



Effect of cationic PVA characteristics on fiber and paper properties at saturation level of polymer adsorption

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ABSTRACT

The characteristics of dry strength additives affect their efficiency in improving fiber bonding. In this work, the influence the charge density and molecular weight, MW, of cationic poly (vinyl alcohol), CPVAs, in improving the strength of papers was investigated at equilibrium level of CPVA adsorption. In the case of CPVAs with the charge density of 0.75 meq/g, the small CPVAs ($h_y < 8$ nm) did not alter the paper properties, though they adsorbed more than the large CPVAs. The large CPVAs ($h_y > 8$ nm) improved the paper properties to some extent, but the hydrodynamic size of CPVAs did not affect their efficiency in improving the paper properties. Also, the low-charged (0.4 meq/g) high molecular weight (MW) CPVA improved the paper properties more than the high-charged high MW ones, even though the total charges introduced to fibers were less by applying low-charged CPVA than by applying high-charged ones. Similar trends were obtained by adsorbing various CPVAs on refined fibers. However, the properties of papers made from unmodified refined fibers were generally superior to those of papers made from CPVA-modified refined fibers, probably due to the coverage of fibrils on the fiber surface.

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1. Introduction

Nowadays, dry strength additives are routinely used in paper-making. By applying a dry strength additive, extra hydrogen bonds are developed between fibers, which improves the paper strength (Bobu, Benea, & Bacaran, 1997). Dry strength additives are mainly applied to increase the strength of paper, to compensate for the decrease in paper strength that results from using fillers (Gaiolas, Mendes, Silva, Costa, & Belgacem, 2005), or to use less pulp by decreasing the basis weight of papers (Retulainen & Kaarina, 1996).

There is still great demand from industry for making new synthetic dry strength additives. The new polymers can be made in a variety of charge densities and molecular weights. However, the effects of such characteristics on paper properties have not yet been fully understood. To identify the influence of polymer characteristics, their interaction with fibers under various conditions should be identified.

The molecular weight (MW) of polymers significantly affects their efficiency in improving fiber bonding (Pelton, Zhang, Chen, & Moghaddamzadeh, 2003; Zhang & Pelton, 2000; Zhang, Pelton, Wagberg, & Rundlof, 2001). Generally, the large polymers may branch off from the fiber surface more than the small ones. However, at the saturation level of polymer adsorption, the small polymers adsorb more than the large ones on the fiber surface. In this

case, it is not clear if the greater adsorption of small polymers could compensate for their smaller size in improving the fiber bonding.

The charge density of polymers significantly affects the configuration of polymers on the fiber surface (Einarson, Aksberg, Ödberg, & Berg, 1991; Li, Du, Wu, & Zhan, 2004; Lofton, Moore, Hubbe, & Lee, 2005; Petlicki & van de Ven, 1994; Tanaka, Ödberg, Wagberg, & Lindström, 1990; Wagberg & Hägglund, 2001). Since the charged polymers should bridge the neighboring fibers, the low-charged polymers, which mainly develop the tail-and-loop configuration, seem to possess a higher efficiency than the high-charged ones on improving the fiber bonding (Fatehi & Xiao, 2008a). Additionally, by adsorbing charged polymers on the fiber surface, the surface chemistry of fibers is changed significantly, which may alter the efficiency of polymers in improving fiber bonding. At the saturation level of adsorption, the low-charged polymers adsorb more than the high-charged ones (Petlicki & van de Ven, 1994; Tanaka et al., 1990; Wagberg & Hägglund, 2001). The higher the adsorption of polymers, the higher the charges introduced on fibers. In this scenario, it is not clear if the fiber bonding is affected by the charge density of the polymer itself, or by the total charges introduced on fibers by adsorbing various dosages of the charged polymers.

In our previous work, the effects of CPVA characteristics on fiber and paper properties under various conditions were analyzed (Fatehi & Xiao, 2008a, 2009a, 2009b; Fatehi, Ward, Ates, Ni, & Xiao, 2009). In the present work, we aim at understanding the effect of

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the MW and charge density of CPVA in improving the paper properties at the saturation level of adsorption. This analysis helps understanding the influences of polymer charge density and MW on fiber bonding improvement, which leads to a better design of synthetic polymers, used as dry strength additives for papermaking.

2. Experimental

2.1. Raw materials and fiber analysis

Poly (vinyl alcohol) (PVA) samples, with a MW of 146–186k, 99% hydrolyzed, polydispersity (PD)=1.47; with a MW of 88–98k, 99% hydrolyzed, PD=1.40; with a MW of 13–23k, 99% hydrolyzed, PD=1.29; and with a MW of 9–10k, 80% hydrolyzed; PD=1.24, glycidyl-trimethylammonium chloride (GTMAC), 75% in water were all obtained from Aldrich Co., and applied as received. Anionic poly vinyl sulfate potassium (PVSK) with a MW of 100–200k, 97.7% esterified, was provided by Wako Pure Chem. Ltd., Japan. Poly ethylene oxide (PEO) with a MW of 22k was obtained from Viscotek, Houston, TX. Also, bleached sulfite softwood pulp was received from Fraser Papers Co., NB, Canada. The pulp refining was carried out according to TAPPI T 248 by a PFI refiner, No. 158, Norway, under different revolutions. The pulp characteristics were analyzed using a Fiber Quality Analyzer (FQA), Optest Equipment Inc., ON, Canada, as listed in Table 1. The fibers smaller than 200 μm are accounted as fines by FQA. The pulp freeness was measured by using a Canadian Standard Freeness (CSF) according to TAPPI T 227.

2.2. CPVA preparation

The cationic modification of PVA was carried out according to the procedures detailed in our previous work (Fatehi & Xiao, 2008a, 2008b). A chosen amount (7.25 g) of PVAs having various MWs were first dissolved in water (100 ml) at 80 °C, and stirred for 1 h. Then, 5 ml of NaOH (5 N) was added to the solutions. In the case of the PVA with the MW of 9–10k, the stirring under the alkaline condition was prolonged for 30 min to ensure the conversion of acetylated groups to hydroxyl groups, which was confirmed by ^1H NMR previously (Fatehi & Xiao, 2008b). The ratio of GTMAC to PVA was 0.5 (mol) for all samples, except for sample 4, which was 0.375 (mol). The reaction was conducted for 60 min for all samples at 80 °C, except for sample 6 at 90 °C. Unreacted GTMAC was separated using membrane tubes with a MW cutoff of 1000, while changing water every 2 h for the first 6 h and then once a day for 2 days.

2.3. Hydrodynamic size analysis

The hydrodynamic size of CPVAs in solutions was measured using a Gel Permeation Chromatography (GPC), Viscotek GPCmax VE2001 (Houston, TX, USA) coupled with an online VE 3580 refractive index (RI) detector and a Viscotek 270 dual laser light scattering detector. The columns were poly [analytic], AquaGel™ series, PAA 202, 204, and 206 used in series. The degassed NaNO_3 solution

in water (0.05 M) was used as an eluent. The concentration of polymer solutions was kept at 4 mg/ml. The polymer solutions were filtered using 0.2 μm pore size syringe filters prior to analysis. The flow rate and the operating temperature were 1 ml/min and 35 °C. Also, PEO was used for GPC calibration.

2.4. Adsorption and charge density analyses

The pulp sample was first washed three times with deionised distilled (DD) water and fiber fines were collected and added to the pulp afterwards. It was observed in our previous work that the optimum consistency for CPVA adsorption was 3% (Fatehi & Xiao, 2009a). Various amounts of CPVAs were mixed with approximately 1.0 g (o.d.) of fibers in suspensions using DD water at 3% consistency and a neutral pH in the absence of salt in 125 ml Erlenmeyer flasks. The adsorption of CPVAs reached equilibrium in 3 h time interval and also dropped dramatically by adding a small amount of salt, e.g., 10^{-3} mol (Fatehi & Xiao, 2008b). The mixtures were then shaken in a water bath shaker (Innova 3100, New Brunswick Scientific) at 30 °C for 3 h. Control samples without fibers were prepared under the same conditions. The titration was conducted with the PVSK solution (0.5 mN) using a Particle Charge Detector, Mütek PCD 03 (Herrsching, Germany). The adsorption amounts were calculated based on the concentration differences of CPVA in filtrates and in their corresponding control samples according to the following equation:

$$\Gamma = \frac{(V_1 - V_2) \times m_H}{V_1 \times m_f} \quad (1)$$

where Γ is the amount of CPVA adsorbed (mg/g), V_1 and V_2 are the volume (ml) of PVSK used for titration of the blanks and of the filtrates. The m_H and m_f are the mass (oven dried) of CPVA and fibers used in the experiment. Three repetitions were conducted to get an average value for each sample. Meanwhile, the charge density of CPVAs was measured using the above-mentioned PCD titrator with PVSK solution.

2.5. Fiber modification with CPVAs

The cationic modification of unrefined or refined fibers was conducted in a 2 L three-neck flask by adding 100 mg/g of CPVAs under the same conditions addressed in Section 2.4. CPVA-modified fibers were washed with DD water twice after the treatments. Handsheets were made from each pulp sample according to TAPPI T 205. The handsheets were kept in a conditioning room specified in TAPPI T 402. The above procedure was conducted for unmodified fibers to prepare the handsheets of the control sample.

2.6. Paper properties

The light scattering coefficient and the brightness of handsheets were tested according to TAPPI T 425 and T 452, respectively, employing an optical tester named Technibrite Micro TB-1C (Indiana, USA). Tensile and tear strengths were measured according to TAPPI T 494, T 403, and T 414, respectively, using Lorentzen & Wetters (L&W) tensile and tear testers (Sweden). The burst strength of

Table 1
Properties of refined fibers and of their resulting papers.

Refining revolutions	Fiber length (LW) (mm)	Fines content (%)	CSF (ml)	Tensile index (Nm/g)	Burst index (kPam ² /g)	Tear index (Nm ² /kg)	Apparent density (kg/m ³)	Light scattering coefficient (m ² /kg)
0	1.82 ± 0.05	23.3 ± 2.1	700 ± 15	27.7 ± 4.2	1.8 ± 0.1	18.9 ± 4.2	649.8 ± 6.2	30.5 ± 0.4
3000	1.67 ± 0.04	27.4 ± 1.3	585 ± 12	74.3 ± 2.1	5.4 ± 0.1	12.2 ± 4.3	821.7 ± 5.3	19.3 ± 0.7
8000	1.45 ± 0.02	37.8 ± 3.2	385 ± 15	87.6 ± 3.8	6.5 ± 0.3	9.5 ± 3.1	863.5 ± 8.2	16.5 ± 0.4

paper was also measured according to TAPPI T 403, using a Burst-o-Matic, Lorentzen and Wettre (L&W), Sweden, burst tester.

3. Results

3.1. Fiber analysis

Usually fiber fragments smaller than 75 μm are classified as fines. Due to the fact that a broader range was used to identify fines by FQA in our analysis (see Section 2.1), the fines content of pulp seemed to be high. The characteristics of refined fibers and their resulting paper properties are listed in Table 1. As expected, by increasing the refined revolutions, the fiber length, tear index, and light scattering coefficient were reduced, whereas the fines content, tensile and burst indices, as well as apparent density were increased.

3.2. Adsorption of CPVAs on fibers

The hydrodynamic size and charge density of various CPVAs are listed in Table 2. As expected, by increasing the MW of CPVAs, the hydrodynamic size of them was increased. In contrast, the charge density of CPVAs did not alter their hydrodynamic size significantly.

Fig. 1 shows the adsorption isotherms of CPVAs having various hydrodynamic sizes and charge densities on fibers. As seen, by increasing the hydrodynamic size or charge density of CPVA, the amount of CPVA adsorbed on fibers at the saturation level of adsorption was reduced. Similar behaviors were reported upon applying various cationic polymers on cellulose fibers (Petlicki & van de Ven, 1994; Zhang & Pelton, 2000). The characteristics of CPVA adsorption on sulfite fibers was discussed in our previous work (Fatehi & Xiao, 2008b). The amounts of CPVA adsorbed on various refined fibers are listed in Table 3. As seen, the higher the refining revolutions, the more CPVA adsorbed on fibers.

3.3. Effect of CPVA hydrodynamic size on paper properties

The modification of fibers by CPVAs varied the mechanical properties of papers. According to the results of the control sample in Table 1, the variations in the mechanical properties of papers as a result of CPVA modification can be calculated. Fig. 2 shows the variations in the mechanical properties of the papers made from the fibers modified with CPVAs (charge density ≈ 0.75 meq/g) versus the hydrodynamic size of CPVAs. If the hydrodynamic size of CPVAs was smaller than 8 nm, tensile and burst indices of the papers made from the unrefined CPVA-modified fibers were marginally changed. If the hydrodynamic size of CPVAs was larger than 8 nm, similar improvements in tensile and burst indices were obtained for the papers made from unrefined CPVA-modified fibers. These results are in agreement with the findings in the literature (Zhang et al., 2001).

Additionally, similar trends were obtained by applying CPVAs on unrefined and refined CPVA-modified fibers. However, CPVAs generally tended to reduce the tensile and burst indices, but to in-

Table 2

The hydrodynamic size (h_y) and charge density of various CPVAs.

Sample No.	MW $\times 1000$	h_y (nm)	Charge density (meq/g)
1	9–10	4.5 ± 0.2	0.74 ± 0.02
2	13–23	5.8 ± 0.3	0.73 ± 0.03
3	88–98	8.5 ± 0.2	0.77 ± 0.05
4	124–186	12.4 ± 0.7	0.38 ± 0.04
5	124–186	12.7 ± 0.6	0.75 ± 0.08
6	124–186	12.9 ± 0.5	1.05 ± 0.09

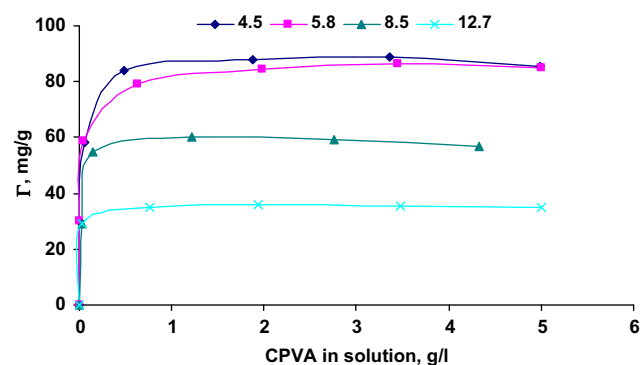


Fig. 1a. Adsorption isotherms of CPVAs having various hydrodynamic sizes (nm), but similar charge densities (≈ 0.75 meq/g) on unrefined fibers at equilibrium level.

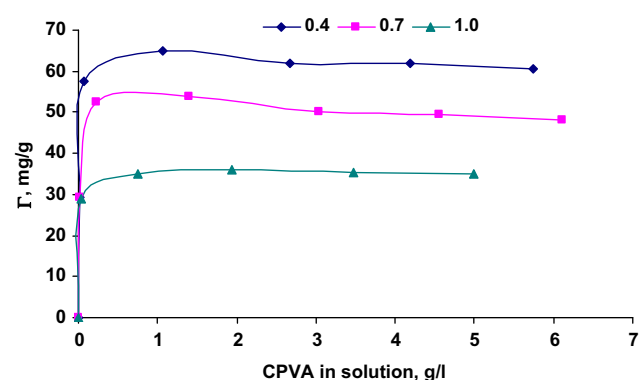


Fig. 1b. Adsorption isotherms of high MW CPVAs ($h_y \approx 12.7$) having various charge densities (meq/g) on unrefined fibers at equilibrium level.

Table 3

Amount of CPVA adsorbed (mg/g) on various refined fibers (addition = 100 mg/g on fibers).

Refining revolutions	Adsorption of various CPVAs (samples)					
	1	2	3	4	5	6
3000	92 ± 3	89 ± 3	67 ± 4	74 ± 2	67 ± 2	49 ± 5
8000	97 ± 4	92 ± 2	72 ± 5	79 ± 3	71 ± 3	53 ± 6

crease the tear index, of papers made from the refined fibers, regardless of the CPVA hydrodynamic size. Similar results were obtained by adsorbing 20 mg/g CPVAs on fines-free fractionated refined fibers (Fatehi & Xiao, 2009b).

The apparent density and light scattering coefficient of the papers made from the CPVA-modified fibers are listed in Table 4. The apparent density and light scattering coefficient of the papers made from the unrefined fibers, modified with small CPVAs ($h_y < 8$ nm) (samples 1 and 2), were similar to those of the papers made of the control sample (Table 1). However, the large CPVAs ($h_y > 8$ nm) (samples 3 and 5) tended to increase the apparent density, but somehow to decrease the light scattering coefficient, of the papers made from unrefined fibers compared with those of the papers made from the control sample (Table 1).

Additionally, similar trends were observed upon applying CPVAs having various hydrodynamic sizes on refined fibers. However, the apparent density was generally lower, but the light scattering coefficient was higher, for the papers made from fiber modified with various CPVAs than those for the papers made from the control samples (Table 1).

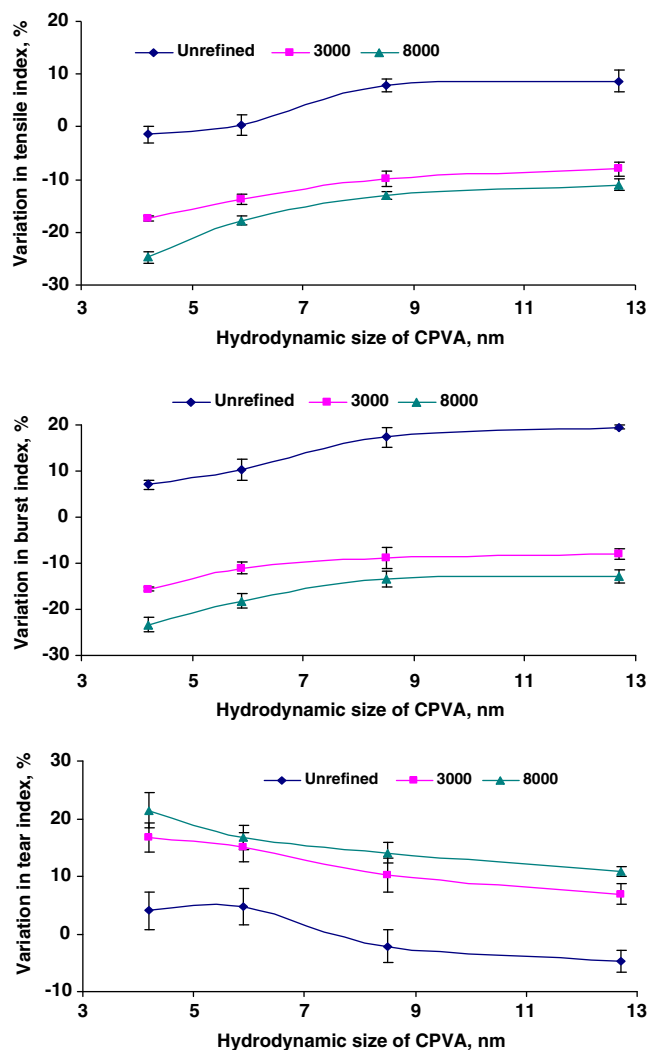


Fig. 2. Variations (%) in tensile, burst, and tear indices of papers made from CPVA-modified fibers (charge density ≈ 0.75 meq/g) versus the hydrodynamic size of CPVAs.

3.4. Effect of CPVA charge density on paper properties

Fig. 3 shows the variations (%) in the mechanical properties of the papers made from the fibers, modified with high MW CPVAs ($h_y \approx 12.5$ nm) having various charge densities, versus the charge density of high MW CPVAs. By increasing the charge density of CPVA, the improvement in the tensile and burst indices of papers was reduced, whereas the tear index was increased more significantly, regardless of the refining revolutions. Regardless of the charge density of CPVAs, however, CPVA generally decreased the tensile and burst indices, but increased the tear index, of papers made of refined fibers.

Table 4

Apparent density and light scattering coefficient of papers made from fibers modified with various CPVAs (samples).

Sample No.	1		2		3		4		5		6	
Refining revolution	AD ^a	LS ^b	AD	LS	AD	LS	AD	LS	AD	LS	AD	LS
0	638.2 \pm 4.2	30.9 \pm 0.3	645.2 \pm 7.1	30.1 \pm 0.4	654.2 \pm 10.2	29.1 \pm 0.5	675.1 \pm 10.1	28.2 \pm 0.3	660.1 \pm 5.4	29.1 \pm 0.3	655.2 \pm 4.3	29.4 \pm 0.4
3000	760.4 \pm 5.1	22.4 \pm 0.6	762.4 \pm 4.3	22.2 \pm 0.3	775.3 \pm 8.5	19.9 \pm 0.3	795.2 \pm 8.2	20.2 \pm 0.4	781.2 \pm 6.2	20.2 \pm 0.3	779.3 \pm 3.2	20.7 \pm 0.4
8000	822.7 \pm 4.1	19.2 \pm 0.5	824.9 \pm 6.5	18.6 \pm 0.5	832.1 \pm 6.5	18.2 \pm 0.6	844.6 \pm 7.6	17.2 \pm 0.2	838.6 \pm 7.2	18.1 \pm 0.2	828.3 \pm 7.5	18.5 \pm 0.5

^a Apparent density, kg/m³.

^b Light scattering coefficient, m²/kg.

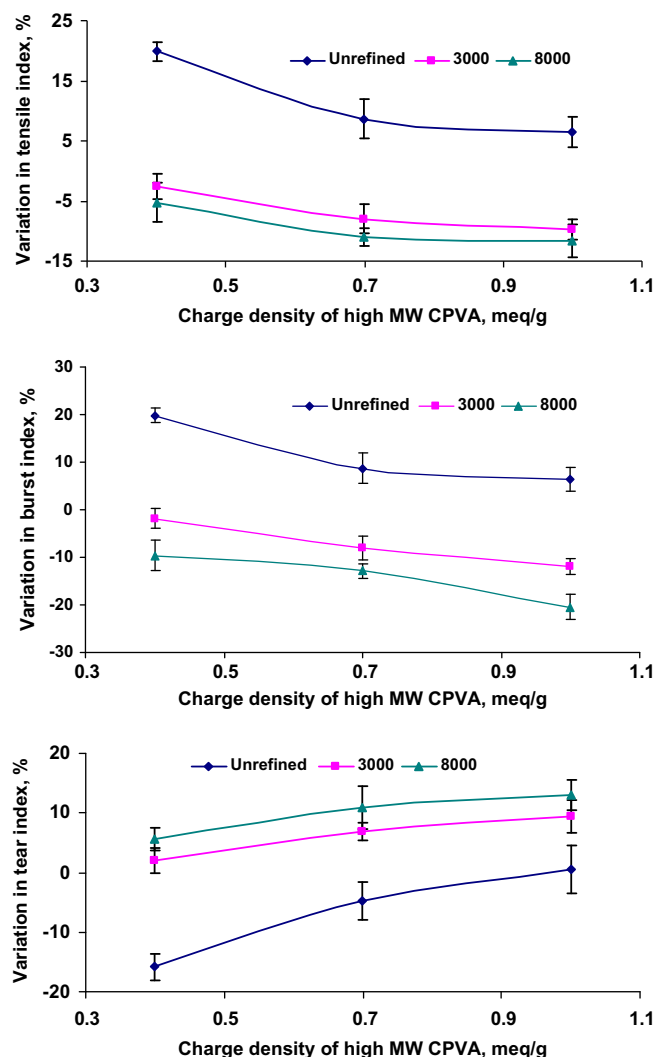


Fig. 3. Variations (%) in the tensile, burst, and tear indices of papers made from fibers, modified with various high MW CPVA ($h_y \approx 12.5$ nm), versus the charge density of CPVAs.

As also seen in Table 4, by increasing the charge density of high MW CPVAs ($h_y \approx 12.5$ nm) (samples 4–6), the apparent density and light scattering coefficient of the papers made from the CPVA-modified fibers were decreased and increased, respectively, regardless of the refining revolutions.

4. Discussion

4.1. Adsorption analysis

It was comprehensively demonstrated in the literature that the small polymers adsorbed more than the large ones on the cellulose

fibers (Tanaka et al., 1990; Van de Ven, 1994; Wagberg & Hägglund, 2001). This behavior is partly due to the greater diffusion of small polymers, compared with the large ones, into the pores of cellulose fibers (Tanaka et al., 1990; Van de Ven, 1994).

In terms of CPVAs having similar hydrodynamic sizes, the low-charged ones adsorbed more than the high-charged ones on fibers. Such a phenomenon is due to the fact that polymers, having various charge densities, develop different configurations on fibers (Li et al., 2004; Petlicki & van de Ven, 1994; Tanaka et al., 1990; Van de Ven, 1994; Wagberg & Hägglund, 2001). In other words, the low-charged polymers might develop the tail-and-loop configuration, whereas the high-charged ones might develop the flattened configuration on fibers. Thus, the low-charged polymers may extend and occupy less surface area than the high-charged ones on the fibers. Therefore, more of the low-charged ones can be adsorbed on the surface. Another reason may be the repulsion force developed between the already adsorbed polymers on the fiber surface and the polymer approaching to the fibers from the bulk for adsorption (Fatehi & Xiao, 2008b). The higher the charge density of polymers, the higher such repulsion force is developed, which impairs the adsorption of polymers and leads to a lower maximum adsorption (Zhang & Pelton, 2000). Furthermore, it was reported that the low-charged polymers diffuse more than the high-charged ones into the fiber pores (Horvath, Horvath, Lindström, & Wagberg, 2008a, 2008b). Therefore, a relatively larger surface area is available for the adsorption of low-charged polymers.

Additionally, the refining of pulp decreased the fiber length and CSF and increased the fines content of pulp, which confirmed the increase in the available surface area of fibers (Table 1). Therefore, the increase in the adsorption of CPVA on refined fibers (Table 3) is due to the increase in the available surface area of fibers.

4.2. Impact of CPVA hydrodynamic size

Since the CPVAs had various charge densities, the surface morphology and chemistry of fibers should be varied differently upon adsorbing various CPVAs, which alter the efficiency of CPVAs on developing fiber bonding. It was hypothesized in the literature that the fiber bonding develops at the scale of 10 nm (Pelton, 2004). Therefore, the larger the CPVAs, the more efficiently they improve the fiber bonding. This phenomenon was observed in improving paper strength by applying (20 mg/g) of various CPVAs (Fatehi & Xiao, 2008a). Zhang et al. (2001) reported that the MW of cationic dextran, ranging from 80 to 2000k, did not change its efficiency in improving fiber bonding at the saturation level of adsorption. Our results also showed that if the MW of CPVA was higher than 80k ($h_y > 8$ nm), similar improvements in paper properties can be achieved at the saturation level of adsorption, regardless of the MW (or hydrodynamic size) of CPVAs. These results imply that the thickness of the coating layer, created by CPVAs on the fiber surface, was similar for CPVAs with the hydrodynamic sizes of 8.5 and 12.7 nm. In other words, the relatively higher adsorption of CPVA with the hydrodynamic size of 8.5 nm could compensate for its smaller size by covering the fiber surface. This hypothesis is confirmed by considering the similar apparent density and light scattering coefficient of papers made of such CPVAs (samples 3 and 5 in Table 4). However, the small CPVAs ($h_y < 8$ nm) could not improve the paper strength (Fig. 2), even though their maximum adsorption was higher than larger ones (Fig. 1). This behavior might be attributed to the greater diffusion of small CPVAs into the fiber pores and probably a thinner coating layer of CPVAs on the fiber surface. In other words, the higher adsorption of the small CPVAs could not compensate for their small size in improving the paper strength. The marginal changes in the apparent density and light scattering coefficient of papers confirms this phenomenon (compare samples 1 and 2 in Table 4 with the control sample in Ta-

ble 1). Also, we reported that the high MW CPVA ($h_y = 12.5$) tended to improve the retention of fiber fines in papers, which can be another reason for the considerable influence of high MW CPVAs in improving the paper strength (Fig. 2) (Fatehi et al., 2009).

4.3. Impact of CPVA charge density on paper strength

By adsorbing CPVAs on fibers, a repulsion force is developed between the neighboring CPVA-modified fibers in handsheets, which affects the fiber bonding development during drying (Fatehi & Xiao, 2009a). Considering the total amount of CPVA adsorbed on fibers (Fig. 1) and the charge density of CPVAs (Table 2), the total charges, originating from the cationic groups of CPVA that were introduced to the fibers, can be calculated. Below the saturation level of CPVA adsorption, we observed that the total charges introduced on fibers were not the influencing factor in fiber bonding (Fatehi & Xiao, 2009a). At the saturation level of adsorption, the total charges introduced on fibers by applying high MW CPVAs having the charge densities of 0.4, 0.7, and 1.0 meq/g were approximately 24, 36 and 32 $\mu\text{eq/g}$ on fibers, respectively. As discussed in Section 4.1, more of the low-charged CPVA (0.4 meq/g) than the high-charged ones might diffuse into the fiber pores, which implies that a charge lower than 24 $\mu\text{eq/g}$ was introduced on the outer surface of fibers. Thus, the total charges introduced on the outer surface of fibers by adsorbing various high MW CPVAs should vary significantly. Therefore, at the saturation level of CPVA adsorption, the outer surface charge density of fibers is less affected by applying the low-charged CPVA than by applying the high-charged ones, even though it adsorbed more. In other words, the higher adsorption of low-charged CPVA did not increase the surface charge density of fibers at the same level as the high-charged ones did. Instead, the low-charged CPVA improved the surface morphology (or increased the surface roughness) of fibers so that fiber bonding was developed more significantly, as confirmed by the decrease in light scattering coefficient (compare samples 5 and 6 of unrefined fibers in Table 4 with those of the control sample in Table 1). Therefore, at the saturation level of adsorption, the total charges introduced on fibers, which affect the fiber chemistry, and also the charge density of CPVA, which affects the configuration of CPVAs adsorbed on the fiber surface, influence the fiber bonding improvement. It was stated in the literature that polymers having higher charge densities tended to retain more fines, due to the charge reversal of the fiber surface (Chi, Li, Liu, & Zhan, 2007; Oulanti, Chabot, Brouillette, & Daneault, 2009). However, since the adsorption level of various high MW CPVAs ($h_y \approx 12.5$ nm) were different (Fig. 1), no clear conclusion can be made on the effect of the charge density of CPVAs on retaining fines at the saturation level of adsorption.

4.4. Impact of CPVA on refined fibers

As seen in Figs. 2 and 3, CPVA affected the properties of papers made from the unrefined and refined fibers similarly. However, the paper strength and apparent density were generally reduced, while the light scattering coefficient was increased, by adsorbing CPVAs on refined fibers. These changes were more pronounced for the fibers refined under 8000 revolutions than for those refined under 3000 revolutions. A similar behavior was observed by applying CPVAs (20 mg/g) on fines-free fractionated refined fibers (Fatehi & Xiao, 2009b), and by applying carboxymethyl cellulose (CMC) to fibers (Jokinen, Niinimäki, & Ammala, 2006). CPVA increases the shear strength of fiber bonding through developing extra hydrogen bonding, while refining increases both shear strength of fiber bonding and contact area of fibers. It was reported that refining is more influential than applying CPVAs in improving the strength of papers made from bleached sulfite fibers (Fatehi et al., 2009). The application of CPVA

on refined fibers increased the shear strength of fiber bonding in one hand, and reduced the contact area of fibers by covering the fibrils on the other hand (Fatehi & Xiao, 2009b). The changes in the light scattering coefficient and apparent density (Table 4) imply that the improvement in the fiber bonding, as a matter of CPVA application, could not compensate for the coverage of fibrils by CPVAs and for the reduction in the contact area of refined fibers, which reduced the paper strength.

5. Conclusions

By increasing the hydrodynamic size or charge density of CPVA, its adsorption on fibers was reduced. By increasing the refining revolutions, the CPVA adsorbed more, due to the increase in the surface area of fibers for adsorption. In the case of CPVAs with similar charge densities (0.75 meq/g), both small CPVAs ($h_y < 8$ nm) did not improve the fiber bonding. However, the large CPVAs ($h_y > 8$ nm) improved the fiber bonding to some extent, and the size of CPVAs did not affect their efficiency in improving the fiber bonding at the saturation level of adsorption. The low-charged high MW CPVA ($h_y \approx 12.5$ nm) improved the fiber bonding more than the high-charged ones, and it introduced lower maximum charges on fibers. Similar trends were observed by adsorbing various CPVAs on refined fibers. However, the properties of the papers made from unmodified refined fibers were generally superior to those of papers made from the CPVA-modified refined fibers, probably due to the coverage of fibrils on the fiber surface.

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