

Polyelectrolyte multilayering of fibers with different polymer combinations and a comparison of its effect on paper strength with a conventional dry strength agent treatment

Seong Min Chin, Hye Jung Youn, Jaeho Ryu, and Kyujeong Sim

KEYWORDS: Polyelectrolyte multilayering, Pulp fiber, Adsorbed amount of polymer, Paper strength, Dry strength agent

SUMMARY: Pulp fibers were modified by polyelectrolyte multilayering with different polyelectrolyte combinations and its effects on the mechanical properties of sheets were investigated in a comparison with a typical addition of a dry strength agent in a papermaking process. Bleached hardwood kraft pulp was used as a substrate with the four polyelectrolyte combinations of polydiallyldimethylammonium chloride (poly-DADMAC)/poly-sodium 4-styrenesulfonate (PSS), cationic starch (C-starch)/PSS, cationic polyacrylamide (C-PAM)/PSS, and C-PAM/anionic polyacrylamide (A-PAM).

The mechanical properties of handsheets made of bleached hardwood kraft pulp fibers modified by polyelectrolyte multilayering increased with an increase in the number of layers owing to the increased cumulative adsorbed amount of the polymers as well as better interaction in the contact zone between fibers. In particular, a multilayer including C-starch was the most effective at improving the strength. Polyelectrolyte multilayering was more effective at improving the mechanical properties compared to a conventional polymeric treatment.

ADDRESSES OF THE AUTHORS: **Seong Min Chin** (saint.chin@samsung.com), Department of Forest Sciences, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul, 151-921, Korea. Now at Samsung Electro-Mechanics Co. Ltd., Suwon-Si, Gyeonggi-Do, 443-743, Korea. **Hye Jung Youn** (page94@snu.ac.kr), Department of Forest Sciences, Research Institute for Agriculture and Life Sciences, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul, 151-921, Korea. **Jaeho Ryu** (yapyam2@snu.ac.kr) and **Kyujeong Sim** (blaze86@snu.ac.kr): Department of Forest Sciences, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul, 151-921, Korea.

Corresponding author: Hye Jung Youn

According to the Page's theory (Page 1969), the tensile strength of paper is determined by the intrinsic strength of the pulp fibers and their ability to form bonds when compressed in a wet state and then dried. The tensile strength of paper is increased with the increases in the fiber length, fiber strength, bonding strength, and relative bonded area (RBA) (Niskanen, Kärenlampi 1998). Many researchers have studied methods of improving the RBA and bonding strength through a mechanical treatment to create high-strength paper. However, an increase of the RBA through a mechanical treatment such as refining requires much energy. In addition, mechanically treated fibers lead to wet-end performance troubles such as poor

dewatering and low fines retention. Another means of modifying the characteristics of pulp fibers to improve the strengths of paper is a chemical treatment or an enzyme treatment. Conventional polymeric treatment in the papermaking process involves a one-time addition of polymer to the pulp slurry in the mixing or machine chest, the typical application of which is the application of a dry strength agent. Dry strength agents such as starch or polyacrylamide (PAM) are typically and widely used in the papermaking process for this purpose. It improves the tensile, burst, and internal strength of the paper remarkably, but occasionally it deteriorates the strain and tear strength (Hofreiter 1981) or the dewatering performance in wire or press sections. Layer-by-Layer (LbL) polyelectrolyte multilayering (PEM), as was introduced by Decher et al. (1992), has been suggested as an advanced polymeric treatment to improve the paper strength. Polyelectrolyte multilayering is one of the most useful methods of modifying or providing specific tailored functions on the surface of substrates. This technology can be applied in various fields on account of its simplicity and versatility.

LbL polyelectrolyte multilayering technology is known for its ability to improve the mechanical properties of paper and modify the pulp fiber characteristics (Wågberg et al. 2002). According to Wågberg et al. (2002), the dry and wet strength of paper made of unbeaten fibers or beaten fibers could be increased through the consecutive adsorption of cationic polyallylamine and anionic polyacrylic acid. Grozidts et al. (2006) and Lvov et al. (2006) applied this technology to improve the bonding ability of broken fibers for the success of paper recycling. The addition of 10% nanocoated broken fiber with polyallylamine hydrochloride and sodium polystyrene sulfonate increased the tensile index by 24%. Excellent strength enhancement using a polyelectrolyte multilayering technique has been recognized by many researchers and papermakers (Eriksson et al. 2005a; 2005b; 2006; Lingström et al. 2006; Lingström, Wågberg 2008; Pettersson et al. 2007). However, many continue to doubt the efficiency of this technology compared to a conventional dry strength agent treatment in papermaking, and the research community in this area is curious about which polymer shows the best effect and why the multilayering has better performance. Therefore, this study aims to investigate the effect of the polyelectrolyte types on the improvement of the strength properties of paper and elucidate the strong and weak points for application to the paper industry through comparisons with conventional polymeric treatments.

Materials and Methods

Materials

An industrially produced, dried bleached mixed hardwood kraft pulp (Hw-BKP) which was supplied by Moorim P&P (Korea) was used as a raw material. Major hardwood species was oak. As cationic polyelectrolytes, poly-diallyldimethylammonium chloride (poly-DADMAC, $M_w < 100,000$ according to the supplier, Sigma-Aldrich), cationic polyacrylamide with a low molecular weight (C-PAM, $M_w \sim 50,000$ according to the supplier, OCI-SNF Co., Korea) and cationic starch (C-starch, DS 0.08, according to the supplier, Samyang Genex Co., Korea) were used. Poly-sodium 4-styrene-sulfonate (PSS, $M_w \sim 70,000$ according to the supplier, Sigma-Aldrich) and anionic polyacrylamide with a low molecular weight (A-PAM, $M_w \sim 50,000$ according to the supplier, OCI-SNF Co., Korea) were used as anionic polymers to build up the polyelectrolyte multilayers. The concentration of all of polyelectrolytes was adjusted to 5 g/l. The charge density of the poly-electrolyte was determined using a Particle Charge Detector (Mütek Co., Germany), and it was +6.2 meq/g, +3.1 meq/g, +0.6 meq/g, -4.6 meq/g, and -2.3 meq/g for poly-DADMAC, C-PAM, C-starch, PSS, and A-PAM, respectively.

Stock preparation

Hw-BKP fibers were disintegrated in deionized water for 15 min using a laboratory Valley beater (Daeil Machinery Co., Korea) without load. The length weighted average fiber length was 1.04 mm. A thoroughly washed stock was prepared after removing dissolved and colloidal materials (DCMs) by passing through a vibration screen (Sweco Co., USA) with 400-mesh wire and washing twice with deionized water. Finally, the stock consistency was diluted to 10 g/l with and its conductivity was adjusted to $1000 \pm 10 \mu\text{S/cm}$ with 10 mM of NaCl.

Determination of polymer dosage

To build up successive polyelectrolyte multilayers on the cellulosic fibers, the addition dosage of all of the polyelectrolytes was initially determined. The zeta potential of fibers was evaluated using System Zeta Potential (SZP, Mütek Co., Germany) with varying addition amount of polyelectrolyte. The appropriate addition dosage of polymer was determined as the required amount that the zeta potential of fibers reaches the plateau after reversion to opposite charge. The appropriate addition levels for poly-DADMAC, C-PAM, and C-starch were 0.4, 0.4 and 1.0% on oven dried (OD) weight of fibers, respectively. The appropriate addition levels of the anionic polyelectrolytes were also determined as 0.6% for PSS and 0.4% for A-PAM.

Pulp fiber modification by LbL polyelectrolyte multilayering

The fibers were treated consecutively with cationic and anionic polyelectrolytes. After the adsorption of cationic polyelectrolyte on the fibers for 20 min, the fibers were washed twice for each 5 min with deionized water. The adsorption of anionic polyelectrolytes followed, and the

modified fibers were washed twice in the same manner. In each step, multilayering was carried out at a conductivity of $1000 \pm 10 \mu\text{S/cm}$ and the pH of 7.7. PEM was carried out with four combinations of cationic and anionic polyelectrolytes – poly-DADMAC/PSS, C-starch/PSS, C-PAM/PSS, and C-PAM/A-PAM.

Conventional polymeric treatment

To evaluate the effectiveness of the polyelectrolyte multilayering process, the performance of the polyelectrolyte multilayering treatment was compared with that of a conventional polymeric treatment in a papermaking process. Various cationic natural or synthetic polymers were used for the development of the dry strength of paper. Therefore, this study focused on the performance of the cationic polyelectrolyte and compared the effect of the multilayering adsorption and one-time addition treatment methods. A conventional polymeric treatment was carried out by adding each cationic polyelectrolyte to the prepared fiber slurry at once under conditions similar to polyelectrolyte multilayering (i.e., the same adsorption time and conductivity). In a conventional treatment, the amount of cationic polyelectrolytes corresponding to the total amount of polycation added during the multilayering treatment was added. For example, the addition level of poly-DADMAC in the multilayering treatment with 5 layers of poly-DADMAC/PSS corresponds to 1.2% of poly-DADMAC on OD pulp fibers, as 5 layers means that poly-DADMAC was adsorbed thrice and 0.4% of poly-DADMAC was added to the OD fibers for each odd layer.

Evaluation of adsorbed amount of polyelectrolyte onto pulp fiber

The zeta potential of the pulp fibers modified by PEM was measured using the System Zeta Potential after adjusting the conductivity of the fiber slurry to $125 \mu\text{S/cm}$ using a NaCl solution. Conductivity of $125 \mu\text{S/cm}$, corresponding to that of tap water, was adjusted, as handsheet forming in this case was done using tap water. The adsorbed amount of polyelectrolyte onto the pulp fiber was evaluated by measuring the charge demand of the filtrate after an adsorption with a Particle Charge Detector and a calculation according to Eq 1.

$$\text{Adsorbed amount of polyelectrolyte, mg/g} = (A-B)/A \times C \quad [1]$$

where, A is the charge demand of the polyelectrolyte without pulp fibers, B is the charge demand of the filtrate after the adsorption of polyelectrolyte on the fibers, and C is the addition amount of polyelectrolyte on the OD fibers.

Handsheets preparation and evaluation of mechanical properties

Handsheets with a basis weight of 80 g/m^2 were prepared with chemically treated Hw-BKP fibers using laboratory rectangular handsheet former (Daeil Machinery, Korea). At least 10 sheets were prepared for each variable. After couching five times, wet sheets were pressed at 3.5 bar using a laboratory press machine. Subsequently, cylinder drying was conducted at 120°C . The handsheets were pre-conditioned at 23°C and 50% RH before their

properties were tested. The grammage and apparent thickness (caliper) of the handsheets were measured in accordance with TAPPI test methods T410 and T411, respectively. The apparent thickness was measured using a micrometer (L&W Co., Sweden). The density was calculated by dividing the basis weight by the apparent thickness. The tensile strength and strain at break were evaluated using a tensile tester according to TAPPI test method T494. The Elmendorf tearing strength of the handsheets was measured according to TAPPI test method T414. An evaluation of the peel strength is considered to be a good approach to investigate the fiber-fiber interaction and fiber bonding ability. The testing method was modified based on Zhao and Pelton's work (2005). First, a peel paper strip of 25 mm×50 mm in size was prepared. The paper strip was fixed on a stainless steel panel of 50 mm×150 mm using a commercial double-sided tape (18 mm wide, Model 665, 3M Korea). Commercial single-sided adhesive tape (18 mm wide, Model 810, 3M Korea) was also stuck onto the paper strip. The tail of the single-sided adhesive tape extended above 100 mm to attach the strip to the clamps of a Texture Analyzer (Stable Micro Systems Co., UK). As in Zhao and Pelton's work (2005) a rubber-coated roller (2 kg) was hand rolled over the sample 10 times. After the tail of the adhesive tape was attached to the instrument, the peel forces were measured using a Texture Analyzer equipped with a 50 N load cell. A peel rate of 600 mm/min was used according to the preliminary test. The average steady-state peel force was used as the peel force result in this study.

Evaluation of thickness of polyelectrolyte multilayer on a model substrate

To find the mechanism of strength development by different polyelectrolyte combinations by predicting the conformation of the polyelectrolyte, the multilayer thickness was evaluated using atomic force microscopy (AFM, XE-150, ParkSystems Co., Korea). Because the fiber surface was not even, the cellulose model film was formed on a silicon wafer by the spin coating of cellulose whiskers which was produced by the sulfuric acid hydrolysis of Hw-BKP. The cellulose film was 5.8 nm thick. The multilayering process was conducted with four combinations of polyelectrolytes via spin coating at 4000 rpm for 15 s. To remove excess or incompletely adsorbed polyelectrolytes from the substrate, the substrate were washed twice with deionized water under the same spinning conditions after each adsorption of the polyelectrolyte. The polyelectrolyte multilayered substrates were analyzed in air using AFM. In this experiment, a silicon nitride (Si_3N_4) tip attached to the end of the cantilever (NP-S, Veeco Co., USA) having a very low spring constant ($k=0.12$ N/m) was used in contact mode. The normalized radius of the Si_3N_4 tip was 10 nm (specifications according to the manufacturer). The scan rate was 1.0 Hz. The Z-servo gain was kept constant at 1.0. The scan size was $5 \mu\text{m} \times 5 \mu\text{m}$. The obtained images were low-pass filtered at $0.20 \mu\text{m}$. The thickness of the PEM was directly calculated from the step height between the bare substrate and the PEM on the cellulose film by scratching with a razor blade.

Results and discussion

Polyelectrolyte multilayering of pulp fiber

The surface of pulp fibers was modified by successive adsorption of polycation and polyanion. Fig 1 shows the streaming zeta potential of fibers with polyelectrolyte multilayer, which was affected by the type of the adsorbed polymer at the outermost layer. The zeta potential of fibers showed a positive charge at 1 layer which has cationic polyelectrolyte in the outermost layer, and moved to the negative charge at 2 layer after adsorption of polyanion. With further layering, the zeta potential showed the repetitive change of charge. It indicated that all four combinations of polyelectrolytes were successfully adsorbed onto fibers. The poly-DADMAC/PSS combination gave the relatively constant zeta potential to fibers, but C-PAM/PSS and C-starch/PSS combinations showed the decreased zeta potential at odd layer with the increase in the layer number. In particular, fibers with 7 layer of C-starch/PSS had a charge near neutral point because of the lowest charge density of C-starch (0.6 meq/g).

Fig 2 shows the adsorbed amount of polyelectrolyte on the pulp fibers at each layer. Of these polyelectrolyte combinations, poly-DADMAC was least adsorbed on the fibers compared to the other cationic polymers used in this study. C-starch recorded the highest adsorbed amount of cationic polymers due to the lowest charge density (0.6 meq/g), and the adsorbed amount of C-PAM was constant at 0.71 ± 0.02 mg/g regardless of the anionic polymer type of the multilayer. As the poly-DADMAC had the highest charge density (+6.2 meq/g) of these cationic polyelectrolytes, its adsorbed amount was relatively low. When C-PAM was used as a cationic polyelectrolyte, the adsorbed amount of APAM was higher than that of PSS due to its weaker negative charge density (-2.3 meq/g) compared to the PSS (-4.6 meq/g).

Thickness of polyelectrolyte multilayer on cellulose model film

The thickness of the polyelectrolyte multilayer on the cellulose model film was measured by the scratch height method using AFM. Fig 3 shows the thickness of the polyelectrolyte multilayer on the cellulose film, showing topological images. The thickness value in Fig 3 consisted of the thickness of the polyelectrolyte layer and

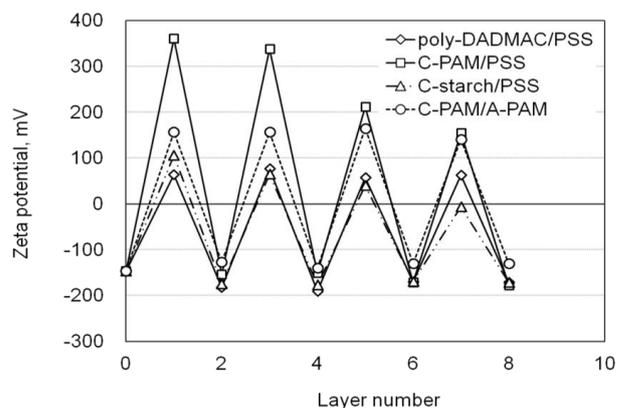


Fig 1. Zeta potential of Hw-BKP fibers modified by different polyelectrolyte multilayer.

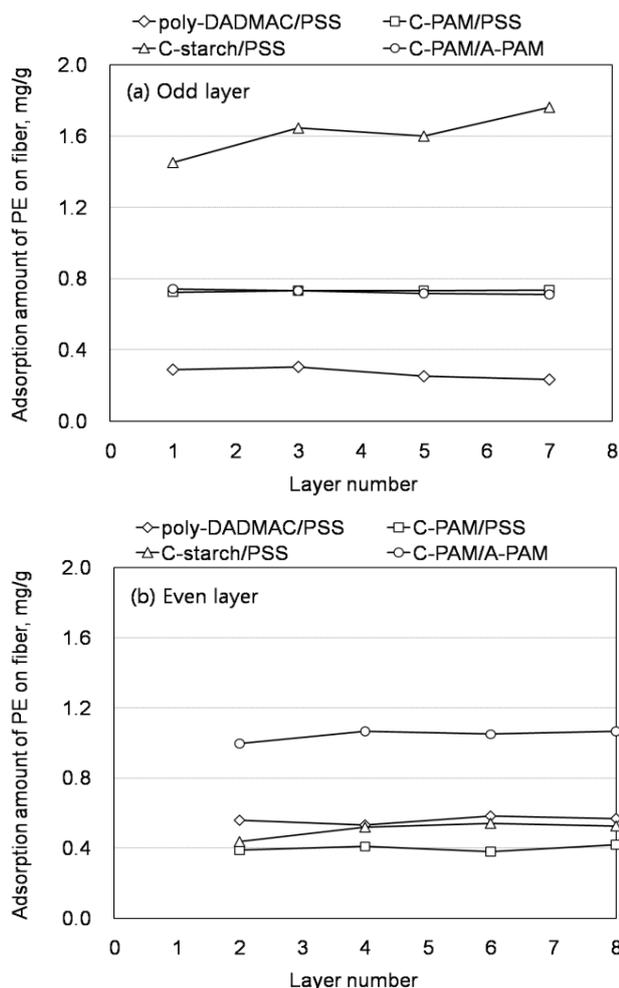


Fig 2. Adsorbed amount of polymer onto the Hw-BKP fibers with layer number ((a) adsorption of cationic polymer, (b) adsorption of anionic polymer).

that of the cellulose film (5.8 nm). The poly-DADMAC/PSS layer had the lowest thickness, and C-starch/PSS showed the greatest thickness of the multilayer. The characteristics of polyelectrolyte appeared to cause the difference in the thickness of the multilayer. Because highly charged poly-DADMAC and PSS are liable to stretch out in a flat conformation, their layer has the most compact structure. However, C-PAM and C-starch formed a rough, bulkier structure due to the lower charge density. Particularly, the branched structure and high molecular weight of C-starch resulted in the formation of the multilayer with the highest thickness.

Effect of polyelectrolyte type on mechanical properties of paper

Four combinations of polyelectrolytes were examined to investigate the appropriate polyelectrolyte type for the enhancement of the mechanical properties. Fig 4 shows the apparent density of handsheets made of modified Hw-BKP fibers by polyelectrolyte multilayering with different polymers. During repeated polyelectrolyte multilayering, the apparent density was kept constant or was slightly decreased. Polymeric multilayer treatments did not increase the density of the paper, as in the result

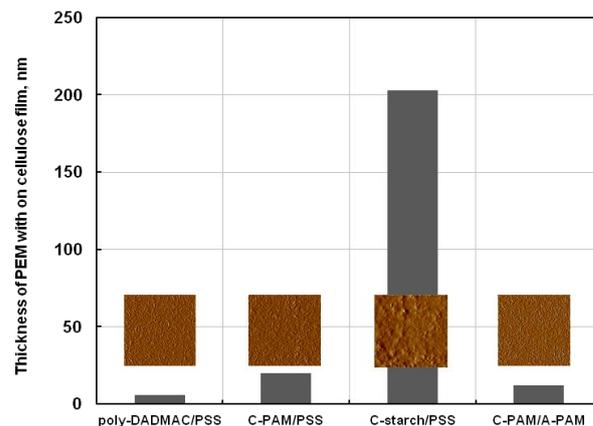


Fig 3. Thickness and topological image (5 μm x 5 μm) of polyelectrolyte multilayer (4 layer) depending on polymer combinations.

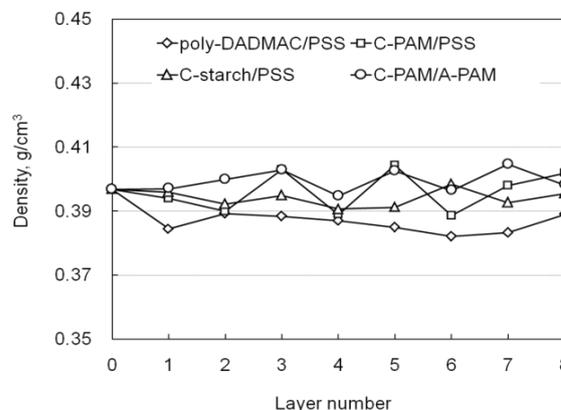


Fig 4. Apparent density of handsheets made of modified Hw-BKP fibers by polyelectrolyte multilayering with different polyelectrolyte combinations.

of Wågberg et al. (2002). It was likely due to relatively low adsorbed amount of polyelectrolyte and use of unbeaten fiber.

The tensile index of the paper is illustrated in Fig 5. The tensile indices of the paper in this study were smaller than expected. According to Colodette et al. (2002), paper from unrefined lab-bleached hardwood kraft pulp had a value of around 20 Nm/g, whereas the results in this study ranged from 6 Nm/g to 11 Nm/g. Low values like these may have resulted because the pulp was supplied in dried-form and unbeaten. Li et al. (2011) also reported similar results for unbeaten bleached hardwood pulp, and Eriksson et al. (2006) showed paper with a tensile index of about 10 Nm/g for dried, totally chlorine-free bleached, softwood kraft fibers. It was expected that the higher value could be obtained if never-dried, beaten fibers were used for the experiment. The formation of the sheet was not significantly affected by the polymer treatment. The formation, the LT value, which is the result from a TechPAP formation tester (TechPAP, France), ranged from 43 to 53 for sheets made of untreated fibers and PEM treated fibers, respectively. For all of polyelectrolyte compositions, the tensile index increased with an increase in the number of layers. When the cationic polymer was adsorbed into the outermost layer of the fiber, i.e. an odd-numbered layer, more

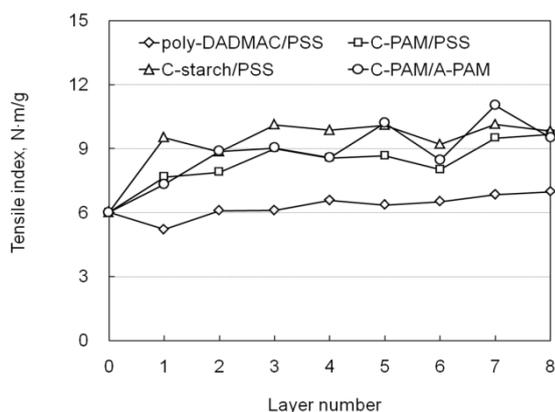


Fig 5. Tensile index of handsheets made of modified Hw-BKP fibers by polyelectrolyte multilayering with different polyelectrolyte combinations.

improvement in the tensile strength was observed. These results agreed with the description in many references (Eriksson et al. 2005a; Lingström et al. 2006; Lingström, Wågberg 2008; Lingström et al. 2007; Notley et al. 2005; Wågberg et al. 2002), despite the fact that the polyelectrolytes used were different in this study. The degree of strength enhancement depended on the polyelectrolyte type. When poly-DADMAC/PSS was adsorbed onto the fiber surface, the tensile strength maintained constant and increased very slightly. This may have resulted due to the low molecular weight and low adsorption of the poly-DADMAC. Lingström et al. (2008) also reported a slight improvement in the tensile strength and strain when using poly-DADMAC with a low molecular weight. In contrast to the poly-DADMAC/PSS result, an improvement in the tensile strength was shown with C-PAM/PSS, C-starch/PSS and C-PAM/A-PAM multilayers. When C-starch/PSS was built up on the fiber, the tensile strength increased up to 5 layers and remained at this level upon further multilayering. The greatest improvement in the tensile index was obtained when C-starch/PSS multilayers were fabricated up onto pulp fibers up to the first 5 layers. On the other hand, a multilayer of C-PAM/A-PAM improved the tensile index of the paper continuously up to 8 layers. The C-PAM/PSS multilayer showed lower strength than the C-PAM/A-PAM multilayer. The mechanism of the strength improvement by PEM has been explained from a multitude of perspectives: the increased number of fiber-fiber joints (Eriksson et al. 2006), an increase in the adsorbed amount (Eriksson et al. 2005a; Eriksson et al. 2005b), a healing effect on a rough or cracked surface (Lvov et al. 2006; Lingström et al. 2008), and electrostatic interaction and covalent bonding between polyelectrolytes (Wågberg et al. 2002). In this paper, the influence of the polyelectrolyte type on the performance of polyelectrolyte multilayering was drawn from the relationship between the adsorbed amount and the paper strength and multilayer structure. In terms of the adsorbed amount, a high adsorbed amount of polymer resulted in greater improvement in the strength (Eriksson et al. 2005a) in a given system, i.e. given the same type and molecular weight of polymer. When polyelectrolyte forms a viscoelastic and thick layer, it would lead to better conformability on fiber surface resulting in great strength

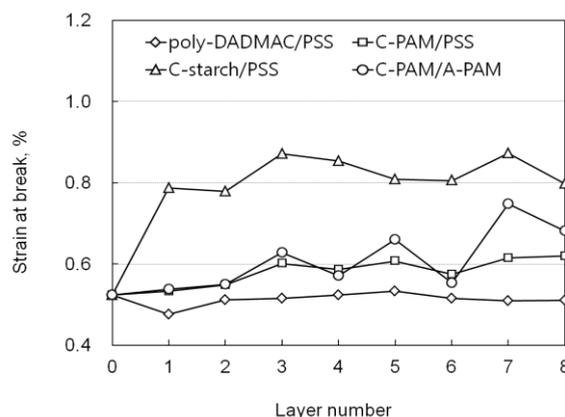


Fig 6. Strain at break of handsheets made of modified Hw-BKP fibers by polyelectrolyte multilayering with different polyelectrolyte combinations.

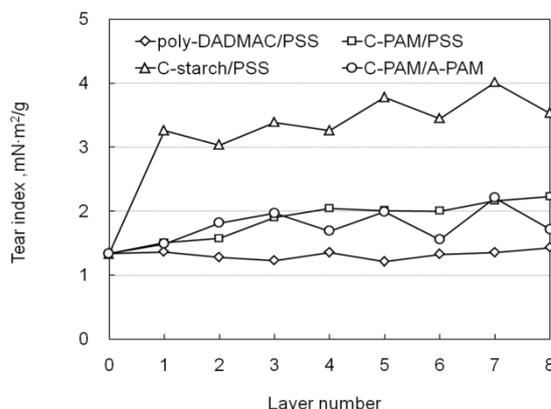


Fig 7. Tear index of handsheets made of modified Hw-BKP fibers by polyelectrolyte multilayering with different polyelectrolyte combinations.

of paper (Notley et al. 2005). A polyelectrolyte layer can enhance the contact area and develop adhesion in fiber-fiber bonds. According to previous studies (Lundström-Hämälä et al. 2010, Lingström and Wågberg, 2008), a multilayer containing C-starch forms a thicker, viscoelastic layer on pulp fibers compared to a poly-DADMAC/PSS multilayer. Therefore, a greater improvement in the mechanical strength of the paper was observed with the C-PAM/A-PAM and C-starch/PSS multilayers compared to others.

The C-PAM/A-PAM combination showed a significant improvement in the tensile strength, but the strain at break was not greatly improved (Fig 6). The strain at break was increased with the C-starch/PSS combination, especially for 1 or 2 layers. Except for the poly-DADMAC/PSS combination, the multilayer with C-PAM also showed an improvement in the strain at break, but not as much as when C-starch was used. The relatively bulky layer of C-starch owing to the low charge density and its branch structure may have contributed to the increase in the strain at break of the sheet.

The tendency of the tensile strength to increase with the increase in the number of layers was also shown in the tear index (Fig 7) and the peel force (Fig 8). The major reason that the greatest improvement in the mechanical properties appeared with the C-starch/PSS combination could also be explained by the same hypothesis in terms

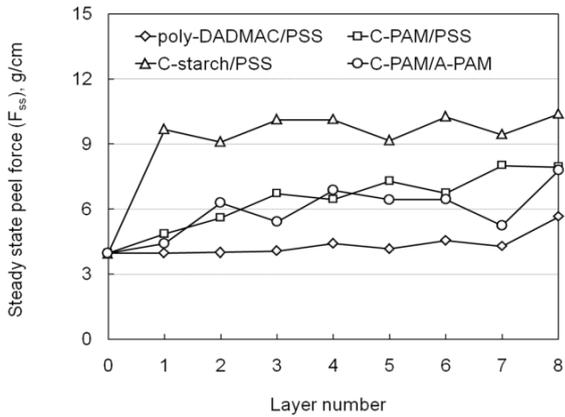


Fig 8. Peel force of handsheets made of modified Hw-BKP fibers by polyelectrolyte multilayering with different polyelectrolyte combinations.

of the adsorbed amount of cationic polymer. In particular, the C-starch/PSS multilayer showed an excellent ability to improve the out-of-plane strength of the handsheet. The tear index was also affected by the friction between the pulp fibers. The increase in the tear index appeared to arise because its multilayer had a relatively bulky and rough layer compared to the other polyelectrolyte combinations, which caused high friction between the cellulose fibers. The simultaneous improvement of the tensile strength and the tear strength was the desirable result. Generally, a change in the tear strength of a paper has an opposite tendency to that of the tensile strength (Hofreiter 1981). A conventional treatment with a dry strength agent frequently has an adverse effect on the tear strength despite the increase in the tensile strength. However, the tensile strength and the tear strength were simultaneously improved through polyelectrolyte multilayering on pulp fibers. The positive effect with polyelectrolyte multilayering on the improvement of the tensile and tear strength was also supported by subsequent peel force result (Fig 8). The peel force is considerably affected by the bonding strength between the fibers. Therefore, it is demonstrated that C-starch/PSS layering onto the pulp fibers clearly improved the inter-fiber bonding.

Comparison of polyelectrolyte multilayering treatment with conventional polymeric treatment for paper strength

To evaluate the performance of the multilayering treatment, it was compared with the conventional polymeric treatment used in papermaking. The adsorbed amount of cationic polymer in each step can be calculated according to Eq 1. Fig 9 shows the total cumulative adsorption amount of the only cationic polymer on the Hw-BKP fibers. When repeated polyelectrolyte multilayering was done to the fiber, the cumulative adsorbed amount of polymer increased linearly. In other words, it was possible to increase the adsorbed amount of the polymer by increasing the number of layers. However, in the conventional treatment, the total adsorbed amount increased with the addition level of the cationic polymer, eventually reaching a plateau just past some addition level of polymer. This indicated that the surface was

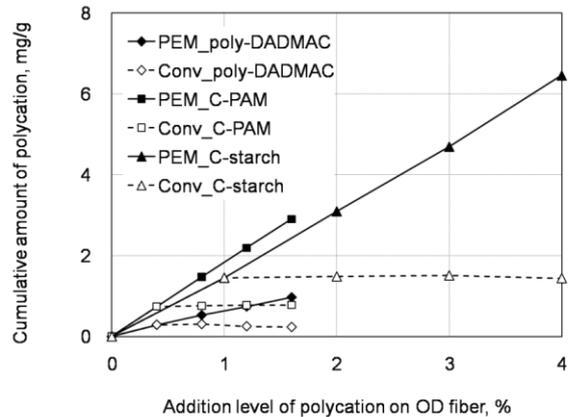


Fig 9. Cumulative adsorbed amount of cationic polymer onto the Hw-BKP fibers (solid line: polyelectrolyte multilayering; dash line: conventional treatment).

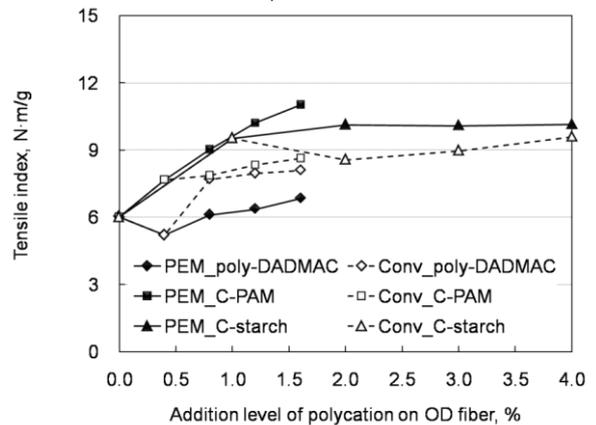


Fig 10. Tensile index of handsheets made of Hw-BKP fibers modified by the different polymeric treatments.

saturated with polyelectrolyte above a certain amount of polymer regardless of how much polymer was added to the stock, thus showing Langmuir adsorption behavior. A higher adsorption of polymer is expected to contribute to a greater improvement of the mechanical strength of the paper.

Fig 10 shows the tensile index of the handsheet depending on the polymeric treatment method. With an increase in the addition level of cationic polymer, the tensile index was improved slightly or significantly depending on the treatment method and polymer type. When polyelectrolyte multilayering was conducted on the fibers, a higher tensile index was obtained, with the exception of the poly-DADMAC. The lowest improvement in the tensile index was shown for both the polyelectrolyte multilayering and the conventional treatment of poly-DADMAC. This may arise because poly-DADMAC has a low inter-fiber bonding which results from its low molecular weight and more compact multilayer structure, compared to the other two cationic polymers used in this study. As demonstrated earlier, the adsorbed amount of poly-DADMAC was very low, whereas the C-starch was highly adsorbed by the fibers. This high adsorbed amount of C-starch and improved interaction in the contact zone between the fibers (Lindström et al. 2005) enabled a stronger sheet to be obtained compared to the conventional method. The

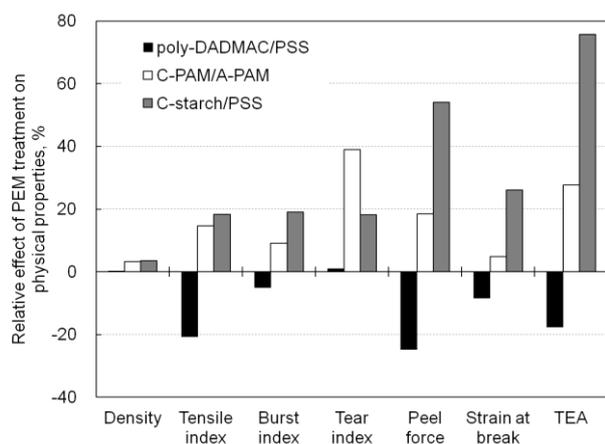


Fig 11. Relative effect of polyelectrolyte multilayering on physical properties of handsheets made of Hw-BKP fibers compared to conventional treatment.

tensile index of a handsheet made of C-PAM- treated Hw-BKP fibers increased linearly both in the case of polyelectrolyte multilayering and the conventional treatment. The increase was more remarkable in the polyelectrolyte multilayering of C-PAM/A-PAM than it was by a single treatment of C-PAM. This was likely affected by the increased cumulative adsorbed amount of C-PAM on the fibers through polyelectrolyte multilayering.

Fig 11 shows the relative effect of physical and mechanical properties of a handsheet made of Hw-BKP fibers modified by polyelectrolyte multilayering compared to the conventional treatment. The pulp fibers were treated with 3 layers, i.e. containing two layers of cationic polyelectrolyte. Polyelectrolyte multilayering enabled a continuous increase of the adsorbed amount of the polyelectrolyte and improved interaction in the contact zone between fibers. It also led to improved mechanical properties of the paper compared to the conventional polymeric treatment. As shown in Fig 11, there was no significant difference in the apparent density of paper. However, the best relative improvements (18 – 75%) were generally obtained through polyelectrolyte

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Literature

Colodette, J.L., Gomide, J.L., Girard, R., Jääskeläinen, A.-S., and Argyropoulos, D.S. (2002): Influence of pulping conditions on eucalyptus kraft pulp yield, quality, a bleachability, Tappi J 1(3), 14-20.

Decher, G., Hong, J.D., and Schmitt, J. (1992): Build up of ultrathin multilayer films by a self-assembly process III: Consecutively alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces, Thin solids film 210, 831-835.

Eriksson, M., Notley, S.M., and Wågberg, L. (2005a): The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibers, J. Colloid Interface Sci. 292, 38-45.

multilayering except for the poly-DADMAC/PSS composition. It was supposed that the effect can be more significant when the paper is made of beaten fibers. Although the polyelectrolyte multilayering treatment greatly improved paper strength, it has some disadvantages in terms of workability and cost in mass production because it involves a repeated process and requires a rinsing process. Therefore, it is necessary to make the process more efficient and simple through the development of a washless PEM treatment.

Conclusions

In this study, pulp fibers were modified by polyelectrolyte multilayering with different polyelectrolyte combinations and the effects of this treatment on the mechanical properties of handsheets were investigated through comparisons with the conventional addition of a dry strength agent in the papermaking process.

The mechanical properties of handsheets made of Hw-BKP fibers modified by polyelectrolyte multilayering were increased with an increase in the number of layers owing to the increased cumulative adsorbed amount of polymers. In particular, the tensile strength, and strain at break, and tear strength were improved in unison by polyelectrolyte multilayering without a significant change in the density. Moreover, a multilayer including C-starch was the most effective at improving the mechanical properties due to the highest adsorbed amount and the high interaction in the contact zone due to its thick, rough layer. A multilayer containing C-PAM was also effective at improving the strength.

Polyelectrolyte multilayering was more effective at improving the mechanical properties compared to the conventional polymeric treatment, as the polyelectrolyte multilayering process enabled a continuous layer growth, which increased the amount of polymer adsorbed on the pulp fibers, whereas the conventional single cationic polymer treatment showed limited saturation adsorption.

Eriksson, M., Petterson G., and Wågberg, L. (2005b): Application of polymeric multilayers of starch onto wood fibres to enhance strength properties of paper, Nord. Pulp Paper Res. J. 20(3), 270-275.

Eriksson, M., Torgnysdotter, A., and Wågberg, L. (2006): Surface modification of wood fibers using the polyelectrolyte multilayer technique: Effects on fiber joint and paper strength properties, Industrial & Chemical Research 45(15), 5279-5286.

Grozidts, G., Eadula, S., Gibson, M., and Lvov, Y. (2006): Nanotechnology for paper recycling, 2006 TAPPI International Conference on Nanotechnology for the Forest Products Industry, Atlanta, USA, TAPPI.

- Hofreiter, B.T.** (1981): Pulp and Paper Chemistry and Chemical Technology, Casey, J.D. (Ed.), Vol. 3, John Wiley & Sons, New York, p. 1493.
- Li, L., Lee, S., Lee, H.L., and Youn, H.J.** (2011): Hydrogen peroxide bleaching of hardwood kraft pulp with adsorbed birch xylan and its effect on paper properties, *BioResources* 6(1), 721-736.
- Lindström, T., Wågberg, L., and Larsson T.** (2005): On the nature of joint strength in paper – A review of dry and wet strength resins used in paper manufacturing, FRC Symposium, Cambridge, UK, p.457-562.
- Lingström, R., Wågberg, L., and Larsson P.T.** (2006): Formation of polyelectrolyte multilayers on fibres: Influence on wettability and fibre/fibre interaction, *J. Colloid Interface Sci.* 296, 396-408.
- Lingström, R., Notley, S.M., and Wågberg, L.** (2007): Wettability changes in the formation of polymeric multilayers on cellulose fibres and their influence on wet adhesion, *J Colloid Interf Sci* 314, 1-9.
- Lingström, R. and Wågberg, L.** (2008): Polyelectrolyte multilayers on wood fibers: Influence of molecular weight on layer properties and mechanical properties of papers from treated fibers, *J Colloid Interf Sci* 328, 233-242.
- Lundström-Hämälä, L., Johansson, E., and Wågberg, L.** (2010): Polyelectrolyte multilayers from cationic and anionic starch: Influence of charge density and salt concentration on the properties of the adsorbed layers, *Starch/Starke* 62, 102-114.
- Lvov, Y.M., Grozdits, G.A., Eadula, S., Zheng, Z., and Lu, Z.** (2006): Layer-by-layer nanocoating of mill broken fibers for improved paper, *Nord. Pulp Paper Res. J.* 21(5), 552-557.
- Niskanen, K. and Kärenlampi, P.** (1998): Paper Physics, Niskanen K. (Ed.), Fapet Oy, Helsinki, p.163.
- Notley, S.M., Eriksson, M., and Wågberg, L.** (2005): Viscoelastic and adhesive properties of adsorbed polyelectrolyte multilayers determined in situ with QCM-D and AFM measurements, *J Colloid Interf Sci* 292, 29-37.
- Page, D.H.** (1969): Theory for the tensile strength of paper, *Tappi* 52(4), 674-681.
- Pettersson G., Sjöberg, J.C., Wågberg, L., Höglund, H., Averheim, A.** (2007): Increased joint-forming ability of ductile kraft pulp fibres by polyelectrolyte multilayer treatment-Influence of refining and drying strategies, *Nord. Pulp Paper Res. J.* 22(7), 228-235.
- Wågberg, L., Forsberg, S., Johansson, A. and Juntti, P.** (2002): Engineering of fibre surface properties by application of the polyelectrolyte multilayer concept, Part 1: Modification of paper strength, *J. Pulp Paper Sci.* 28(7), 222-278.
- Zhao, B. and Pelton, R.** (2005): The initiation of tape peeling-induced paper delamination, *J Pulp Pap Sci* 31, 33-38.

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