

# Effect of pH and conductivity in weak polyelectrolytes multilayering on paper properties

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**KEYWORDS:** Weak polyelectrolyte, Multilayer, Sheet property, Bonding ability, pH, Conductivity

**SUMMARY:** Pulp fibers can be modified through a Layer-by-Layer polyelectrolyte multilayering process. The properties of pulp fibers are affected by the multilayering conditions including the conductivity and pH of the aqueous solution. In this study, we evaluated the properties of the handsheets made of multilayered fibers with weak polyelectrolytes at different pH and conductivity levels. We prepared handsheets from modified pulp fibers by means of multilayering with polyallylamine hydrochloride and polyacrylic acid and evaluated their bonding ability and structural properties. The bonding ability of the fibers was improved remarkably after the polyelectrolyte multilayering due to the increased conformability and electrostatic bonding between the polycation and polyanion on the fiber surface. An outstanding increase of the tensile index was observed at pH 10 when the pulp fibers were treated by polyelectrolyte multilayering. The sheet thickness increased depending on the pH condition. The formation of the paper deteriorated slightly after the polyelectrolytes multilayering process.

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An improvement in paper strength can be achieved by two approaches: a mechanical treatment or a chemical treatment (Pu et al. 2007). A typical mechanical approach is refining. This method can very effectively increase the tensile and burst strength of paper, but negative effects on the tear strength and drainage ability arise during the papermaking process. To avoid the disadvantages of refining, chemical treatments such as the addition of a dry strength agent or oxidation have long been used. In addition, it was reported that the paper strength can be greatly improved by polyelectrolyte multilayering (Wågberg et al. 2002). Layer-by-Layer (LbL) polyelectrolyte multilayering (PEM) technology is a simple process which was introduced by Decher et al. (1992). It is accomplished by consecutive adsorption of polycations and polyanions onto the substrate. The PEM technique has been applied to the papermaking area to increase the paper strength, and its use has been increasing. The strength of the paper is improved through the PEM application of weak polyelectrolytes (Eriksson et al. 2005a; Eriksson et al. 2006), strong polyelectrolytes (Lingström et al. 2006) or cationic and anionic starches (Eriksson et al. 2005b). Lvov et al. (2006) showed that the paper strength can be improved by adding the

recycled fibers or broken fibers nanocoated with polyelectrolytes. Pettersson et al. (2007) showed that Scott bond strength was increased by applying PEM to unbleached kraft pulp. It is also possible to produce new paper products by the deposition of functional materials on the fiber surface using the PEM technique. For example, the deposition of nano clay and polyelectrolyte onto fibers increases the thermal stability of the fibers (Lin et al. 2008). Consequently, polymer multilayering can be a useful and powerful tool to develop functional papers by modifying the fiber surface.

A polyelectrolyte multilayering treatment can modify the electrochemical properties of fibers (Youn et al. 2007; Chin et al. 2008; Ryu et al. 2008). During the multilayering process, the physical and chemical properties of the raw pulp fibers, the polyelectrolyte types, and the treatment conditions including the pH and salt concentration are important factors to determine the electrochemical properties of the modified fibers. In particular, the pH and salt concentration have a considerable influence on the zeta potential of the resultant fibers and adsorption ratio of the polymer, as they affect the conformation and degree of dissociation of the polyelectrolyte and the fibers (Ryu et al. 2008). According to Ryu et al. (2008), a higher zeta potential was obtained when pulp fibers were multilayered at a high pH and a high salt concentration; the final zeta potential of the pulp fiber modified by the multilayering process was dependent on the adsorption ratio. The electrochemical characteristics of the modified pulp fibers are likely to be important when considering the paper strength. It is known that fiber with a higher surface charge results in higher strength paper (Torgnysdotter et al. 2007). Eriksson et al. (2005a) demonstrate that the sheet strength is dependent on both the pH during adsorption and the type of polyelectrolyte in the outer layer when bleached softwood fibers are modified with polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA) under the pH conditions of 3.5, 5.0 and 7.0. By increasing the joint strength between the fibers, the amount of the adsorbed polyelectrolyte on the pulp fiber has a positive effect on the tensile strength of paper made of PEM-treated fibers (Eriksson et al. 2006). Eriksson et al. (2005a) adjusted the amount of PAH and PAA adsorbed onto the fibers by changing the pH of the solution. Weak polyelectrolytes such as PAH and PAA are very useful materials for PEM because of their pH-dependent characteristics. According to Choi and Rubner (2005), the solution  $pK_a$  of PAH is estimated to be between 8.0 and 9.0 and the effective  $pK_a$  of the weak polyelectrolytes in a multilayer assembly can be influenced by the type of polyelectrolyte in the multilayer. By controlling a solution pH, it is possible to vary the thickness of an adsorbed weak polyelectrolyte (Shiratori and Rubner 2000). Thus far, investigations of the effect of the pH on sheet property have been restricted

to limited pH conditions and sheet properties. Therefore, this study sought to evaluate the effect of the pH and conductivity in the multilayering of PAH and PAA on the bonding ability of fibers and the structural properties of the sheet.

## Materials and Methods

### Materials

Bleached hardwood kraft pulp (Hw-BKP) was used for experiments. The fibers to be used as stock for the polyelectrolyte multilayering treatment were beaten to 470 mL CSF in a laboratory Valley beater. The weak polyelectrolytes, PAH with a molecular mass of 15,000 (according to the supplier) and PAA with a molecular mass of 1,800 (according to the supplier) were purchased from Sigma Aldrich and used in the multilayering process on the fibers. The polyelectrolytes were dissolved in deionized water at a concentration of 3 g/L.

Sodium hydroxide and hydrochloric acid were used to adjust the pH and sodium chloride was used to control the conductivity of the solution.

### LbL multilayering of polyelectrolytes

The LbL multilayering of the polyelectrolytes was carried out by repeated alternate adsorption of polycation and polyanion onto the pulp fiber. The consistency of the pulp stock was 0.5%. The pulp fibers were treated with PAH with an addition level of 0.3% based on the oven dried weight of the fibers. After the adsorption for 20 min, the stock was washed two times for 5 min with deionized water to remove unadsorbed polyelectrolyte. The washed pulp was then treated with PAA at an addition level of 0.3% and was then rinsed again. This created one bi-layer of polyelectrolytes. The subsequent layers were prepared in the same way. *Fig 1* schematically depicts the procedure of the polyelectrolytes multilayering. The multilayering process was carried out at the different pH and conductivity conditions shown in *Table 1*. Conductivities of 111  $\mu\text{S/cm}$  and 520  $\mu\text{S/cm}$  were adjusted with 0.001 M and 0.005 M NaCl solutions.

The adsorption ratio of an adsorbed polyelectrolyte onto fibers was evaluated by measuring the charge demands of the polyelectrolyte solution without pulp fibers and the unadsorbed polyelectrolyte which was obtained by filtering the fiber suspension after adsorption process, according to *Eq 1*. The charge demand was measured by particle charge detector (PCD 03, Mutek Co.).

$$\text{Adsorption ratio, \%} = (A-B)/A \times 100 \quad [1]$$

where, A is the charge demand ( $\mu\text{eq/L}$ ) of a polyelectrolyte solution without pulp fiber and B is the charge demand ( $\mu\text{eq/L}$ ) of filtrate of pulp suspension after treating with the polyelectrolyte.

### Preparation of handsheet and evaluation of sheet properties

Handsheets with a grammage of 75  $\text{g/m}^2$  were made of fibers with a multilayer of PAH and PAA using a laboratory handsheet former. Although the pH change can affect the properties of a polyelectrolyte layer such as the conformation and charge density, the handsheets were made with tap water under a neutral pH condition in this

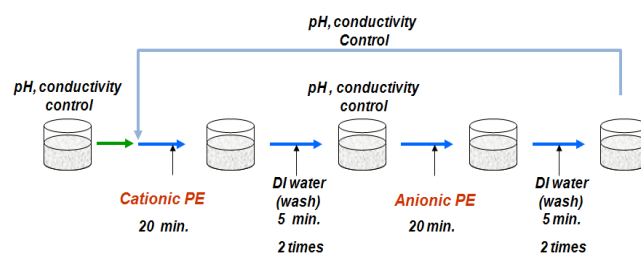


Fig 1. Schematic of the procedure of the polyelectrolytes multilayering onto the pulp fibers.

Table 1. Multilayering variables.

pH	4, 7, 9, 10
Conductivity, $\mu\text{S/cm}$	111, 520
Layer number	2, 10

study. As most papermaking processes are carried out under a neutral pH, the results from this study must be useful to predict the performance of the modified fibers. They were pressed at 3.5  $\text{kg/cm}^2$ , dried at 120°C, and preconditioned at a constant temperature (23°C) and humidity (RH 50%) before testing.

The bonding ability of the fibers and the structural properties of the handsheets were evaluated. The bonding ability was evaluated by measuring the tensile strength of a handsheet in accordance with TAPPI Test Method T494 om-96. The thickness, air permeability and PPS roughness were evaluated as structural properties in accordance with TAPPI Test Methods. The formation was measured using a TechPAP Formation tester, and the air permeability was tested using a Gurley permeability tester.

### Evaluation of layer thickness on model substrate

To measure the thickness of the polyelectrolyte layer adsorbed on a substrate, a slide glass was used as a model substrate. The slide glass was cleaned by RCA process (Kern 1993) before use to remove contaminants and increase the hydrophilicity, and it was then multilayered up to 10 layers of PAH and PAA in accordance with the dipping method introduced by Decher (1997) at different pH conditions as noted in *Table 1*. The adsorption thickness of the polyelectrolyte layers was measured by a NV-E1000 device (NanoSystem Co., Korea) which works according to the principle of a white light scanning interferometer (WLSI). The resolution of the height was 0.1 nm.

## Results and Discussion

### Bonding ability

The bonding ability of a sheet was evaluated by measuring the tensile strength. According to Page's theory, the tensile strength of paper is determined by two key factors: the intrinsic fiber strength and the interfiber bonding ability as determined by the bonded area and the bonding strength (Page 1969). Because polyelectrolyte multilayering does not change the fiber strength, the changes in the tensile strength of the paper can be regarded as indicating the changes in the bonding ability between fibers.

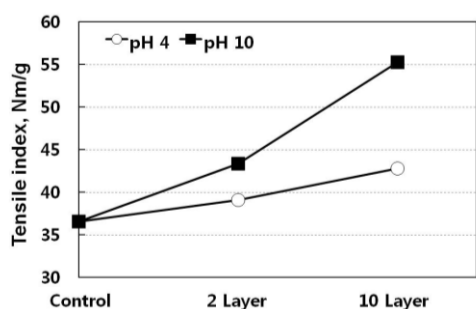


Fig 2. Effect of layer number on tensile index of sheet (conductivity of 111  $\mu\text{S}/\text{cm}$ ).

A polyelectrolyte multilayering had a good effect on the bonding ability of the fibers, as shown in *Fig 2*. The tensile index showed a remarkable improvement with 10 layers of polyelectrolytes. The densities were  $0.45 \text{ g}/\text{cm}^3$  and  $0.44 \text{ g}/\text{cm}^3$  for the control and PEM-treated sheets with 10 layers. Although the density of handsheet was insignificantly changed by PEM treatment, the strength of the handsheets increased with increasing number of layers and its enhancement was dependent on the multilayering pH. The effect of the number of layers on the tensile index was similar to the result obtained by Wågberg et al. (2002). They reported that this improvement was caused by the increased joint strength and the contact degree between fibers when layer number increased. Eriksson et al. (2005a; 2006) showed that the joint strength was increased and leveled off for pH 7.5/7.5 strategy PEM treatment when the number of layers increased. However, *Fig 2* shows that there was improvement in the tensile strength of the sheets with 2 and 10 layers for pH 4 and 10 conditions. This discrepancy may be due to the different pH in multilayering and handsheet forming.

*Fig 3* represents the tensile index of handsheets made of PEM-treated fibers with 10 layers at different pH and conductivity conditions. The bonding ability as described by the tensile index was generally improved as the multilayering pH increased, except for pH 9. Especially at pH 10, the bonding ability was improved by approximately 60%. This showed the same tendency as the average adsorption ratio of PAH onto the fibers for all layers, as shown in *Fig 4*. This means that the changes of the bonding ability of fibers might be correlated with the adsorption ratio of PAH. The average adsorption ratio was calculated by dividing the total adsorption ratio by the layer number of PAH or PAA (for this case, the layer number is 5). However, the average adsorption ratio of PAA showed the different behavior from that of PAH. As the PAA is not fully dissociated at pH 4 (Choi and Rubner 2005), the adsorption ratio of PAA at pH 4 was the highest among the examined pH conditions. The high adsorption ratio of PAA at pH10 appears to be associated with a high adsorbed amount of the cationic PAH layer. *Figs 3 and 4* demonstrate that the bonding ability of the fibers with a higher adsorption ratio of PAH is superior. This was most likely due to the increased joint strength caused by the interpenetration of the polyelectrolytes, as reported by Wågberg et al. (2002). Eriksson et al. (2005a) also demonstrated a positive relationship to the adsorbed amounts of PAH. They indicated that the adsorption ratio

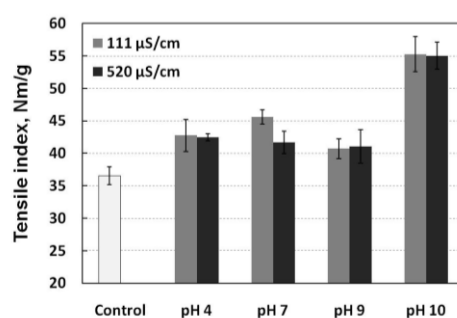


Fig 3. Effect of pH and conductivity in multilayering on tensile index of sheet (10 layers).

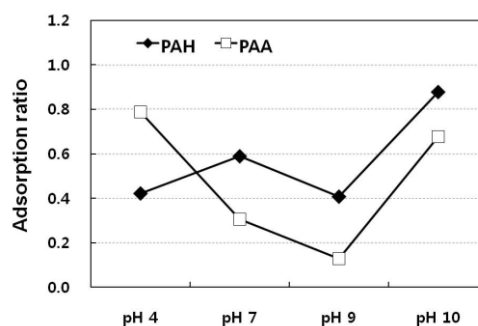


Fig 4. Average adsorption ratio of PAH and PAA on fiber at different pH conditions and 111  $\mu\text{S}/\text{cm}$ .

of PAH was a determinant factor in the bonding strength.

Although the adsorption ratio was higher at a conductivity of 520  $\mu\text{S}/\text{cm}$  owing to the 'coiled-up' conformation of the polyelectrolytes in the aqueous solution (Ryu et al. 2008), the effect of the conductivity during the multilayering process on the bonding ability was insignificant (*Fig 3*).

### Structural properties

We evaluated the structural properties of the sheets, including the formation, thickness, air permeability and roughness. *Fig 5* represents the formation of a handsheet made of the pulp fibers with 10 layers. The formation was evaluated via the  $L_T$  values. The formation was deteriorated by polyelectrolyte multilayering, but it did not show an obvious dependence on the pH in the multilayering process. When pulp fibers were treated at pH 10 or at higher conductivity levels, however, the handsheet showed better formation.

*Figs 6 and 7* show the thickness and density of the handsheets made of the PEM-treated fibers. Polyelectrolyte multilayering increased the sheet thickness by 3%-12%. The density of sheets was slightly decreased by PEM treatment, but its decrease appeared insignificant. When pulp fibers were consecutively adsorbed with polycation and polyanion at 111  $\mu\text{S}/\text{cm}$  (0.001 M NaCl solution), polyelectrolyte multilayering did not lead to a significant change of the handsheet thickness under the various pH conditions. However, it caused an apparent increase in the thickness at 520  $\mu\text{S}/\text{cm}$ , with different behavior depending on the pH.

To investigate the effect of the pH and conductivity in the multilayering on the sheet thickness, we evaluated the thickness of the adsorption layer using a model substrate and the WLSI method. *Fig 8* shows the adsorption

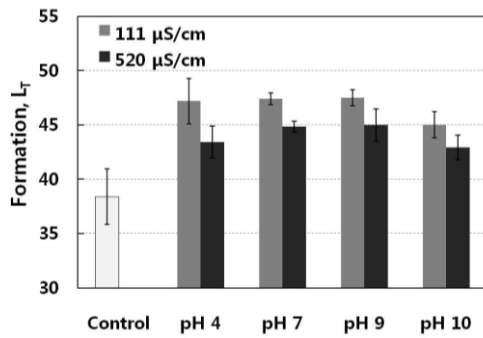


Fig 5. Effect of pH and conductivity in multilayering on sheet formation (10 layers).

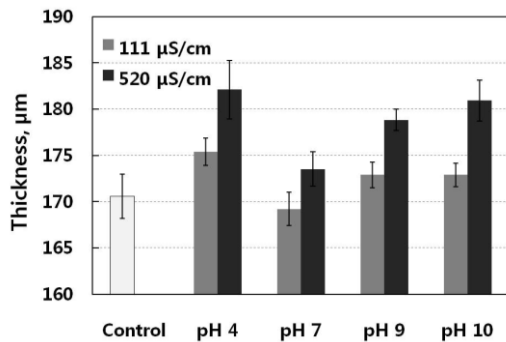


Fig 6. Effect of pH and conductivity in multilayering on sheet thickness (10 layers).

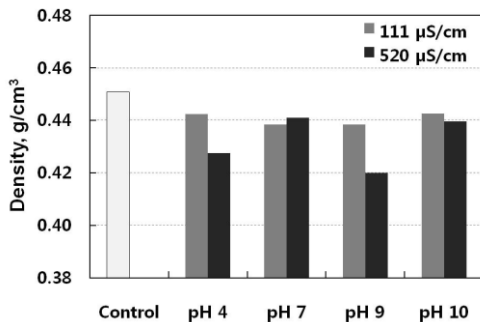


Fig 7. Effect of pH and conductivity in multilayering on sheet density (10 layers).

thickness of 10 layers at different pH and conductivity conditions. It is notable that the change of the PEM thickness with pH looks similar to the sheet thickness change, although the thickness of the polyelectrolyte multilayer is definitely very small and the sheet thickness is mainly determined by the consolidation process. This behavior can be seen at high conductivity. PAH and PAA are weak polyelectrolytes, and their dissociation degree is dependent on the pH. The PAH was fully charged but the PAA was not fully ionized at pH 4. At pH 10, the PAA was adsorbed in a fully ionized state while the degree of ionization of PAH was low. Because both PAA and PAH were nearly fully and fully ionized, respectively, at pH 7, however, they were deposited with a flat conformation. This led to a low adsorption thickness of the polyelectrolytes and a narrow sheet thickness. The dependence of the pH on the adsorption thickness of weak polyelectrolytes was also demonstrated by Shiratori and Rubner (2000).

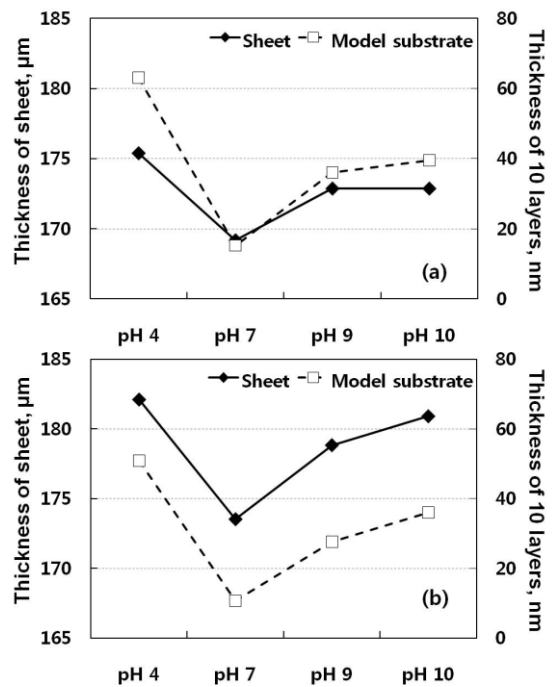


Fig 8. Handsheet thickness and polyelectrolyte multilayer thickness on slide glass with the change of pH at different conductivity of 111 μS/cm (a) and 520 μS/cm (b) (10 layers).

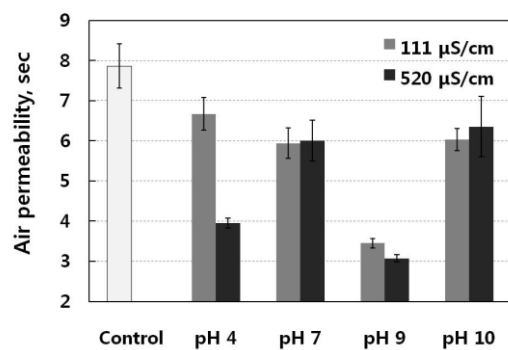


Fig 9. Air permeability of handsheet made of fibers treated at different pH and conductivity conditions (10 layers).

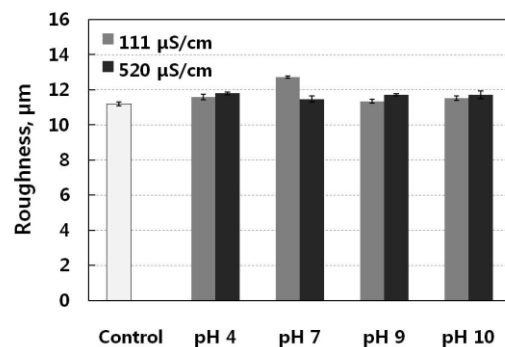


Fig 10. Effect of pH and conductivity in multilayering on sheet roughness (10 layers).

Fig 9 shows the air permeability of the handsheet. The air permeability was evaluated by measuring the required time to pass an air volume of 300 cc using a Gurley densometer. Air permeability is generally affected by the densification and flocculation, but we could not find a clear relationship between the treatment conditions of the

pH and the conductivity and the air permeability of a handsheet in this study. This would require further investigation. The sheet roughness was not significantly changed by polyelectrolyte multilayering (Fig 10). The pH and conductivity during multilayering had little influence on the PPS roughness of a handsheet.

## Conclusions

The effects of the pH and conductivity during the multilayering of PAH and PAA on the bonding ability of the fibers and the structural properties of the sheet were investigated. The bonding ability of the fibers was improved remarkably by polyelectrolyte multilayering. The behavior of the bonding ability with the multilayering pH was correlated with the adsorption amount of PAH. The sheet thickness became thicker upon higher conductivity and was dependent on the multilayering pH. The change of the sheet thickness with multilayering pH was similar to the change of the polyelectrolyte multilayer thickness. The sheet formation was deteriorated by the PEM treatment, and the PPS roughness of handsheet was not significantly changed by changes in the pH and conductivity during the multilayering process.

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