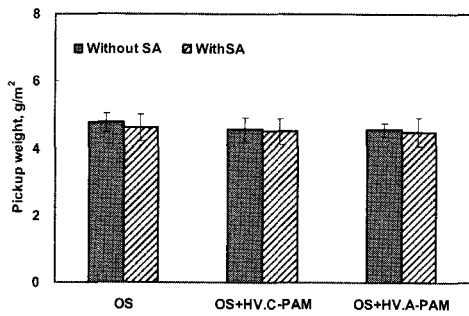


Fig. 3. Effect of addition of high and low viscosity of PAM on the pickup weight.

Bending stiffness increased by 4.6% with the combination use of SA and high viscosity PAM. But the use of SA along with anionic PAM did not improved bending stiffness. This suggests that electrostatic interaction between PAM and starch and SA is important for the improvement of bending stiffness [11]. The use of cationic PAM instead of anionic PAM was desirable to improve bending stiffness. Fig. 5 shows the effects of viscosity of cationic PAMs on bending stiffness. When low viscosity PAM was used, the bending stiffness was increased by 5.9%, while it improved by only 2.7% when high viscosity PAM was used. The combination use of SA and LV.C-PAM substantially increased the bending stiffness. This result suggests that low viscosity PAM, in other words PAM with low molecular weight, is more effective in improving the starch holdout. This may be due to the number of polymer molecules of PAM was far greater when low molecular weight PAM was used. Fig. 6 shows the effects of charge density of cationic PAM on the bending stiffness of paper. The use of high charge density PAM resulted in 5.9% increase of bending stiffness while the application of low charge density

PAM improved 3.9% of bending stiffness. The increase of bending stiffness with the combination of SA and high charge density PAM and low charge density PAM was 9.6% and 7.5%, respectively. The high charge density PAM was more effective in improving bending stiffness probably due to it increased starch holdout on paper surface.

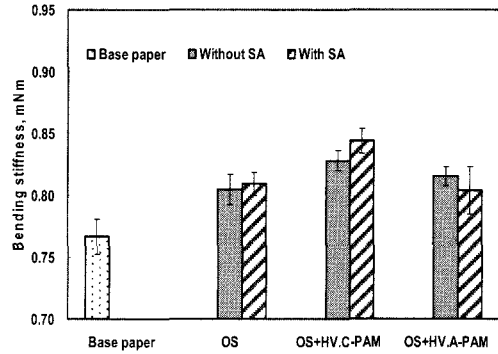


Fig. 4. Effect of addition of cationic and anionic PAM into oxidized starch on bending stiffness of paper.

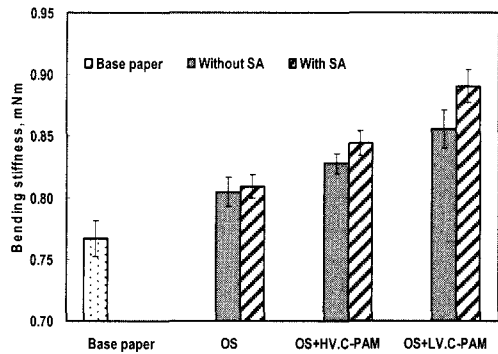


Fig. 5. Effect of addition of high and low viscosity of PAM into oxidized starch on bending stiffness of paper.

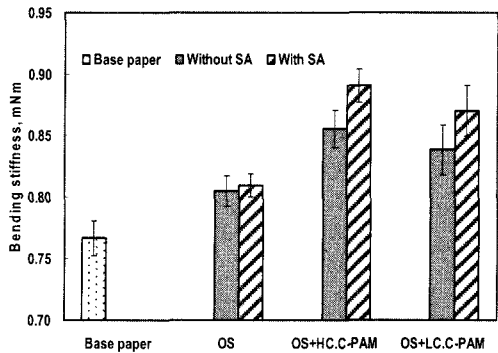


Fig. 6. Effect of addition of high and low charge density of PAM into oxidized starch on bending stiffness of paper.

The effects of addition order of cationic PAM and SA on bending stiffness were evaluated and shown in Fig. 7. Two cationic PAMs with similar charge densities but differed in viscosities were used. Addition of high and low viscosity PAM prior to SA substantially

increased the bending stiffness. The degree of improvement was higher with low viscosity PAM. The addition of cationic PAM after SA showed less improvement of bending stiffness compared to the addition of cationic PAM before SA. Prior addition of SA followed by PAM addition increased the bending stiffness more than the addition of cationic PAM only (Fig. 7).

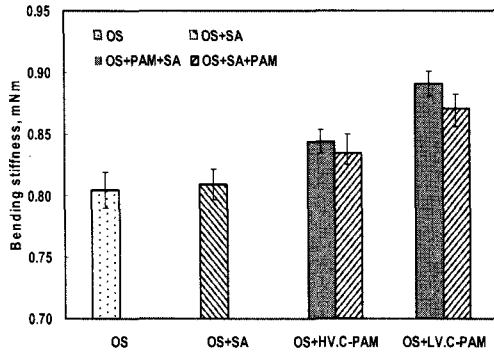


Fig. 7. Effect of addition order of high and low viscosity PAM into oxidized starch on bending stiffness of paper.

The enthalpy change when cationic PAMs with different viscosities was mixed with oxidized starch was investigated by ICT and shown in Fig. 8. The information about interaction between cationic PAM and oxidized starch could be obtained with this method [12, 14, 15]. Enthalpy change between PAM and starch shows that the interaction between low viscosity PAM and oxidized starch was higher than that between high viscosity PAM and starch. The interaction for the high viscosity PAM was low, and led to less improvement of bending stiffness. It appeared that low molecular weight PAM approaches oxidized starch with ease compared to high viscosity PAM.

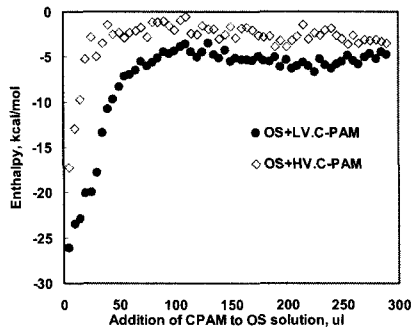


Fig. 8. Enthalpy change between high and low viscosity PAM and oxidized starch.

Fig. 9 shows the effects of low viscosity PAM and SA on penetration of starch solution. Addition of cationic PAM to oxidized starch solution made starch solution stay on paper surface rather than penetrating into paper structure (Fig. 10).

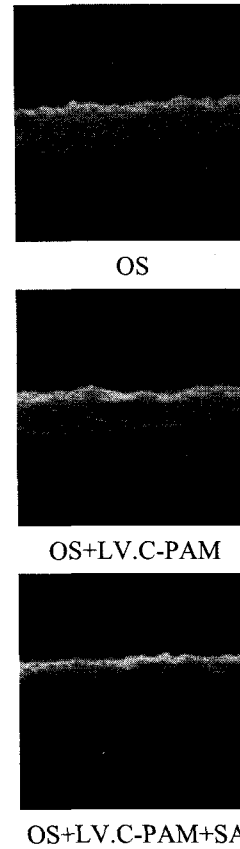


Fig. 9. Effects of addition of cationic PAM and SA on starch penetration into paper structure ($\times 200$).

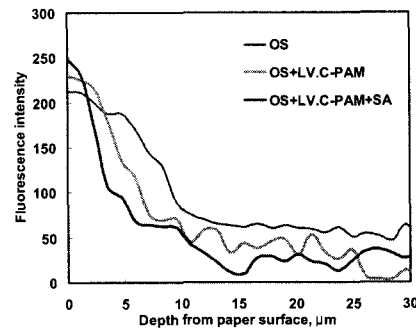


Fig. 10. Effects of addition of cationic PAM and SA on penetration of starch solution.

Conclusions

This study was focused on the use of cationic PAM (Polyacrylamide) as a surface sizing additive to improve the surface sizing properties of paper. Effects of the ionic property, viscosity and charge density of PAM on bending stiffness were investigated. Use of cationic PAM as a surface sizing additive improved bending stiffness while addition of anionic PAM did not show any effect. Viscosity of PAM was one of the most important factors affecting surface sizing due to its influence on the interaction between cationic PAM and

oxidized starch solution. The use of low viscosity and high charge density PAM was effective to improve the bending stiffness. Improved film formation with the addition of cationic PAM and SA was significant factor for increases in physical properties. The different roles of high and low viscosity of PAM were due to their interaction with oxidized starch.

The order of addition was found to have significant influence on the effect of additives since it influence the formation of network structure among starch, cationic PAM, and SA (Styrene acrylic acid copolymer).

After investigating penetration of starch solution by CLSM, addition of cationic PAM to oxidized starch solution made starch molecules stay on the paper surface rather than penetrating into the paper structure because of the electrostatic interaction between negatively charged fibers and positively charged cationic PAM molecules.

Literature cited

1. Mabee, S. W., Controlled filler preflocculation-improved formation, strength and machine performance, 2001 TAPPI papermaker conference
2. Tommey, T., Pruszynski, P. E., Armstrong, J. R., and Hurley, R., Controlling filler retention in mechanical grades, Technical Section CPA, 83rd Annual meeting.
3. Kettuner, K., Ake, K., Norell, M., U.S. Patent 6, 113, 741 (2000).
4. Fairchild, G., Coflocculation of fines and filler particles, *Paperi ja Puu*, 11: 649-653 (1985).
5. Shin, J. H., Han, S. H., S, C., Ow, S. K., and Mah, S., Highly branched cationic polyelectrolytes: filler flocculation, *TAPPI J.*, 80(11):179 (1997).
6. Bown, R., Particle size, shape and structure of paper fillers and their effect on paper properties, *Paper Technol.* 39: 44-48 (1998).
7. Casey, J. P, *Pulp and paper*, vol 3, New York, USA, (1981).
8. Lee, H. L, Shin, J. Y., Koh, C. H., Ryu, H., Lee, D. J., and Sohn, C. M., Surface sizing with cationic starch; its effect on paper quality and papermaking process, *TAPPI*, 1(1):34-40 (2002).
9. Kajanto, *Paper physics*, TAPPI press, 193-221 (2000).
10. Kolger, W., Spielmann, D., and Huggenber, L., Cationic coating colors present state and outlook, 1992 TAPPI papermaker conference.
11. Gees, J. M., Retention of fines and fillers during papermaking, TAPPI Press, Atlanta, USA (1998).
12. Gaudreault, R., Van de Ven, T., G, M., and W., M. A., Mechanisms of flocculation with poly(ethylene oxide) and novel cofactors, *Colloids and surfaces A:Physicochem Eng. Aspects*, 235:1-16 (2005).
13. Lipponen, J., Grön, J., Bruun, S. E., and Laine, T., Surface sizing with starch solutions at solids contents up to 18%, *JPPS J*, 30(3):82-90 (2004).
14. Weber, A., Herold, M., Brunner, H., and Tovar, G., E. M., Bioconjugative polymer nanosphere studied by isothermal titration calorimetry, *Thermochimica acta.*, 415:69-74 (2004).
15. Nyström, R., Hedström, G., Gustafsson, J., and Rosenholm, R. B., Mixtures of cationic starch and anionic polyacrylate used for flocculation of calcium carbonate-influence of electro, *Colloids and surfaces A:Physicochem Eng. Aspects*, 234:85-93 (2004).