Penetration Control of Surface Sizing Starch Using Cationic PAM and Its Effect on the Bending Stiffness of Paper

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Surface sizing is employed to increase the wetting resistance against liquids and to improve strength and surface properties of paper. Starch solution is the most widely used for surface sizing, and its effect is highly dependent upon how deep the starch solution penetrates into the paper structure. Better tensile strength can be obtained when starch penetrates deep into the thickness direction of paper. However, holdout of starch solution is beneficial for improving the stiffness and air or liquid resistance. This study was focused on the use of cationic polyacrylamide (PAM) as a surface sizing additive to control the penetration of starch solutions into paper, thus improving bending stiffness of paper. The effects of the ionic property, viscosity, and charge density of PAM on starch penetration and bending stiffness of surface sized papers were investigated. The penetration of starch solution was investigated with confocal laser scanning microscopy. The enthalpy changes accompanying the mixing of cationic PAMs with oxidized starch was determined using an isothermal titration calorimeter to see the molecular level interaction between PAM and starch in mixing. The addition of cationic PAM to oxidized starch solution made starch molecules stay on the paper surface rather than penetrating into the paper structure.

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INTRODUCTION

Increasing the filler content in printing paper is one of the most effective approaches to achieve cost savings in papermaking because it allows the substitution of expensive fibers with low cost fillers (Hubbe and Gill 2016). Increasing filler content also provides opportunities to improve many paper properties such as opacity, brightness, smoothness and printability. However, conventional ways of increasing filler loading often result in decreases of mechanical properties, which limits the filler level in paper products (Gill and Hagemeyer 1992; Hubbe and Gill 2016). Stiffness is the most seriously affected property with the increase of filler content in paper. To alleviate the problem of strength reduction associated with the increase of filler content, papermakers have developed various methods including lumen loading, shape modification and agglomeration of fillers, coflocculation of fillers and fiber fines, preflocculation of fillers, and coating of filler particles with dry strength polymers, *etc.* (Fairchild 1985; Tommey *et al.* 1997; Kettuner *et al.* 2000;

Porubská *et al.* 2002; Chauhan *et al.* 2011; Kumar *et al.* 2011; Im *et al.* 2015). These methods decrease the loss of many strength properties of paper compared with the conventional filler loading system (Bown 1998; Lee *et al.* 2002; Lee and Lee 2006; Hubbe and Gill 2016). It is unavoidable, however, to lose strength properties of papers with the increase of filler contents even though above-mentioned various approaches are employed. This indicates that new methods or technologies should be found to solve the problem of strength reduction associated with the increase of filler content of paper.

Surface sizing compensates for 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. Many surface sizing agents including starch, polyvinyl alcohol copolymers of styrene and acrylate (SAE), water-soluble polyurethane (PUD), copolymers of styrene and acrylate (SAA), copolymers of styrene and maleic anhydride (SMA) have been developed and used (Hodgson 1994; Samyn *et al.* 2010). Among them, oxidized starch is the most widely used for surface sizing because it is available at low cost and shows excellent resistance against retrogradation and good fiber bonding capability (Kearney 2005). Oxidized starch solution, however, tends to penetrate deeply into the paper structure, leaving less starch film on the surface. Thus, it has a marginal effect on improving the bending stiffness (Kajanto 1998; Lee *et al.* 2002). Layer structure is the most effective way to obtain high bending stiffness, and this can be made by surface sizing when the size does not penetrate into the sheet (Kolger *et al.* 1992). To reduce the penetration of starch solution into paper, it is necessary to increase the solids content of sizing solution or to promote interaction between starch and fiber. Lipponen *et al.* (2004) have shown that by increasing the surface size solids content, the penetration of the starch into the sheet can be decreased, which improves surface strength and bending stiffness. Because the fiber is negatively charged, cationic starch or additives increase the interaction of the sizing agents with fiber. The application of cationic additives to increase the holdout of coating colors has been studied by Kogler *et al.* (1992). They showed that cationic coating color improved coating holdout, fiber coverage, and printability. Lee *et al.* (2002) showed that the 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. Jun and Lee (2008) have shown that surface sizing with cationic starch improves the coverage and optical properties of coated papers. The overall change of an anionic surface sizing system to a cationic one, however, increases the cost of paper production due to the higher price of cationic starches.

Recently, graft copolymerization of starch by different monomers has been used to modify the surface sizing starch (Kim *et al.* 2017; Rajabi Abhari *et al.* 2017). In starch graft-copolymer, functional groups are attached to the main chain of starch along with their backbone monomers. This modification of starch improves the starch properties because functional groups and various monomers with desirable characteristics can be attached to starch molecules. Acrylic acid, acrylamide, methacrylic acid, and other acrylic/vinyl monomers are used for grafting onto starch. Rajabi Abhari *et al.* (2017) showed that addition of dextrin poly(acrylic acid) copolymer has beneficial effects on starch holdout. Because of its lower penetration into linerboard, higher compressive and bending strengths of sized paper sheet were obtained. This improvement in mechanical properties made it possible to reduce the pickup weight of the surface sizing agent around 23% while keeping the mechanical properties at a same level. Ni *et al.* (2017) showed that surface sizing with enzymatically degraded starch and 3-aminopropyl trimethoxysilane (APMS) improved the physical properties of paper because APMS forms covalent linkages with cellulose. The

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approaches of using starch graft-copolymers or specialty chemicals, however, have a serious economic disadvantage.

It is needed, therefore, to develop a method to improve the holdout of surface sizing agent on paper surface without using cationic or graft starch system that requires complete substitution of low cost oxidized starches with expensive cationic starch or starch copolymers. In other words, a method to improve the surface sizing efficiency with the use of cationic additives is needed. In this study, various cationic polyacrylamides (PAMs) were tested as surface sizing additives for improving starch holdout and stiffness. Penetration phenomena of the surface sizing agents into paper and the enthalpy changes accompanying the mixing of cationic PAMs with oxidized starch were investigated to evaluate the hypothesis that the bending stiffness of paper can be improved by the addition of cationic PAM additives to surface sizing solution.

EXPERIMENTAL

Materials

Oxidized corn starch (Sunsize, Samyang Genex, Daejeon, Korea) in powder form and diverse PAMs (Woojin Industry, Ltd. Kunsan, Korea) with different charge densities, molecular weights, and ionic properties were utilized for surface sizing. PAMs used in this study were liquid solutions, and their solids contents were 20.0± 1.0%. Low shear viscosity and charge density of the polymers and starch are summarized in Table 1. Low shear viscosity in Table 1 was measured using a Brookfield viscometer (DV-IP, Brookfield Engineering Laboratories, Inc., Middleborough, MA, USA) at 20 °C. A no. 1 spindle of the Brookfield viscometer was placed in the 0.5% solution of starch or polymer. Spindle rotation speed of 60 rpm was employed for the measurement. Charge density was determined using a streaming current detector (Mütec PCD, BTG, Germany) with 0.01 N of poly-diallyldimethylammonium chloride (poly-DADMAC) or sodium polyethylene sulfonate (PES-Na) as a titrating solution. Molecular weights of PAMs and SA were provided by the manufacturer. Styrene acrylic acid copolymer (SA, Woojin Industry, Ltd. Kunsan, Korea) was used as an additive for surface sizing.

To examine the effect of molecular weight of PAM, two cationic PAMs with high and low Brookfield viscosities were used. They were HV.C-PAM (high viscosity cationic PAM) and LV.C-PAM (low viscosity cationic PAM). These two PAMs showed similar charge densities, while their viscosity values were quite different. Cationic and anionic PAMs were also used 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 used to investigate the effect of cationic charge density of PAM as a surface sizing additive. The difference of their viscosities was around 12%, while the difference in their charge density was 290%. LV.C-PAM was the same polymer as HC.C-PAM.

Acridine orange (Sigma Aldrich, St. Louis, MO, USA) was used as a fluorescent dye to stain the starch and PAM (Lee *et al.* 2002). Sodium hydroxide solution (1 N) (Sigma Aldrich, St. Louis, USA) was used to control the pH of starch solution. Handsheets made with hardwood bleached kraft pulp (Moorim P&P, Ulsan, Korea) were used for surface sizing experiment.

Table 1. Properties of Polymers Used for Surface Sizing

Polymers	Charge Density (meq/g)	Viscosity (cPs) (0.5%, 20 °C)	Molecular Weight (Dalton)
Oxidized starch (OS)	-0.16	7.0	
Styrene acrylic acid copolymer (SA)	-3.23	5.0	100,000
High viscosity cationic PAM (HV.C-PAM)	1.42	7.6	500,000
Low viscosity cationic 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

Methods

Forming handsheets

Handsheets with basis weights of 100 ± 2.0 g/m^2 were prepared according to TAPPI T205 sp-02 (2002). Hardwood BKP was beaten to 450 mL CSF in a laboratory Hollander beater. Sheets were formed on a square sheet former and pressed under the pressure of 345 kPa for 5 min. Handsheets were cylinder-dried at 120 °C and conditioned at 50% relative humidity (RH) and 23 ± 2 °C for over 48 h.

Preparation of surface sizing agents and surface sizing

Oxidized corn starch was cooked for 30 min at 95 °C at 10 % consistency. The pH of starch solution was controlled to 8.5 using sodium hydroxide solution (1 N). PAM solution was added to the cooked starch solution with mechanical stirring, and then styrene acrylic acid copolymer was added and mixed thoroughly, when specified. The solids content and temperature of the final starch solution were kept constant at 10% and 50 °C, respectively. The amounts of PAM and SA were kept constant at 5 parts per hundred (pph) of the starch weight in all experiments.

During surface sizing, the temperature of the 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., Saitama, Japan). A no. 10 wire-wound rod and coating speed of 53.0 ± 2.0 mm/sec were employed to control the starch pickup at 4.5 ± 0.45 g/m^2. Only one side of the handsheet was surface sized. After surface sizing, it was hot air dried at 105 °C and cylinder dried at 120 °C. Surface sized papers were conditioned at 50% RH and 23 ± 2 °C for over 48 h. After conditioning, the handsheet weight, the pickup weight, and the thickness were measured according to TAPPI standard (T 411 om-97, 1997). Bending resistance of the samples was measured using a bending resistance tester (ISO 5628, 2019). 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 (MicroCal VP-ITC, Malvern Panalytical, Malvern, UK). Before the titration, all samples were degassed using a MicroCal ThermoVac for 5 min. The differential power between the sample cell and the reference cell was 5 μcals^{-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 μL 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. Thus, a positive heat reading indicates an endothermic reaction and a negative reading means an exothermic reaction.

Analysis of starch penetration into paper

Ten mL of 0.05% acridine orange solution was added to 300 mL of 10% starch solution at 50 °C and stirred (Weber *et al.* 2004). Acridine orange absorbs the visible light with wavelengths of 480 nm and emits fluorescence at 530 nm. Surface sizing with starch solutions containing acridine orange was carried out with an automatic rod coater (PI-1210 Film coater, Tester Sangyo Co. Ltd., Saitama, Japan). Starch pickup was controlled at 2.5 ± 0.25 g/m^2, 4.0 ± 0.40 g/m^2, and 6.0 ± 0.60 g/m^2 by controlling the speed of the laboratory rod coater at 60.0 ± 2.0 mm/sec, 55.0 ± 2.0 mm/sec and 48.0 ± 2.0 mm/sec, respectively. The thicknesses of the papers after surface sizing at three different speeds were 5.1 ± 0.38 µm, 7.2 ± 0.63 µm, and 10.2 ± 0.96 µm, respectively. Then the surface sized handsheet was air dried at 105 °C, and cylinder dried at 120 °C. Conditioning of surface-sized papers was carried out in a standard conditioning room for over 48 h, and the pickup weight and thickness of paper after surface sizing were evaluated according to TAPPI standard (T 411 om-97, 1997). Cross sections of the paper were observed using a confocal laser scanning microscope (CLSM). Ar laser (power: 9.5 mW) was used as a light source for CLSM analysis. A dichroic beam splitter, which separates the fluorescent wavelengths from the excitation wavelength of the Ar laser, was used. The pinhole size was set at the optimum value for each objective lens.

RESULTS AND DISCUSSION

Effects of PAM on the Physical Properties of Handsheet

To examine the effect of PAM addition on handsheet properties, starch solutions containing different types of PAM with or without SA were prepared and applied on the handsheet. The effect of PAM to starch solution on pickup weight is shown in Fig. 1.
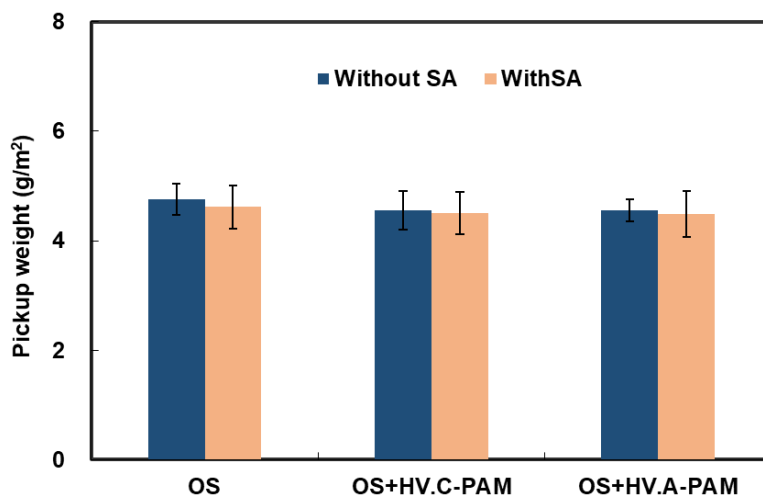
Fig. 1. Effect of addition of high viscosity cationic and anionic PAMs on the pickup weight of surface sizing agents

The effect of ionic properties of PAM on pickup weight was also evaluated. The Brookfield viscosities of cationic and anionic PAMs in Fig. 1 were 7.6 cPs and 7.0 cPs, respectively. Average pickup weights were approximately 4.5 ± 0.45 g/m^2 irrespective of PAM types. The addition of SA into starch solution showed no significant change in pickup weight. Thus, these two additives did not cause significant variations in the pickup weight, which allowed us direct comparison of bending stiffness and penetration of surface sizing solutions into the thickness direction of paper.

The effect of the addition of cationic and anionic PAMs in starch solutions with or without SA on the bending stiffness of paper is shown in Table 2. The bending stiffness of base paper and surface sized paper with oxidized starch only was 0.77 mN·m and 0.81 mN·m, respectively. Surface sizing with oxidized starch improved bending stiffness by 5.1%. The addition of SA to starch solution did not improve bending stiffness, indicating that SA did not change the penetration of starch solution and stiffness of the dried film.

The use of high viscosity cationic PAM as a surface sizing additive improved the bending stiffness by 7.5%. In contrast, there was not much improvement in the bending stiffness when anionic PAM was used as a surface sizing additive. This result suggested that electrostatic interactions between two oppositely charged polymers enhanced the holdout of surface sizing solution and thereby increased the bending stiffness of paper. Table 2 also shows the effects of viscosity of cationic PAMs on bending stiffness. When low viscosity cationic PAM was used, the bending stiffness increased by 11.0%, while high viscosity PAM improved the bending stiffness only by 7.5%. This result suggests that low viscosity PAM was more effective in improving the starch holdout. This was probably because the number of polymer molecules of PAM was far greater when low molecular weight PAM was used, which provided more uniform interaction between two sizing materials.

Kajanto (1998) have shown that the use of short dwell time application leaves the size at the surface, which increases the bending stiffness more than 50% with the same amount of size. Theoretically, higher elastic modulus on the surfaces than in the middle of sheet would give higher bending stiffness. For instance, if each surface layer is 5% of the paper thickness, then doubling their elastic modulus raises bending stiffness by 27% (Kajanto 1998). This suggested that the higher bending stiffness for the low viscosity C-PAM was obtained because it gave either better holdout of sizing solution or better film forming opportunity for greater elastic modulus of the surface layer, or both. The effect of electrostatic interaction between sizing solution and paper substrate has been investigated by Lee *et al*. (2002), and they have shown that an increase in holdout of starch solution can be achieved using cationic starch. Lipponen *et al*. (2004) have shown that the holdout of the starch solution improves surface strength and bending stiffness of paper.

The effects of charge density of cationic PAM on bending stiffness can be seen by comparing the data of LV.CPAM and LC.CPAM. It is clear that the use of high charge density PAM resulted in a greater increase of bending stiffness than low charge density PAM, probably because it increased starch holdout on paper surface. The combined use of cationic PAM and SA further increased the bending stiffness, but the use of SA along with anionic PAM showed a negative effect on bending stiffness. This result shows that electrostatic interaction between starch and surface sizing additives is important for the improvement of bending stiffness (Gaudreault *et al.* 2005).

Table 2. Effect of Oxidized Starch (OS), Cationic and Anionic PAMs and SA on Bending Stiffness of Paper

Surface Sizing Agent Composition	Bending Stiffness (mNm)	Bending Stiffness, mNm (SA was added after PAM)
Base paper	0.770 ± 0.026	
OS	0.809 ± 0.023 (5.1%)	0.810 ± 0.018 (5.2%)
OS + HV. CPAM	0.828 ± 0.017 (7.5%)	0.844 ± 0.019 (9.6%)
OS + HV. APAM	0.816 ± 0.015 (6.0%)	0.804 ± 0.036 (4.4%)
OS + LV. CPAM	0.855 ± 0.030 (11.0%)	0.890 ± 0.026 (15.6%)
OS + LC. CPAM	0.838 ± 0.042 (8.8%)	0.870 ± 0.041 (13.0%)

*OS: oxidized starch, HV; high viscosity, LV; low viscosity, CPAM; cationic polyacryl amide, SA; styrene acrylic acid copolymer

The effect of the addition order of cationic PAM and SA on bending stiffness was examined. When SA was added before HV.CPAM, bending stiffness decreased by 0.01 mNm to 0.834 ± 0.025 mNm. In the case of LV.CPAM, reduction of 0.02 mNm in bending stiffness occurred to give 0.870 ± 0.024 mNm. The addition of cationic PAM after SA gave lower bending stiffness than prior addition of cationic PAM to SA. This result suggests that the interaction between starch and cationic PAM is more effective than the interaction between SA and cationic PAM for improving the bending stiffness. The addition of SA before high viscosity cationic PAM, however, gave higher bending stiffness than when only cationic PAM was used as additive without SA.

The degree of improvement in bending stiffness depended on the PAM viscosity. As shown in Table 1, the charge densities of high and low viscosity PAMs were 1.42 meq/g and 1.19 meq/g, respectively, and their viscosities were 7.6 cPs and 2.5 cPs, respectively. The addition of high viscosity cationic PAM increased the viscosity compared to starch only case. In contrast, the addition of low viscosity cationic PAM decreased the viscosity by 1.3 or 1.4 cPs (Table 3). This result showed that greater bending stiffness increase with low viscosity cationic PAM was not derived from the viscosity increase. The charge density of starch solution containing high and low viscosity C-PAMs were -0.15 meq/g and -0.13 meq/g, respectively. Because the charge density of low viscosity C-PAM (1.19 meq/g) was lower than that of high viscosity C-PAM (1.42 meq/g), low viscosity C-PAM showed greater electrostatic interaction with oxidized starch than high viscosity C-PAM. The viscosity data showed that the intermolecular interaction between oxidized starch and the low viscosity C-PAM was less than that of the high viscosity C-PAM. The charge densities of starch solutions decreased as SA was added because the charge density of SA was -3.23 meq/g.

Sequential addition of 5 pph of a cationic PAM and 5 pph of SA with constant stirring did not give any sticky materials or deposits. The viscosity of starch solution did not change much when cationic PAM and SA were added in order, probably because the cationic PAM interacts uniformly with starch to generate microflocs. However, the addition of SA to starch solution followed by the addition of a high viscosity PAM caused a dramatic increase in viscosity. This indicated that extensive reaction between SA and cationic PAM occurred, which gave large polymer flocs. This showed that the sequential addition of cationic PAM and SA should be made to avoid the formation of polymer complex.

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Table 3. Charge Density and Brookfield Viscosity of Sizing Solutions Containing High and Low Viscosity Cationic PAM and Styrene Acrylic Acid Copolymer (SA)

	Charge density (meq/g)	Viscosity (cPs)		Charge density (meq/g)	Viscosity (cPs)
OS	-0.16	11.5	OS + SA	-0.36	11.8
OS + HV. C-PAM	-0.15	12.7	OS + HV. C-PAM+SA	-0.29	12.0
OS + LV. C-PAM	-0.13	10.1	OS + LV. C-PAM+SA	-0.30	10.5

The penetration of starch affects the optical properties of paper (Lee *et al*. 2002; Hubbe and Gill 2016). To investigate the effect of cationic PAM on optical properties of paper, the brightness and opacity were determined after surface sizing using cationic PAMs and SA as additives (Fig. 2). The brightness of unsized base paper was 83.1%. Surface sizing with oxidized starch decreased brightness because the oxidized starch is less white in color and its brightness was lower than hardwood bleach pulp. More importantly, penetration of starch solutions into the pore caused a reduction of light scattering, which is crucial for brightness. It has been shown that brightness reduction with surface sizing increases as the amount of starch pickup increases (Lee *et al*. 2002). The paper surface sized with cationic PAM showed relatively high brightness. The addition of low viscosity cationic PAM gave the highest brightness, which was further increased with SA addition. It is interesting to see that the brightness change accompanied with the use of PAM in surface sizing was very similar to the change of bending stiffness. This suggested that the holdout of surface sizing materials on paper surface is important for bending stiffness and optical properties of paper.
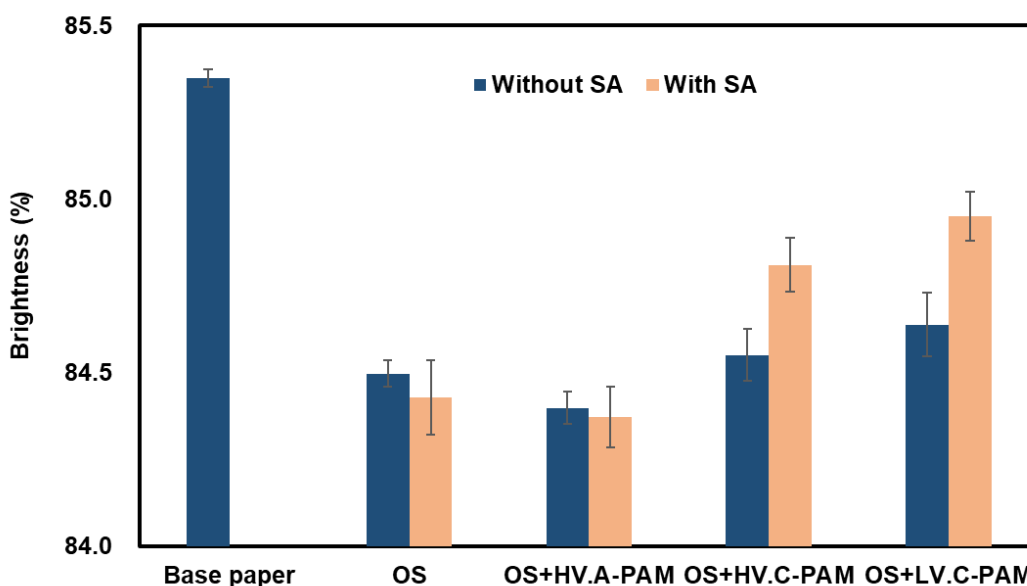
Fig. 2. Effect of addition of anionic and cationic PAMs on pickup weight of surface sizing agents

The enthalpy changes when low and high viscosity cationic PAMs were mixed with oxidized starch were investigated using ITC and shown in Fig. 3, which showed the level of thermodynamic interaction between cationic PAM and oxidized starch (Lipponen *et al.* 2004; Nyström *et al.* 2004; Seo *et al.* 2012). Enthalpy change between low viscosity PAM

and oxidized starch was higher than that between high viscosity PAM and starch. This indicates that low molecular weight PAM interacts with oxidized starch more actively compared to high viscosity PAM, which probably provide much stronger interaction between two components. Less interaction between the high viscosity PAM and starch led to less improvement of bending stiffness.
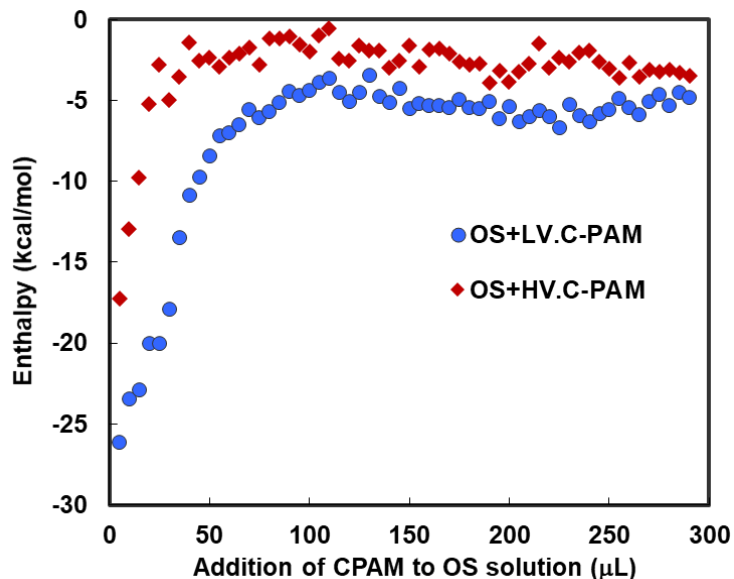

Fig. 3. Enthalpy change between high and low viscosity PAM and oxidized starch

Z-Directional Distribution of Starch

Results of bending stiffness and optical properties suggested that addition of cationic PAM increased the surface holdout of surface sizing starches. To obtain more direct evidence on the holdout of surface sizing solutions associated with the use of cationic PAMs, CLSM images of the cross section of surface sized papers were obtained. This method is very useful to investigate the z-directional distribution of starch in the paper (Lee *et al*. 2002).
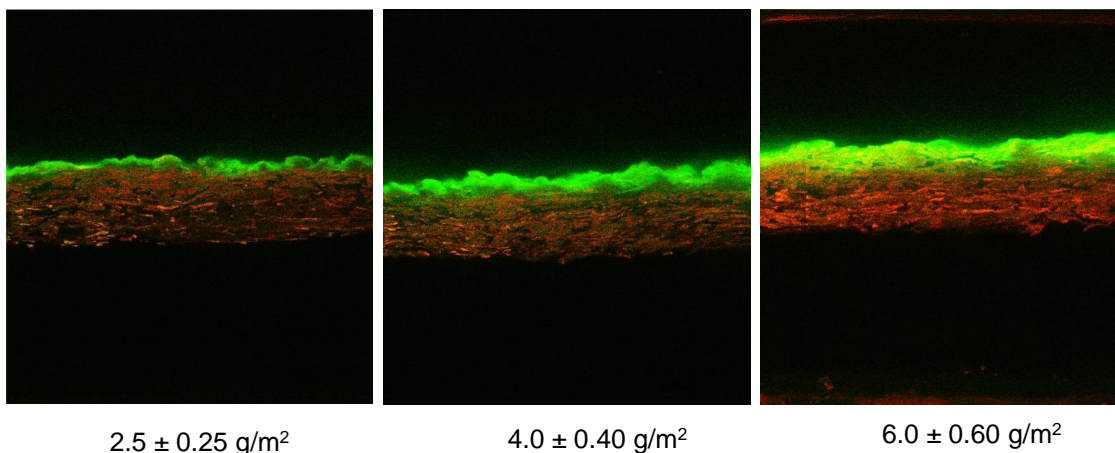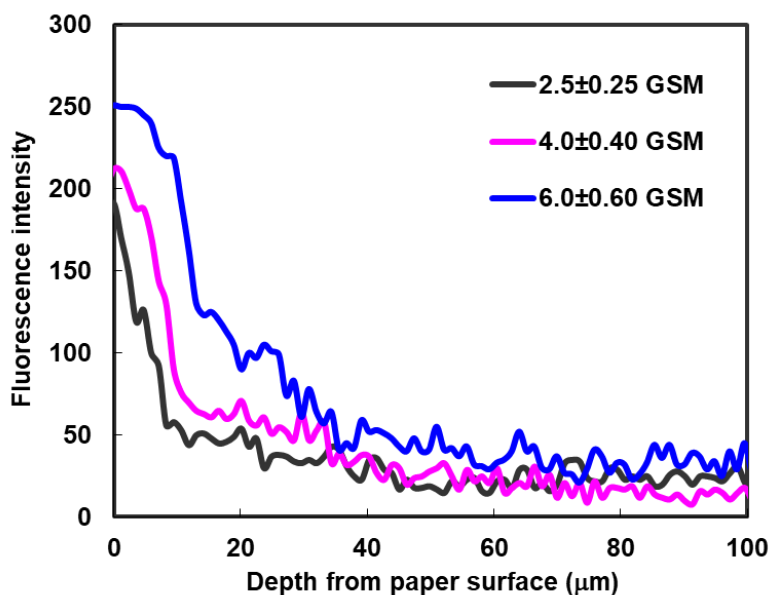

2.5 ± 0.25 g/m^2 $\qquad$ 4.0 ± 0.40 g/m^2 $\qquad$ 6.0 ± 0.60 g/m^2

Fig. 4. CLSM image of paper surface sized with starch solution containing acridine orange. Green color shows the presence of acridine orange which was applied with starch solution

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Acridine orange (Sigma Aldrich, St. Louis, MO, USA) was used as a fluorescent dye to stain the starch and PAM. Acridine orange that possesses anionic charge density (-2.30 meq/g) was added to starch slurry during the cooking process to stain the starch. The acridine orange stained starch can be detected because it emits fluorescence at 530 nm.

CLSM images of the surface sized handsheets with different pickup weights are shown in Fig. 4. Basis weight and thickness of the handsheet before surface sizing were 100 ± 2.0 g/m², and 148 ± 1.69 μm, respectively, and the density of paper was 675 kg/m³. The images in Fig. 4 clearly show that fluorescence intensity increased with an increase of pickup weight. The depth of fluorescence also increased with starch pickup weight.

Because the green color in CLSM images indicates the presence of acridine orange contained in starch solution, the distribution of starch solution in z-direction can be evaluated by the intensity of the green color. The fluorescence intensity profile is shown in Fig. 5. The amount of the surface sizing agent remained on paper surface was high, but it decreased as the distance from the paper surface increased. This agrees with the results reported by Lee *et al*. (2002). They pointed out that the starch content was quite high in the vicinity of the surface, and decreased abruptly inside of the paper. The CLSM image showed that surface sizing starch did not penetrate all the way to the back side. The penetration depth of starch solution has been investigated by Lipponen *et al*. (2004). Starch penetration into paper depends on the viscosity and temperature of the solution, pressure applied to the solution, time of absorption, and interaction between the solution and paper substrate. Of course, the pickup weight is another important factor of the penetration depth.

Fig. 5. Fluorescence profile of the surface sized papers with pickup weights of 2.5 ± 0.25 g/m², 4.0 ± 0.40 g/m² and 6.0 ± 0.60 g/m²

Figure 6 shows the fluorescence intensity profile for the papers surface sized with starch solutions containing low viscosity cationic PAM and SA as additives. The addition of cationic PAM to oxidized starch solution made the starch solution remain on paper surface rather than penetrating into paper structure. The use of SA further decreased starch penetration. The change of starch distribution agrees well with the improved bending stiffness of the paper by cationic PAM and SA (Table 2).
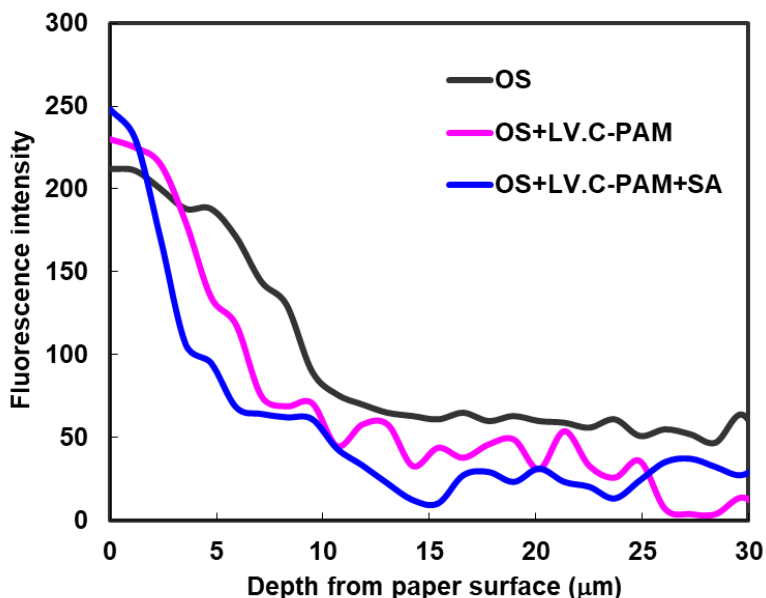
Fig. 6. Effects of addition of cationic PAM and SA on the penetration of starch solution into paper determined from the fluorescence intensity of acridine orange

CONCLUSIONS

1. This study was focused on the use of cationic PAM as a surface sizing additive to improve the surface sizing properties of paper. The effect of various cationic PAMs as surface sizing additives for improving starch holdout and bending stiffness was investigated.

2. Penetration phenomena of the surface sizing agents into paper and the enthalpy changes accompanying the mixing of cationic PAMs with oxidized starch have been investigated using confocal laser scanning micrometry (CLSM) and an ultra-sensitive thermal titration method, respectively.

3. The cationic PAM surface sizing additive improved bending stiffness and brightness, while anionic PAM did not show any effect. This supports the finding that cationic sites of c-PAM increased starch holdout on paper surface because of the electrostatic interaction with negatively charged fiber surface.

4. The viscosity and charge density of PAM were found to be important factors in surface sizing. Low viscosity PAM was more effective in improving the bending stiffness. High charge density PAM gave greater increase of bending stiffness than low charge density PAM probably because it increased the starch holdout.

5. The combined use of cationic PAM and SA further increased the bending stiffness, but the use of SA alone with anionic PAM showed a negative effect on bending stiffness.

6. The sequence of addition of PAM and SA was found to have great influence to the viscosity of starch solution. The addition of SA prior to high viscosity PAM caused a dramatic increase of viscosity indicating the strong electrostatic interaction between these two polyelectrolytes.

7. The penetration of starch solution was examined with CLSM, and it was shown that

the addition of cationic PAM to oxidized starch solution increased the holdout of starch.

8. The enthalpy changes accompanying the mixing of cationic PAMs with oxidized starch was used to determine the molecular level interaction between PAM and starch in mixing. Low viscosity PAM showed greater enthalpy change in mixing with oxidized starch than high viscosity PAM, indicating that much stronger interaction between low viscosity PAM and oxidized starch.

ACKNOWLEDGMENTS

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