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A DISSERTATION FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Polyelectrolytes Multilayering of Fillers for Strength Improvement of Filled Paper and Their Functionality

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Abstract

Polyelectrolytes Multilayering of Fillers for Strength Improvement of Filled Paper and Their Functionality

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Inorganic filler particles are one of the most important additives in papermaking industry, typically for printing and writing paper grades. Advantages of fillers are to improve optical properties, smoothness, printability of papers, and to save final cost and drying energy. To maximize the advantages of fillers, demand for the increase in filler content of paper, so-called “high filler loading”, has been increased. However, fillers give negative effect on strength of paper. High filler loading is mainly focused on minimization of the negative effect of fillers on paper strength. Polyelectrolytes multilayer (PEM) technique is regarded as one of the surface modification techniques to increase paper strength. Even though there are many researches about application of PEM technique into papermaking science, these previous researches are mostly focused on surface modification of pulp fibers and its effect on paper without fillers. In this study, therefore, possibility of PEM technique for high filler loading was investigated. Furthermore, applicable model of PEM process to
papermaking industry and antibacterial paper with high strength using PEM fillers were proposed.

Firstly, strengthening effect of PEM treatment for highly filled paper was investigated. PEM treatment can be performed on either fibers or fillers. Two approaches gave strength improvement of filled paper. Even though PEM treatment on fibers improved strength of filled paper, this strengthening effect become weaker as filler content increased. However, PEM treatment on fillers was more effective for strength improvement of highly filled paper. This was because PEM treatment on fillers improved bonding strength between fiber and filler as well as bonding strength between fillers. This was confirmed by evaluation of specific debonding factor between fiber and filler, and measurement of breaking strength of dense film composed of fillers.

Factors affecting strength improvement of filled paper were investigated depending on characteristics of multilayer and morphological properties of fillers. The characteristics of multilayer were controlled by salt concentration during PEM treatment, and different types of polyelectrolytes. High salt concentration up to 0.1 M NaCl enabled to increase amounts of PDADMAC and PSS in multilayer onto GCC, and thickness of the multilayer, resulting in greater strengthening effect at given filler content. The multilayer with cationic starch showed greater strengthening effect than the multilayer with PDADMAC at given layer number, but PDADMAC /PSS 7 layers at 0.1 M NaCl gave similar strengthening effect with C-starch/A-PAM 3 layers. It was considered that strengthening mechanism was due to creation of additional hydrogen bonding in the case of multilayer with C-starch, and more interdiffusion of polymer chains and creation of van der Waals and coulombic bonding in the case of multilayer with PDADMAC. PEM treatment was performed onto three types of fillers, irregular type of GCC, scalenoahedral type of PCC, and platy type of kaolin. PEM treatment on the platy type of kaolin provided the highest
strengthening effect on filled paper. It was considered that the smoother surface of fillers showed the higher strengthening effect of multilayer on filled paper.

To suggest mill application model for PEM treatment on fillers, inline washless PEM system was designed for fast and continuous PEM treatment. The inline washless PEM system consisting of three inline mixers and pumps can form multilayer onto fillers up to 3 layers. Zeta potential and particle size of washless PEM fillers can be controlled by addition level of polyelectrolytes, and shear, respectively. The washless PEM fillers provided a little more effective for strength improvement of filled paper than conventional PEM fillers. Therefore, it was considered that this inline washless PEM system would be proper to apply to papermaking industry.

As one of the application of PEM technique in the papermaking, antibacterial paper using PEM treated fillers was proposed. PVAm is known to be one of the polyelectrolytes that shows antibacterial activity, thus PVAm/PAA multilayer was formed onto kaolin particles. Internal addition of the PEM kaolin to paper showed antibacterial activity less than 90%, and great strengthening effect on the filled paper. Surface treatment of the PEM kaolin on paper gave great antibacterial activity more than 99%. This PEM kaolin with antibacterial activity is expected to be used as strengthening fillers of filled paper as well as fabrication of antibacterial paper.

Keywords : Polyelectrolytes multilayering, fillers, filled paper, mechanical properties, strengthening mechanism, washless polyelectrolytes multilayering, antibacterial activity

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List of Papers

This dissertation is written based on the following published papers or papers in submission:

Paper I

Strengthening effect of polyelectrolytes multilayer on highly filled paper
Jegon Lee and Hye Jung Youn
Nordic Pulp & Paper Research Journal (SCI), In preparation
-Designed and performed the experiments, wrote the paper.

Paper II

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Paper III

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Jegon Lee, Kyujeong Sim, Hak Lae Lee, and Hye Jung Youn

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- Designed and performed the experiments, wrote the paper.

Paper V

Effect of ground calcium carbonate modified by washless multilayering of polyelectrolytes on paper quality

Jegon Lee, Wanhee Im, Kyujeong Sim, Hak Lae Lee, and Hye Jung Youn

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- Designed and performed the experiments, wrote the paper.
Contents

Chapter 1
Introduction ................................................................. 1
1. Introduction ............................................................. 2
2. Objectives ............................................................... 7

Chapter 2
Literature review ......................................................... 9
1. Influences of fillers on strength of paper ......................... 10
2. High filler loading techniques ...................................... 12
3. Polyelectrolytes multilayering (PEM) ............................ 14
   3.1 General aspects for PEM ....................................... 14
   3.2 PEM in the papermaking ....................................... 18
   3.3 PEM for high filler loading .................................... 20
4. Mechanism for strengthening effect of polyelectrolytes ......... 21

Chapter 3
Investigation on strengthening effect of polyelectrolytes multilayer
on filled paper ............................................................ 23
1. Introduction ............................................................. 24
2. Materials and methods ............................................... 26
   2.1 Materials .......................................................... 26
   2.2 Formation of polyelectrolytes multilayer on filler particles 28
   2.3 Formation of polyelectrolytes multilayer on pulp fiber ..... 30
2.4 Properties of PEM GCC and PEM fiber ........................................ 31
  2.4.1 Zeta potential and particle size ............................................. 31
  2.4.2 Adsorbed amount of polyelectrolytes ................................... 31
2.5 Preparation and properties of filled handsheets ............................. 32
  2.5.1 Handsheets preparation ..................................................... 32
  2.5.2 Properties of filled handsheets ............................................ 35
    2.5.2.1 Structural properties ............................................... 35
    2.5.2.2 Mechanical properties ............................................. 35
    2.5.2.3 Optical properties .................................................. 36
2.6 Bonding ability of PEM fillers ............................................... 36
  2.6.1 Measurement of bonding force between fibers and fillers ........... 36
    2.6.1.1 Preparation of model fibers sheets ................................. 37
    2.6.1.2 Preparation of a filler layer between the model fibers sheets .... 37
    2.6.1.3 Delamination test .................................................... 39
2.6.2 Measurement of bonding strength between fillers ..................... 40
3. Results and discussion ............................................................ 41
  3.1 Properties of PEM fibers and PEM GCC ................................. 41
3.2 Effect of PEM treatment on properties of filled handsheets ............ 43
    3.2.1 Influence of PEM treated fibers on paper properties ............... 43
    3.2.2 Physics properties of filled paper ................................... 45
    3.2.3 Improvement on mechanical properties of filled paper .......... 48
    3.2.4 Optical properties of filled paper ................................... 59
3.3 Mechanism for improvement on strength of filled paper by PEM treatment ................................................. 63
    3.3.1 Determination of improvement on bonding strength between fibers-fillers ................................................. 63
3.3.2 Bonding ability between PEM treated fillers

4. Summary

**Chapter 4**

**Factors affecting properties of PEM fillers and strength of filled paper**

1. Introduction

2. Materials and methods

2.1 Materials

2.2 Formation of polyelectrolytes multilayer on filler particles

2.3 Properties of PEM fillers

2.3.1 Zeta potential and particle size of PEM filler

2.3.2 Adsorbed amount of polyelectrolytes

2.3.3 Charge demand of PEM GCC

2.3.4 Monitoring of growth of PD/PSS multilayer using Quartz Crystal Microbalance with Dissipation

2.4 Preparation and properties of filled handsheets

2.4.1 Handsheets preparation

2.4.2 Properties of filled handsheets

2.5 Bonding ability of PEM fillers

2.5.1 Measurement of bonding force between fibers and fillers

2.5.2 Measurement of bonding strength between fillers

3. Results and discussion

3.1 Effect of multilayer characteristics on properties of PEM GCC and strength of filled paper

3.1.1 Effect on properties of PEM GCC depending on salt concentration
3.1.2 Effect on strength of filled paper .................................. 102
3.2 Effect of nature of polyelectrolytes on strength of filled paper .... 108
3.3 Effect of filler morphology on strength of filled paper .......... 117
  3.3.1 Properties of PEM fillers ........................................... 117
  3.3.2 Effect of types of fillers on handsheets properties .......... 126
4. Summary ................................................................. 133

Chapter 5
Application of polyelectrolytes multilayering:
washless polyelectrolytes multilayering for mill application and
antibacterial effect of PEM fillers ....................................... 135
1. Introduction .......................................................... 136
2. Materials and methods ............................................. 139
  2.1 Materials ......................................................... 139
    2.1.1 Pulp fibers ............................................... 139
    2.1.2 Fillers ....................................................... 139
    2.1.3 Polyelectrolytes .......................................... 139
    2.1.4 Bacteria .................................................. 140
  2.2 Washless polyelectrolytes multilayering ....................... 141
    2.2.1 Inline washless polyelectrolytes multilayering .......... 141
    2.2.2 Handsheets preparation .................................. 142
    2.2.3 Measurement .............................................. 143
      2.2.3.1 Properties of inline washless PEM GCC ....... 143
      2.2.3.2 Handsheets properties ............................. 144
  2.3 Antibacterial PEM fillers ...................................... 145
    2.3.1 Formation of PVAm/PAA multilayer on kaolin .......... 145
Chapter 6

Overall conclusions .................................................... 180

References ........................................................................ 187

초록 ............................................................................. 201
List of Tables

Table 3-1. Nitrogen content in C-starch/A-PAM 3 layers fibers and GCC excluding nitrogen content of raw materials ........................................ 42
Table 3-2. Properties of handsheets without fillers ........................................ 44
Table 3-3. The coefficients obtained from empirical equation of peel force versus filler loading ...................................................... 68
Table 3-4. Estimated average peel force calculated from empirical equation 68
Table 4-1. Characteristics of fillers ............................................................ 81
Table 4-2. Description of PEM fillers used for handsheets preparation ...... 87
Table 4-3. Characteristics of untreated GCC and PEM GCC applied to filled paper ...................................................................... 108
Table 4-4. Summary of coefficients fitting peel force versus filler loading obtained from Microsoft excel trend line function .......... 109
Table 4-5. Polyelectrolyte amount adsorbed in multilayer (mg/g) .......... 119
Table 5-1. Variables of treatment conditions for inline washless PEM ...... 150
Table 5-2. Properties of untreated GCC and two types of PEM GCC ...... 161
Table 5-3. Paper conditions for antibacterial tests .................................. 169
Table 5-4. Antibacterial activity described as reduction ratio of bacteria population compared to remaining bacteria population of blank condition ........................................................ 174
List of Figures

Fig. 1-1. Types of inorganic filler particles .................................................. 3
Fig. 1-2. Trend of paper strength depending on filler content .................. 3
Fig. 2-1. (a) Bracing mechanism in which filler debonds the paper, and (b) covering mechanism in which the proportion of direct contact between fibers is reduced ...................................................... 11
Fig. 2-2. (A) Schematic of the film deposition process using slides and eakers. (B) Simplified molecular picture of the first two adsorption steps. (C) Chemical structures of two typical polyions, the sodium salt of poly(styrene sulfonate) and poly(allylamine hydrochloride) .............................................................................. 15
Fig. 2-3. Model of the segment distribution in multilayers along the surface normal ................................................................. 15
Fig. 2-4. Formation of multilayer in salt solution ................................. 17
Fig. 3-1. Chemical structure of polyelectrolytes used for PEM treatment, (a) cationic starch and (b) anionic polyacrylamide (A-PAM) .......... 27
Fig. 3-2. Process of polyelectrolytes multilayer treatment on filler particles .................................................................................. 29
Fig. 3-3. Process of preparation for filled hadnsheets ......................... 34
Fig. 3-4. Illustration of the laminate ......................................................... 37
Fig. 3-5. The final model sheets for measurement .............................. 38
Fig. 3-6. (a) Sample preparation of the measurement, and (b) sample placed in 90° peel fixture ......................................................... 39
Fig. 3-7. Dried fillers structure ................................................................. 40
Fig. 3-8. Size distribution of untreated GCC and PEM GCC (C-starch/A-PAM 3 layers) .......................................................... 42
Fig. 3-9. Apparent density of filled handsheets as a function of ash content 46
| Fig. 3-10. Surface images of filled handsheets with range of 27.9-29.4% fillers content | 47 |
| Fig. 3-11. Tensile index of filled handsheets as a function of ash content | 48 |
| Fig. 3-12. Illustration of bonding between PEM treated fibers and untreated GCC | 51 |
| Fig. 3-13. Illustration of bonding between untreated fibers and PEM treated GCC | 51 |
| Fig. 3-14. Internal bond strength of filled handsheets as a function of ash content | 54 |
| Fig. 3-15. Tear index of filled handsheets as a function of ash content | 54 |
| Fig. 3-16. Strain of filled handsheets as a function of ash content | 57 |
| Fig. 3-17. Tensile energy absorption (TEA) index of filled handsheets as a function of ash content | 57 |
| Fig. 3-18. Tensile stiffness index of filled handsheets as a function of ash content | 58 |
| Fig. 3-19. Bending stiffness index of filled handsheets as a function of ash content | 58 |
| Fig. 3-20. Opacity of the filled handsheets as a function of ash content | 60 |
| Fig. 3-21. Light scattering coefficient of the filled handsheets as a function of ash content | 58 |
| Fig. 3-22. Brightness of the filled handsheets as a function of ash content | 58 |
| Fig. 3-23. Light absorption coefficient of the filled handsheets as a function of ash content | 58 |
| Fig. 3-24. Surface images of fillers-laminated fiber model layer | 64 |
| Fig. 3-25. Delamination peel force of the laminate depending on filler loading | 67 |
| Fig. 3-26. Flexure stress of untreated GCC and PEM treated GCC | 70 |
| Fig. 3-27. Cross section images of the filled handsheets made of untreated fibers and C-starch/A-PAM 3 layers GCC | 72 |
Fig. 4-1. Chemical structure of polyelectrolytes used for PEM treatment 80
Fig. 4-2. Morphology of (a) GCC, (b) PCC, (c) kaolin and (d) size distribution 81
Fig. 4-3. Zeta potential of GCC depending on salt concentration of GCC suspension 92
Fig. 4-4. Zeta potential of GCC with a PDADMAC layer formed at different salt concentration 92
Fig. 4-5. Zeta potential of PDADMAC/PSS GCC depending on salt concentration during PEM treatment 95
Fig. 4-6. Charge demand of PDADMAC/PSS GCC depending on salt concentration 96
Fig. 4-7. Adsorbed amount of (a) PDADMAC and (b) PSS per gram of GCC 99
Fig. 4-8. QCM-D data of the fifth overtone (25 MHz), (a) change in frequency and dissipation as a function of time and (b) thickness obtained from the change in frequency 100
Fig. 4-9. Average particle size of PDADMAC/PSS GCC depending on salt concentration 101
Fig. 4-10. Size distribution of untreated GCC and PDADMAC/PSS 7 layers GCC 101
Fig. 4-11. Tensile index of filled handsheets 104
Fig. 4-12. Internal bond strength of filled handsheets 104
Fig. 4-13. Relationship between adsorbed amount of PDADMAC and tensile index at 25±1% ash content 106
Fig. 4-14. Relationship between adsorbed amount of PDADMAC and internal bond strength at 25±1% ash content 106
Fig. 4-15. Schemes of multilayer structure with (a) PDADMAC/PSS 0 M and (b) PDADMAC/PSS 0.1 M 107
Fig. 4-16. Delamination peel force of the laminate 110
Fig. 4-17. Flexure strength of the dense film composed of fillers 111
Fig. 4-18. Tensile index of the filled handsheets 115
Fig. 4-19. Internal bond strength of the filled handsheets 115
Fig. 4-20. Wet tensile index of the filled handsheets 116
Fig. 4-21. Zeta potential of (a) PDADMAC/PSS GCC, PCC, and kaolin, and
(b) C-starch/A-PAM GCC and PCC 118
Fig. 4-22. Adsorbed amount of (a) PDADMAC and (b) PSS in the outermost
layer of PDADMAC/PSS multilayer 120
Fig. 4-23. Average particle size of (a) PDADMAC/PSS GCC, PCC, and
kaolin, and (b) C-starch/A-PAM GCC 123
Fig. 4-24. Size distribution of PEM fillers 124
Fig. 4-25. Morphology of (a) untreated GCC, (b) PDADMAC/PSS 7 layers
GCC, (c) untreated PCC, (d) PDADMAC/PSS 7 layers PCC (e)
untreated kaolin, (f) PDADMAC/PSS 7 layers kaolin, (g) C-
starch/A-PAM 3 layers GCC, and (h) C-starch/A-PAM 3 layers
PCC 125
Fig. 4-26. Apparent density of filled handsheets 127
Fig. 4-27. Light scattering coefficient at 457 nm of filled handsheets 127
Fig. 4-28. Surface images of handsheets filled with (a) untreated GCC, (b) PD7
(0.1M) GCC, (c) untreated PCC, (d) PD7 (0.1M) PCC, (e) untreated
kaolin, and (f) PD7 (0.1M) kaolin at 25% ash content 128
Fig. 4-29. Tensile index of filled handsheets 131
Fig. 4-30. Internal bond strength of filled handsheets 131
Fig. 4-31. Tensile index (a) and internal bond strength (b) of handsheets
filled with C-starch/A-PAM 3 layers GCC and C-starch/A-PAM 3
layers PCC 132
Fig. 5-1. Scheme of laboratory inline system for inline washless
polyelectrolytes multilayering 137
Fig. 5-2. Effect of addition level of cationic starch on (a) zeta potential, (b) adsorbed level of cationic starch, (c) average particle size, and (d) size distribution of treated GCC ........................................... 152

Fig. 5-3. Effect of addition level of A-PAM onto cationic starch-treated GCC on (a) zeta potential, (b) adsorbed level of cationic starch, (c) average particle size, and (d) size distribution .............................. 154

Fig. 5-4. Properties of inline washless 3 layers GCC as a function of flow rate of GCC suspension, (a) zeta potential, (b) total adsorbed amount of CS and A-PAM, (c) average particle size, and (d) size distribution ................................................................. 156

Fig. 5-5. Zeta potential of inline washless 3 layers GCC (a) and adsorbed amount of cationic starch and A-PAM (b) depending on rotation speed ................................................................. 158

Fig. 5-6. Particle size of inline washless 3 layers GCC ........................................ 169

Fig. 5-7. Optical microscopic images of inline washless 3 layers GCC prepared at (a) 12.5 m/sec, (b) 18.7 m/sec, (c) 27.4 m/sec, and (d) 36.1 m/sec ................................................................. 169

Fig. 5-8. Patterns of (a) zeta potential and (b) average particle size of C-starch/A-PAM GCC (conventional treatment) and inline washless C-starch/A-PAM GCC ................................................................. 160

Fig. 5-9. Surface images of handsheets filled with (a) untreated GCC, (b) C-starch/A-PAM 3 layers GCC, and (c) inline washless C-starch/A-PAM 3 layers GCC at around 25% ash content ............... 163

Fig. 5-10. Apparent bulk of filled handheets ............................................. 163

Fig. 5-11. Tensile index (a) and internal bond strength (b) of filled handsheets ................................................................. 165

Fig. 5-12. Properties of PVAm/PAA kaolin, (a) zeta potential, (b) average particle size, and (c) amount of PVAm in the multilayer ................................................................. 167

Fig. 5-13. Tensile index (a) and internal bond strength (b) of handsheets filled with PVAm/PAA kaolin ................................................................. 168
Fig. 5-14. Surface images of (a) FU, (b) F3L, (c) F7L, (d) PL_F3L, (e) PH_F3L, and (f) PH_FU ................................. 171

Fig. 5-15. Alive bacteria population for (a) *E.coli* O157:H7 and (b) *L. monocytogenes* in handsheets-soaked bacteria suspension after 18 hr incubation ..................................................... 173

Fig. 5-16. Bacteria membrane integrity of *E.Coli* O157:H7 on filled handsheets with untreated kaolin ((a) and (b)) and pigmentized handsheets treated with 3 layers PEM kaolin ((c) and (d)) after exposure for 2 hr  ......................................................... 177
Chapter 1.

Introduction
1. Introduction

Fillers defined as water-insoluble particulate substances (Hubbe and Gill 2016) are one of most important additives in papermaking industry. Inorganic mineral particles such as ground calcium carbonate (GCC), precipitated calcium carbonate (PCC), and clay (Fig. 1-1) are typically used as fillers in various paper grades such as printing and writing paper grades. These fillers give better optical properties, smoothness, printability, and appearance to papers (Shen et al. 2009). Another benefit of the use of fillers in paper is to reduce product cost and drying energy consumption. Therefore, paper makers have been interested in an increase in filler content of paper in order to maximize the advantages of fillers.

The increase in filler content of paper, so-called “high filler loading”, should overcome disadvantages of the use of fillers. The most important negative issue is that fillers weaken the strength of paper. As described in Fig. 1-2, mechanical properties of filled paper is decreased with an increase in filler content. According to Page’s theory (1969), tensile strength of paper is related to the intrinsic strength of fibers and the strength of bonds between fibers. It is expected that fillers negatively affect the strength of the bonds because of interference in the bonded area between fibers and weak bonding strength between filler particle and fiber (Hubbe and Gill 2016).
Fig. 1-1. Commonly used inorganic filler particles.

Fig. 1-2. Trend of paper strength depending on filler content (Mohlin and Olander 1986).
There are two strategies to overcome the negative effect of fillers on paper strength. One is focused on the bonded area between fibers. Preflocculation of filler particles before adding them to fibers stock (Mabee and Harvey 2000, Lee and Lee 2006, Gaudreault et al. 2009, Seo et al. 2012, Im et al. 2013) and lumen loading of filler particles (Middleton et al. 2003, Kumar et al. 2011) are related to less interference in inter-fiber bonding, thus filler content can be increased without severe decrease in strength of paper. The other strategy is surface modification of filler particles to increase the weak bonding strength like the bonding strength between fiber and filler and the bonding strength between fillers. There are numerous surface modification techniques to improve strength of filled paper such as modification with starch or starch derivatives (Yan et al. 2005, Zhao et al. 2005, Yoon and Deng 2006), cellulose derivatives (Shen et al. 2010), and inorganic compounds (Lourenco et al. 2014). It is considered that these surface modification techniques promote the fiber-to-filler bonding, thus contribute to improve strength of filled paper at a given filler content.

Polyelectrolytes multilayering (PEM) technique, first introduced by Decher and Hong (1991), is one of the surface modification techniques. Polyelectrolytes multilayer can be formed onto various types of substrate by alternative adsorption of oppositely charged polyelectrolytes. It was considered that this consecutive polyelectrolytes treatment was very similar to the treatment of various additives in papermaking industry in terms of sequential addition of polyelectrolytes. In addition,
papermakers have long experience about strategy to apply various types of polyelectrolytes such as dry and wet strength agent, retention aids, and fixing agent. Therefore, PEM technique was regarded as an adoptable technique to papermaking industry.

This PEM technique has been already applied for surface modification of cellulose fibers to improve paper strength (Wågberg et al. 2002, Chin et al. 2012). It has been demonstrated that numbers of deposited layers, amount of polyelectrolytes in the multilayer, and nature of the outermost layer are key factors affecting strength of paper (Eriksson et al. 2005a, Eriksson et al. 2006, Lingström and Wågberg 2008, Ryu et al. 2011, Chin et al. 2012). It has been also suggested that PEM technique can provide versatile functionality to paper such as electronic conductivity (Agarwal et al. 2006, Wistrand et al. 2007, Peng et al. 2008, Lee et al. 2012) and antibacterial activity (Imani et al. 2011, Illergård et al. 2012, Illergård et al. 2015).

Most of previous researches about application of PEM technique to the papermaking industry are focused on surface modification of pulp fibers. There are several researches about surface modification of filler particles using PEM technique focused on charge inversion of GCC (Lee et al. 2011), strength improvement of filled paper (Ahn et al. 2012a, Ahn et al. 2012b, Ahn 2014), and retention strategies of PEM treated GCC (Lee et al. 2013a, Lee et al. 2013b). These previous researches provide potential for high filler loading through surface modification of filler particles by using PEM technique. However, there is not sufficient
demonstration why polyelectrolytes multilayering can improve strength of filled paper and how polyelectrolytes multilayering in practice is applied to papermaking industry for high filler loading. It was necessary to examine factors affecting properties of PEM fillers and strength of paper filled with PEM treated fillers. In addition, PEM technique can provide various functionality such as antibacterial activity and electronic conductivity. In order to apply PEM technique practicably for high filler loading and wide application, therefore, more studies about those perspectives should be carried out.
2. Objectives

The objectives of this study is to understand mechanism for strengthening effect of polyelectrolytes multilayer on filled paper, and to propose application of polyelectrolytes multilayering (PEM) technique for field application and antibacterial activity as functionality. It was necessary to identify why PEM was treated on filler particles for high filler loading rather than PEM treatment on pulp fibers. It was also important to investigate mechanism for strengthening effect of polyelectrolytes multilayer on filled paper and factors affecting improvement on strength of paper with PEM treated fillers in aspect of characteristics of multilayer constructed onto filler particles, and morphological effect of applied fillers. Appropriate PEM process for field application would be also suggested to apply PEM technique successfully to papermaking industry. In addition, it would be investigated for potential that can give antibacterial activity as well as strength improvement using PEM technique.

- In the first part, more effective approach between PEM treatment on pulp fibers and PEM treatment on filler particles and influences of PEM on bonding abilities were investigated for enhancement of strength of highly filled paper
- In the second part, factors affecting strength improvement of filled paper were investigated in terms of characteristics of multilayer and morphological properties of fillers. The characteristics of multilayer were controlled by salt concentration during polyelectrolytes multilayering and different types of polyelectrolytes. Three types of different fillers were selected for the different morphology.

- In the last part, two different application of PEM were discussed, washless polyelectrolytes multilayering for mill application and fabrication of antibacterial paper using PEM treated fillers.
Chapter 2.

Literature review
1. Influences of fillers on strength of paper

According to Page’s theory (1969), tensile strength of paper depends on the strength of fibers and the strength of the bonds between fibers. Hubbe and Gill (2016) insisted that fillers affect the strength of the bonds between fibers related to the relative bonded area (RBA) and the adhesive strength per unit of bonded area. Hubbe and Gill (2016) proposed that there are two mechanisms by which fillers interfere with the strength of paper. One is “bracing” mechanism that means a filler particle sandwiched between fibers, which tend to make space between the fibers (Fig. 2-1 (a)). The other is “covering” mechanism that means interference of the fillers in direct contact between adjacent fibers (Fig. 2-1 (b)). These two mechanisms are that fillers give less RBA between fibers and weak bonding strength between fiber and filler.

Böhmer (1981) proposed that addition of 10 percent fillers results in 20 – 25% reduction of tensile or burst strength of paper. However, this degree of strength loss is affected by properties of fillers such as particle size, specific surface area, and morphology of fillers (Li et al. 2002, Hubbe and Gill 2016). In general, large particle size is less harmful for strength of paper than small particle (Adams 1993, Han and Seo 1997, Li et al. 2002). Lindström and Florén (1987) reported that the size effect on paper strength is related to specific surface area of fillers. Li et al. (2002) also suggested that specific debonding factor obtained from delamination test of model laminates is linearly increased with an
increase in specific surface area of precipitated calcium carbonate (PCC). Open structure types of fillers like scalenohedral PCC are more harmful for strength of paper than solid types of fillers such as ground calcium carbonate (GCC) and clay (Fairchild 1992, Li et al. 2002). This is because the scalenohedral PCC provide more open spaces between fibers.

Fig. 2-1. (a) Bracing mechanism in which filler debonds the paper, and (b) covering mechanism in which the proportion of direct contact between fibers is reduced (Hubbe and Gill 2016).
2. High filler loading techniques

High filler loading involve an increase of filler content without decrease in paper strength and filler retention efficiency. High filler loading techniques can be divided into two groups; one is related to less interference in bonded area between fibers and the other is related to improvement on the relatively weak bonding strength between fiber and filler.

Pre-flocculation of filler particles and lumen loading of filler particles involve in the less interference in fiber-to-fiber contact. Pre-flocculation is such technique that flocculates filler particles by using flocculant before addition of the filler particles into fiber stock (Mabee and Harvey 2000). Size and strength of filler flocs are dominant factors to secure inter-fiber bonding (Im et al. 2013). These size and strength of flocs can be controlled by types of flocculant (Antunes et al. 2010, Rasteiro et al. 2010), molecular weight and charge density (Sang and Englezos 2012), addition level (Lee and Lee 2006, Gaudreauit et al. 2009), and shear condition (Seo et al. 2012). Lumen loading of fillers is firstly introduced by Green et al. (1982). Filler particles can be loaded inside lumen of fibers with sequential procedures of agitation of pulp fibers in concentrated filler suspension and washing filler particles attached to exterior surfaces of fibers (Middleton et al. 2003). Loading level of fillers inside lumen can be controlled by pulp consistency, impregnation time, and polyelectrolytes additives (Middleton and Scallan 1989, Petlicki and...
Vandeven 1994, Middleton et al. 2003, Othman et al. 2010). These two techniques can provide strength improvement of filled paper. However, Lumen loading is possible to apply to only softwood fibers. Preflocculation has been still being studied for application to papermaking industry.

Surface modification of filler particles is regarded as the technique that can improve the relatively weak bonding strength such as the bonding strength between fiber and filler and the bonding strength between fillers. Zhao et al. (2005) reported that starch gel can be coated on the surface of PCC through a procedure of mixing PCC and starch powder, cooking the mixture, grinding, and breaking up. This starch-coated PCC improves strength of filled paper at given PCC content. Yoon and Deng (2006) suggested that starch-fatty complex modified fillers also provide strength improvement of filled paper. They confirmed that the coated starch-fatty complex provide bonding between fibers and the treated fillers through scanning electron microscope images. Formation of polyelectrolytes multilayer (PEM) onto filler particles is also regarded as the surface modification technique for high filler loading. Ahn (2014) reported that PEM contribute to improve strength of filled paper. This strengthening effect depends on types of polyelectrolytes and layer numbers of multilayering. In addition, positively charged ground calcium carbonate treated with PEM shows better retention efficiency at same retention system than untreated GCC (Lee et al. 2013a, Lee et al. 2013b).
3. Polyelectrolytes multilayering (PEM)

3.1 General introduction to PEM

Polyelectrolytes multilayering (PEM) technique is that oppositely charged polyelectrolytes are alternatively adsorbed onto the surface of a substrate, resulting in formation of multilayer described in Fig. 2-2 (Decher and Hong 1991, Decher et al. 1992, Decher 1997). This PEM is available to versatile substrate such as plane substrate and sphere types of substrate (Radeva 1999, Radeva et al. 2001, Schönhoff 2003a). In addition, PEM can provide various functionality depending on types of materials (Schönhoff 2003a, Lichter and Rubner 2009, Westman et al. 2009b, Wong et al. 2009). Decher (1997) stated that the use of polyelectrolytes rather than small molecules is better because polyelectrolytes can simply bridge over underlying defects. The conformation of the polyelectrolytes adsorbed onto substrate is mainly dependent on characteristics of polyelectrolytes and adsorption condition rather than properties of substrate (Decher 1997). Structural characteristics of multilayer is fuzzy layers rather than layer-by-layer formation as described in Fig. 2-3. Polyelectrolytes segment inside multilayer is overlapped between several layers. This is because polyelectrolytes are interpenetrated into multilayer (Liu et al. 2008, Soltwedel et al. 2010).
Fig. 2-2. (A) Schematic of the film deposition process using slides and beakers. (B) Simplified molecular picture of the first two adsorption steps. (C) Chemical structures of two typical polyions, the sodium salt of poly(styrene sulfonate) and poly(allylamine hydrochloride) (Decher 1997).

Fig. 2-3. Model of the segment distribution in multilayers along the surface normal. Dashed and full lines corresponding to polyanions and polycations, respectively (Schönhoff 2003b).
Characteristics of multilayer depend on various factors such as types of polyelectrolytes, molecular weight and charge density of polyelectrolytes, ionic strength and pH of polyelectrolytes solution, and temperature during construction of multilayer (Schönhoff 2003b). The surface charges of the multilayer is affected by charges of polyelectrolyte in the outermost layer (Decher 1997, Schlenoff et al. 1998, Guzmán et al. 2009). Adsorbed amount of polyelectrolytes, and thickness and viscoelastic properties of multilayer mostly depend on adsorption condition such as salt concentration and pH rather than molecular weight and charge density of polyelectrolytes (Dubas and Schlenoff 1999, Schlenoff and Dubas 2001, Voigt et al. 2003). Salt concentration during construction of the multilayer is one of the most dominant factors for the characteristics of the multilayer. This is because screening effect of counter ions on charges of polyelectrolytes and their overcompensation mechanism (Schlenoff et al. 1998, Schlenoff and Dubas 2001). When salt concentration is relatively low, polyelectrolytes charges are compensated by charges of the opposite polyelectrolytes implying a stoichiometric 1:1 ratio (cationic polymer : anionic polymer) in the multilayer as described in Fig. 2-4 (a) (McAloney et al. 2001). This is so-called “intrinsic compensation”. In the alternate mechanism as salt concentration is increased, “extrinsic mechanism” is that much of charges are compensated by counter ions during builing of the multilayer (Fig. 2-4 (c)). Schlenoff and Dubas (2001) demonstrated that growth of multilayer is strongly affected by these two mechanism depending on salt concentration. McAloney et al. (2001) and Guzmán et al. (2009) also
demonstrated that linear or exponential growth of multilayer is related to salt concentration, and thicker and bulkier multilayer can be formed as salt concentration is increased. For weak polyelectrolytes affected by pH, control of pH provides similar influence on characteristics of multilayer like control of salt concentration (Elzieciak et al. 2009, Bieker and Schonhoff 2010, Lundin et al. 2011). Electrostatic properties of weak polyelectrolytes are dependent on pH condition, and thickness and swelling properties of multilayer are controlled by degree of ionization depending on the pH (Shiratori and Rubner 2000, Choi and Rubner 2005, Itano et al. 2005).

Fig 2-4. Formation of multilayer in salt solution
(Dubas and Schlenoff 1999).
3.2 PEM in the papermaking

Application of PEM technique in the papermaking process is mostly for surface modification of pulp fibers. Wågberg et al. (2002) firstly introduced that polyelectrolytes multilayer can be successfully formed on pulp fibers, and this PEM treatment on pulp fibers provide strength improvement on paper. Wågberg et al. (2002) stated that polyelectrolytes multilayer onto fibers affects at least three aspects of joint strength between fibers such as molecular contact area, molecular interaction, and interpenetration of molecules. Following researches demonstrated dominant factors affecting strength of paper made of PEM treated fibers. Eriksson et al. (2005a) reported that tensile strength of paper and joint strength between fibers are approximately proportional to adsorption amount of cationic polyelectrolytes. Eriksson et al. (2005b) suggested that cationic starches show much better strengthening effect at given layer number than other cationic polyelectrolytes such as poly (allylamine hydrochloride) (PAH) and poly-diallyldimethylammonium chloride (PDADMAC). This is agreed with other researches (Johansson et al. 2009, Chin et al. 2012). Chin et al. (2012) stated that much bulkier and thicker multilayer containing cationic starches provides better conformability between fibers, and this is the reason for outstanding improvement of paper strength. Lingström and Wågberg (2008) suggested that multilayer with high molecular weight of PDADMAC leads to more interdiffusion of polymer chains across the treated fibers,
thus higher strength of paper can be achieved.

PEM can provide not only strengthening effect but also functionality. Electronic conductivity can be given by PEM treatment on fibers using of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) (Agarwal et al. 2006, Wistrand et al. 2007, Lee et al. 2012). Carbon nanotube (CNT) and indium tin oxide (ITO) also provide much higher conductivity than only the use of PEDOT-PSS (Peng et al. 2008, Agarwal et al. 2009). Antibacterial activity also can be given by PEM treatment on pulp fibers. It is known that Polyvinylamine (PVAm) is one of the polyelectrolytes exhibiting antibacterial activity (Westman et al. 2009a, Westman et al. 2009b, Illergård et al. 2010). It is also demonstrated that surface modified cellulose fibers with not only PVAm (Illergård et al. 2012, Illergård et al. 2015) but also other cationic polyelectrolyte such as chitosan (Imani et al. 2011) show antibacterial activity. Formation of multilayer with these polyelectrolytes on pulp fibers provide antibacterial activity (Illergård et al. 2012, Illergård et al. 2015)
3.3 PEM for high filler loading

To achieve high filler loading, polyelectrolytes multilayering can be mainly applied to surface modification of filler particles. Lee et al. (2011) reported that polyelectrolytes multilayer is successfully formed onto surface of GCC particles. Ahn (2014) suggested that cationic starch is the best polyelectrolytes for strength improvement of filled paper in the case of surface modification of GCC. The author also suggested that anionic polyelectrolytes with relatively low charge density is better pair for cationic starch to form stable multilayer than anionic polyelectrolytes with relatively high charge density. Positively charged GCC through PEM treatment shows spontaneous deposition onto pulp fibers, and the deposition behavior of PEM treated GCC depends on types of polyelectrolytes in the outermost layer (Lee et al. 2013a). Retention efficiency of this positively modified GCC is not as much as untreated GCC in the case of single retention system, while the positively modified GCC shows better retention efficiency in the case of microparticle retention system (Lee et al. 2013b).
4. Mechanism for strengthening effect of polyelectrolytes

Polyelectrolytes such as cationic starch, polyacrylamide, polyamideamine epichlorohydrine resins (PAE) are typically used as strength agents in the papermaking. Lindström et al. (2005) stated that the strength agents may work by increasing the specific bond strength, by consolidating the sheet, i.e. affecting the Campbell forces, and by decreasing the local stress concentration in the sheet. The authors suggested that those strength agents contribute to paper strength with a combination of different mechanisms not a single mechanism. It is known that the specific bond strength between fibers is determined by several different factors such as mechanical interlocking, interdiffusion mechanism, hydrogen bonding, and van der Waals force (Wågberg 2009, Hirn and Schennach 2015). Lindström et al. (2005) stated that strength agents may contribute to create additional bonds and more interdiffusion of polymer chains between adjacent fibers. Moeller (1966) demonstrated that cationic starch produces additional bonds between fibers. Gaspar (1982), and Howard and Jowsey (1989) also arrived at the same conclusion. Stratton (1989) reported that both of electrostatic charge attraction force between cationic sites and anionic sites and creation of covalent bonds improve joint strength between fibers. PDADMAC known to be as a fixing agent not a strength agent enable to improve strength of paper depending on adsorption amount and molecular weight of PDADMAC (Lingström and Wågberg 2008). Authors reported that
chains of PDADMAC with large molecular weight contribute to more interdiffusion across fibers.

Starch also contributes to consolidation of paper (Lindström et al. 2005). Lindström et al. (2005) suggested that beating fibers and addition of starch may act in a similar way. It has been also reported that starches release stress concentration of filled handsheets during sheet consolidation through a stick-slip mechanism (Lindström 1985). This stress concentration factor obtained from Zhorkov type life-length experiment is reduced with addition level of cationic starch in the case of filled paper.
Chapter 3.

Investigation on strengthening effect of polyelectrolytes multilayer on filled paper
1. Introduction

Polyelectrolytes multilayering (PEM) treatment on fibers or fillers is suggested as one of the techniques that can improve paper strength (Wågberg et al. 2002, Ahn 2014). It has been already proved that PEM treatment on fibers improves joint strength between fibers (Eriksson et al. 2006). Furthermore, many literatures have included studies on mechanism for PEM effect on the paper strength depending on polyelectrolytes types (Chin et al. 2012), adsorbed amount of polyelectrolytes (Eriksson et al. 2005a), and multilayer characteristics (Lingström et al. 2006, Lingström et al. 2007, Ryu et al. 2011). However, these previous researches about PEM treatment on pulp fibers were focused on properties of paper without fillers rather than those of filled paper.

There are a few studies on the effect of PEM treatment for filler modification. Previous researches about filler modification through PEM treatment were mainly focused on properties of PEM treated fillers and retention of fillers onto pulp fibers (Lee et al. 2011, Lee et al. 2013a, Lee et al. 2013b). Ahn (2014) suggested that surface modification of ground calcium carbonate particles provide strength improvement of filled paper. This previous study, however, does not sufficiently explain why PEM treatment is performed to improve strength of filled paper. PEM treatment can be performed on fibers as well as fillers to improve strength of filled paper. Because high filler loading is focused on an
increase of filler content, it is important to improve strength of highly filled paper. Therefore, more effective approach to PEM treatment for strength improvement of highly filled paper was examined depending on filler content and substrate types, i.e. fibers or fillers, for PEM treatment. In addition, PEM treatment effect on the strengthening of the highly filled paper was investigated. PEM treatment was performed using cationic starch and polyacrylamide system, which was one of the most effective systems on paper strength (Chin 2010, Ahn 2014).
2. Materials & methods

2.1 Materials

Ground calcium carbonate (GCC, Hydrocarb 75K, Omya) was used as inorganic filler particles. Mixed hardwood bleached pulp fibers (Hw-BKP, Moorim P&P) were used after beating to 400±10 mL Canadian Standard Freeness (CSF, TAPPI methods 227 om-99) using a laboratory beater. Cationic starch (C-starch, DS 0.06, charge density +0.6±0.1 meq/g, Samyang), and anionic polyacrylamide (A-PAM, Mw ~70,000 g/mol, charge density -1.7±0.1 meq/g, OCI-SNF) were used for PEM treatment. Charge density of polyelectrolytes was measured using particle charge detector (PCD, PCD-03pH, Mütek, Germany). Chemical structure of the polyelectrolytes for PEM treatment was shown in the Fig. 3-1. Cationic polyacrylamide (C-PAM, Percol 63, Mw ~7,500,000 g/mol, BASF) was used as retention aids. Sodium chloride (NaCl) was used to control salt concentration. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust pH.
Fig. 3-1. Chemical structure of polyelectrolytes used for PEM treatment, (a) cationic starch and (b) anionic polyacrylamide (A-PAM).
2.2 Formation of polyelectrolytes multilayer on filler particles

Polyelectrolytes multilayer (PEM) process is represented in Fig. 3-2. Formation of a polyelectrolyte layer consisted of adsorption step and two times of the washing step. In the adsorption step, polyelectrolyte was added to the filler suspension (30 wt%) under stirring at 3000 rpm and mixed for 5 min. The washing step consisted of removal of excess polyelectrolytes which were not adsorbed on filler particles and re-dispersing process. The unadsorbed polyelectrolytes were removed by sequential process of centrifugation for 20 min at 3000 G using centrifuge (Union 5kr, Hanil, Korea), and decantation of supernatant. After dilution of the sediment fillers to 30 wt%, the suspension was re-dispersed by using an ultrasonicator (VCX 750, frequency: 20 kHz; amplitude: 124 μm; generating power: 750 W; probe diameter: 13 mm, Sonics, USA). This washing step was conducted two times. PEM can be formed with alternate adsorption of a cationic polyelectrolyte layer and an anionic polyelectrolyte layer.

Polyelectrolytes system for PEM treatment was C-starch/A-PAM. C-starch and A-PAM were diluted to 20 g/L and 10 g/L using 0.01 M NaCl solution, respectively. The C-starch solution was used after cooking at 95°C for 30 min. pH of the two solutions was adjusted to pH 9.0±0.5. Addition level of polyelectrolytes based on oven dried weight of GCC was 3.5wt% for C-starch and 1wt% for A-PAM in the C-starch/A-PAM system. Salt concentration during PEM treatment was 0.01 M NaCl, and
the pH was kept at pH 9.0±0.5. Three layers of C-starch/A-PAM/C-starch were formed on GCC particles.

Fig. 3-2. Process of polyelectrolytes multilayer treatment on filler particles.
2.3 Formation of polyelectrolytes multilayer on pulp fiber

The beaten pulp fibers were washed using vibration screen equipped with 100-mesh wire. Only long fibers retained on the 100-mesh wire were used. Consistency of the long fibers slurry was adjusted to 1 wt% using deionized (DI) water. Conductivity of the slurry was adjusted to 1200 μS/cm using NaCl solution. This conductivity was corresponds to 0.01 M NaCl condition.

Formation of a polyelectrolyte layer was performed with adsorption step and two times washing steps. Adsorption step consisted of addition of polyelectrolytes and then reaction for 20 min. After the adsorption step, washing steps to remove excess polyelectrolytes were followed. This washing step was conducted for 5 min twice. First polyelectrolyte layer was formed with addition of C-starch because the charge of the fibers is originally negative. With alternative treatment of C-starch/A-PAM/C-starch, finally three layers of C-starch/A-PAM/C-starch were formed on the long fibers.
2.4 Properties of PEM GCC and PEM fiber

2.4.1 Zeta potential and particle size

Zeta potential of PEM GCC was measured using Zetasizer Nano ZS (Malvern, UK) after dilution of the PEM GCC to 0.1 g/L at 0.01 M NaCl and pH 9. Zeta potential of PEM fiber was measured using system zeta potential (SZP, Mütek Co., Switzerland). The measurement was conducted at 1 wt% stock and 1200 μS/cm of conductivity which was similar with 0.01 M NaCl solution.

Particle size was measured by using Mastersizer 2000 (Malvern, UK). In the measurement, PEM GCC was diluted to 0.01 g/L using 0.01M NaCl, pH was adjusted to pH 9 during measurement. The average particle size was represented as volumetric average particle size under 1500 rpm stirring.

2.4.2 Adsorbed amount of polyelectrolytes

Nitrogen content of C-starch and A-PAM was determined using Kjeldahl Protein/Nitrogen Analyzer (Kjeltec Auto 1035/1038 System, Tecator AB, Sweden). The nitrogen content in both of PEM treated GCC and fibers was analyzed. Total adsorbed amounts of C-starch and A-
PAM in the PEM GCC at each layers were evaluated by change in weight after combustion in furnace at 525 °C for 5 hr. In this combustion system, residues of C-starch and A-PAM was 2.0±0.2%, and residues of untreated GCC was 98.8±0.3%. Individual adsorbed amount of C-starch and A-PAM can be calculated with adsorbed amounts using combustion system and the nitrogen content at each layers.

2.5 Preparation and properties of filled handsheets

2.5.1 Handsheets preparation

To determine more effective approach of PEM treatment for filled paper with high strength, filled hadnsheets were prepared. Process of preparation for the filled handsheets was represented in Fig. 3-3. Control handsheets were prepared with untreated long fibers & untreated GCC. There were two types of control; “Control” condition was handsheet preparation without adding a dry strength agent, and “Control w/ C-starch” was handsheets preparation with adding C-starch as a dry strength agent. “PEM fibers” condition handsheets were prepared with C-starch/A-PAM 3 layers fibers and untreated GCC, and PEM GCC conditions handsheets were prepared with C-starch/A-PAM 3 layers long fibers and untreated GCC. “PEM GCC” condition handsheets were prepared with untreated long fibers and C-starch /A-PAM 3 layers GCC.
For “Control” handsheets, a cationic retention aid (C-PAM) was added to pulp stock before the addition of untreated GCC to deposit negatively charged GCC onto negatively charged fibers without flocculation of the GCC particles by the C-PAM. In the case of control w/C-starch, c-starch was used instead of C-PAM. In the case of PEM fibers and PEM GCC handsheets, filler particles were firstly added to pulp stock, and then C-PAM was added. Addition level of the C-PAM and C-starch was 0.03% and 1.5% based on dried weight of fibers, respectively. Target grammage was controlled to 80±4 g/m². Filler content of the filled handsheets was controlled to 10-30%.

Filled handsheets were prepared using the square handsheets former. After making wet sheets, 5 times couching, pressing at 3.5 bar using a laboratory press machine, and drying at 120°C using a cylinder dryer were conducted. The dried handsheets was pre-conditioned at 23±1°C and 50±2%RH.
Fig. 3-3. Process of preparation for filled handsheets.
2.5.2 Properties of filled handsheets

2.5.2.1 Structural properties

Grammage and apparent thickness of the filled handsheets were measured in accordance with TAPPI test methods T410 om-98 and T410 om-97, respectively. The apparent thickness was measured using micrometer (L&W Co., Sweden). Apparent density of the filled handsheets was calculated using the grammage and thickness values.

Fillers content in the filled handsheets was evaluated by measurement of ash content using furnace in accordance with TAPPI test method T211 om-93. Filler distribution was observed using Field Emission Scanning Electron Microscope (FE-SEM, SUPRA 55VP, Sweden).

2.5.2.2 Mechanical properties

Tensile strength, strain, tensile energy absorption (TEA), and tensile stiffness of the filled handsheets were measured using tensile tester (L&W Co., Sweden) in accordance with TAPPI test method T494 om-96. Tensile index and TEA index were calculated with the measured grammage. Internal bond strength of the filled handsheets was measured in accordance with TAPPI test method T569 pm-00 (Scott type internal bond strength). Tear strength was measured by tear strength tester (L&W Co., Sweden) according to TAPPI test method T414 om-98. Bending
stiffness was evaluated by measurement of bending resistance at bending angle of 15° (TAPPI test method T556 pm-95).

2.5.2.3 Optical properties

Optical properties were evaluated using Elrepho (L&W Co., Sweden) under C light source. Opacity (ISO 2471), brightness (ISO 2470), and light scattering and absorption coefficient (ISO 9416) were measured.

2.6 Bonding ability of PEM fillers

2.6.1 Measurement of bonding force between fibers and fillers

Bonding force between fibers and fillers was evaluated by measuring delamination force of laminate for fibers-fillers bonding. This laminate consisted of model substrates representing fibers in top and bottom layer and a monolayer of fillers in middle layer (Fig. 3-4). This model laminate was designed by modifying one from the previous report (Li et al. 2002).
2.6.1.1 Preparation of model fiber sheet

Cellulose nanofibrils (CNF) was prepared by grinding the beaten Hw-BKP (400±10 mL CSF) using a grinder (Super Masscolooider, Masuko Co., Japan). Softwood bleached kraft pulp (Sw-BKP) was beaten to 400±10 mL CSF. The CNF slurry and the Sw-BKP slurry were mixed with mixing weight ratio of 60:40. The mixed slurry was diluted to 0.5wt% and stirred well. Two wet circle sheets (60 g/m², 75 mm diameter) were prepared each onto mixed cellulose ester (MCE) membrane with an average pore size of 0.2 μm (HYUNDAI Micro CO.) using a vacuum filtration apparatus. The wet sheets were pressed at 3.5 bar for 1 min using a laboratory press machine.

2.6.1.2 Preparation of a filler layer between the model fibers sheets

For the formation of a filler layer, 0.4-1.0 mg of fillers were suspended in 20 mL of DI water. This suspension was filtered onto the MCE
membrane using the vacuum filtration apparatus. After filtration, the membrane containing the filler layer was placed with filler side down on top side of the wet sheet which was sprayed twice with DI water using a sprayer. The sandwich was pressed at 3.5 bar for 1 min using the laboratory press machine. After pressing, the filler side membrane was carefully peeled off. Another wet sheet with being sprayed twice with DI water was place down on filler side of the wet sheet. This two-ply with a filler layer was pressed at 3.5 bar for 1 min, and dried at 105°C using hot press machine under 2 bar. The final model sheet was shown in Fig. 3-5. Filler loading amount at the interplay was evaluated by measurement of potentiometric titration with EDTA after dissolution of the model sheet into 0.01N HCl.

Fig. 3-5. The final model sheets for measurement.
2.6.1.3 Delamination test

The model sheets were cut into strips with 20 mm width, and then double side tape was applied to one side of the sample strip (Bottom side). The bottom side was taped onto steel plate, and end of the strip was peeled off manually. This sample for the measurement of the delamination force was shown in Fig. 3-6 (a).

Delamination force was measured using universal testing machine (5943, Instron, USA) equipped with 90° peel fixture (2820-036, Instron, USA). The steel plate was fixed onto moving zig. Masking tape was applied to the end of peeled strip, and then this strip was placed in the pulling zig (Fig 3-6 (b)). Experiments were conducted at a peeling rate of 40 mm/min. Average peeling forces were obtained from the steady-state range of peeling load versus distance with results of 8 samples.

Fig. 3-6. (a) Sample preparation of the measurement, and (b) sample placed in 90° peel fixture.
2.6.2 Measurement of bonding strength between fillers

To evaluate bonding strength between fillers, dense film composed of fillers was prepared, and breaking strength of the dense film was measured. 33 g of filler suspension (20% of concentration) was vacuum filtered onto the MCE membrane (0.2 μm pore size) using the vacuum filtration apparatus. After the filtration, the wet fillers film was cut into a square shape with 14 mm width and more than 50 mm length, and then dried at 75°C in oven. The dried dense film composed of fillers was shown in Fig 3-7. The grammage and density of the film were 1500±100 g/m² and 1.7±0.1 g/cm³, respectively.

Breaking strength of the dense film was evaluated by measurement of flexure strength using three point bending setup in UTM. Load at break was converted into flexure strength using Eq. [3-1].

\[
\text{Flexure strength (}\sigma\text{)} = \frac{3FL}{2bd^2} \quad [3-1]
\]

Where, F is axial load at fracture point, L is length of span, b is width of specimen, and d is thickness of specimen. The length of specimen was fixed at 30 mm.

Fig. 3-7. Dried film composed of fillers.
3. Results and discussion

3.1 Properties of PEM fibers and PEM GCC

C-starch/A-PAM 3 layers multilayer was formed on each pulp fibers and GCC. The zeta potential of the PEM treated fibers and GCC was 8.9 mV and 3.3 mV, respectively. Both of the PEM treated fibers and GCC showed positive charges because cationic starch that shows cationic charges was in the outermost layer. Average particle size of the PEM GCC was 2.1 μm, which was the same value with untreated GCC (2.0 μm). This particle size result and size distribution (Fig. 3-8) indicated that PEM was mostly formed on each of particles without flocculation during PEM treatment.

Table 3-1 represented nitrogen content of the C-starch/A-PAM 3 layers fibers and GCC. Total nitrogen content of the C-starch/A-PAM 3 layers GCC was 1.4 times higher than that of the C-starch/A-PAM 3 layers fibers. This might be due to higher specific surface area of GCC. This indicated that cationic starch and A-PAM were more adsorbed onto GCC than fibers.
Fig. 3-8. Size distribution of untreated GCC and PEM GCC (C-starch/A-PAM 3 layers).

Table 3-1. Nitrogen content in C-starch/A-PAM 3 layers fibers and GCC excluding nitrogen content of raw materials.

<table>
<thead>
<tr>
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<th>C-starch/A-PAM 3 layers fillers</th>
<th>C-starch/A-PAM 3 layers fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen content, mg/g</td>
<td>0.61±0.06</td>
<td>0.43±0.02</td>
</tr>
</tbody>
</table>
3.2 Effect of PEM treatment on properties of filled handsheets

3.2.1 Influence of PEM treated fibers on paper properties

Properties of handsheets without fillers, i.e. made of only fibers was shown in Table 3-2. “Untreated fibers” and “PEM fibers” represented handsheets consisting of untreated fibers and the PEM treated fibers (C-starch/A-PAM 3 layers), respectively. PEM treatment on fibers contributed to increase handsheets density, tensile index and internal bond strength. This improvement of strength resulting from PEM treatment was similar result with previous studies with PEM treatment using cationic starch on pulp fibers (Eriksson et al. 2005b, Pettersson et al. 2006, Chin et al. 2012).

Table 3-2. Properties of handsheets without fillers

<table>
<thead>
<tr>
<th></th>
<th>Untreated fibers</th>
<th>PEM fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent density, g/m³</td>
<td>0.531±0.003</td>
<td>0.554±0.004</td>
</tr>
<tr>
<td>Tensile index, N·m/g</td>
<td>32.7±1.2</td>
<td>45.6±1.4</td>
</tr>
<tr>
<td>Internal bond strength, J/m²</td>
<td>120.4±2.1</td>
<td>284.3±7.8</td>
</tr>
</tbody>
</table>
Strength improvement of paper due to PEM treatment using cationic starch on pulp fibers was attributed to role of strength agent and effect of PEM. Cationic starch is one of the most widely used dry strength agents. Role of cationic starch on the improvement of paper strength is well described in many researches (Lindström et al. 2005, Hubbe 2006, Wågberg 2009). The strength improvement by cationic starch originates from three mechanisms; sheet consolidation effect, increase in specific bond strength, and decreasing stress concentrations in paper sheets (Lindström et al. 2005). The results with an increase in both of the density and the mechanical properties in Table 3-2 were interpreted in the mechanism of the sheet consolidation effect and the increase in specific bond strength.

Furthermore, it has been suggested that PEM treatment contributes to increase joint strength between fiber surfaces including aspects such as molecular contact area, molecular interactions, and relaxation or interpenetration of molecules on adjacent fiber surfaces (Wågberg et al. 2002). Eriksson et al. (2005a) found that PEM treatment on pulp fibers enables to increase adsorption amounts of polyelectrolytes, and the more adsorbed amount of polyelectrolytes contributes to improve paper strength. It has been also suggested that PEM effect of improving paper strength is due to increase in the joint strength (Eriksson et al. 2006) and better conformability on fiber surfaces with viscoelastic and thick layer characteristics (Notley et al. 2005, Chin et al. 2012). As a results, it can be known that paper strength was improved by PEM effect as well as
strengthening effect of the strength agent.

3.2.2 Physical properties of filled paper

Filled handsheets were prepared to determine more effective approach of PEM treatment for the strength of filled paper. Control condition referred to the filled handsheets prepared with untreated fibers and untreated GCC without a dry strength agent, and control w/ C-starch condition was the filled handsheets prepared with untreated fibers and untreated GCC with a dry strength agent. PEM fibers condition referred to the filled handsheets prepared with PEM (C-starch/A-PAM 3 layers) treated fibers and untreated GCC. PEM GCC condition referred to filled handsheets prepared with untreated fibers and PEM (C-Starch/A-PAM 3 layers) treated GCC.

Apparent density of the filled handsheets was represented in Fig. 3-9. The apparent density of the filled handsheets was increased along with ash content. However, two types of Control, PEM fibers, and PEM GCC condition handsheets showed different tendency of apparent density. Apparent density of the PEM GCC condition handsheets showed relatively steep increase tendency compared to other condition. PEM fibers and PEM GCC condition showed higher density at same ash content compared to Control, and density of PEM GCC condition was higher than that of PEM fibers condition at more than 22% ash content.
Fig. 3-9. Apparent density of the filled handsheets as a function of ash content.
Fig. 3-10. Surface images of the filled handsheets with range of 27.9-29.4% fillers content; (a) Control condition, (b) PEM fibers condition, and (c) PEM GCC condition.
3.2.3 Improvement on mechanical properties of filled paper

Fig. 3-11 showed tensile index of the filled handsheets. The tensile index of the filled handsheets was decreased with an increase in the ash content. The handsheets prepared at PEM fibers condition and PEM GCC condition showed higher strength than handsheets prepared at control condition as well as control with a dry strength agent at the same ash content. This improvement on the strength was due to effect of PEM on the strength.

Fig. 3-11. Tensile index of filled handsheets as a function of ash content.
The effect of PEM treatment on the strength was different depending on the ash content and the substrate type in PEM treatment. The PEM fibers condition which were filled handsheets made of PEM treated fibers and untreated GCC showed higher strength than PEM GCC condition at relatively low ash content less than around 20%. This improvement on the strength of PEM fibers condition handsheets was mainly due to an increase in joint strength between adjacent PEM-treated fibers. It was already described that PEM on the fibers increased the joint strength between the adjacent fibers in Table 3-2. This PEM effect on the joint strength between the adjacent fibers still worked on contact zone between fibers (Fig. 3-12, black narrows). This is agreed with the previous report which has suggested that enhancement of fiber-fiber joint with polymer treatment gives high strength at the low level of PCC content (Xu et al. 2005). It also seemed that cationic starch in the outermost layer on fibers contributed to create additional bonds at the contact zone between PEM-treated fiber and untreated GCC (Fig. 3-12, gray narrows). However, there was still weak bonding strength at interfaces between fillers (Fig. 3-12, transparent narrow). These area would be weak points that caused rupture of paper. Accordingly, paper strength was weakened by an increase in these area along with an increase in ash content.

The PEM GCC condition handsheets, which were made of untreated fibers and PEM-treated GCC, showed higher strength compared to the PEM fibers condition handsheets as ash content was increased more than
20%. As the PEM treatment was done onto the GCC in PEM GCC condition handsheets, there was no contribution of PEM on the inter-fiber bonding (Fig. 3-13, black arrows). Nevertheless, the PEM treatment on GCC led to high strength at relatively high ash content. This was due to creation of bonding between untreated fibers and PEM treated GCC (Fig. 3-13, gray arrows). Interaction between PEM treated GCC particles would also contribute high strength of the filled handsheets (Fig. 3-13, transparent arrow). In other words, PEM on GCC improved strength of filled paper at the relatively weak bond area such as contact zone between fiber and filler, and contact zone between fillers. This explanation was agreed with the gradual decline of strength in the case of PEM GCC condition compared to the PEM fibers condition (Fig 3-11). As a result, the PEM treatment on filler particles was more efficient for improvement on strength of highly filled paper. The mechanism of improvement on strength of filled paper with PEM fillers was described in next section.
Fig. 3-12. Illustration of bonding between PEM treated fibers and untreated GCC.

Fig. 3-13. Illustration of bonding between untreated fibers and PEM treated GCC.
Fig. 3-14 and 3-15 showed two types of out-of-plane strength properties, internal bond strength and tear index of the filled handsheets, respectively. Trend of the internal bond strength and tear index was similar with tensile index in Fig. 3-11, i.e. PEM treatment on fibers or GCC contributed to enhance internal bond strength and tear index at same ash content compared to untreated condition.

In the case of internal bond strength, PEM fibers condition handsheets showed much higher than PEM GCC condition handsheets at relatively low ash content. This great improvement originated from improvement of joint strength between adjacent PEM treated fibers. Nevertheless, there was not big differences between PEM fibers and PEM GCC conditions at relatively high ash content unlike tensile index in Fig. 3-11. The reason for this was that highly filled handsheets was too weak to measure internal bond strength, which was caused by absence of fines due to washing the pulp fibers with 100 mesh wire before stock preparation. The effect of improvement on internal bond strength at high filler content was represented in chapter 3 with properties of filled hadnsheets containing fines.

Tear strength is mainly affected by friction. It was proposed that thick and rough multilayers cause high friction between cellulose fibers (Chin 2010). Extremely high friction between PEM treated fibers contributed to improve tear index of PEM fibers condition handsheets at relatively low ash content. At this range of ash content, Control w/ C-starch also showed relatively high tear index due to effect of c-starch, i.e. dry
strength agent. This effect became lower along with an increase in ash content due to decrease in contact area between adjacent fibers. Nevertheless, tear index of the PEM fibers condition handsheets was still higher than that of Control and Control w/ C-starch condition, which resulted from enhancement of friction between PEM treated fibers and untreated GCC. In the case of PEM GCC condition handsheets, the tear index was improved compared to Control and Control w/ C-starch condition at relatively high ash content. This improvement also originated from improvement of bonding strength between PEM treated GCC and fibers. In addition, bonding ability between PEM treated GCC particles contributed to more improve the tear index at highly ash content compared to the PEM fibers condition.
Fig. 3-14. Internal bond strength of the filled handsheets as a function of ash content.

Fig. 3-15. Tear index of the filled handsheets as a function of ash content.
Fig. 3-16 and 3-17 showed strain and TEA index, respectively. The strain of PEM fibers and PEM GCC condition handsheets was higher than that of two types of control condition handsheets like strength properties such as tensile index, internal bond strength, and tear index. Trend of strain as a function of ash content was also similar with the strength properties. It is known that cationic starches release stress concentrations during sheet consolidation through a stick-slip mechanism (Lindström et al. 1985). It was considered that the improvement of strain originated from a decrease in stress concentration. TEA index that is the integral of the stress-strain curve (Niskanen 1998) showed similar trend with result of tensile index and strain because of an increase in both of the tensile index and strain in the cases of PEM fibers and PEM GCC condition.

Tensile stiffness index and bending stiffness index were presented in Fig. 3-18 and 3-19, respectively. These in-plane and out of plane elastic properties of PEM fibers and PEM GCC condition were improved compared to Control condition, especially at high ash content. Unlike strength and strain properties, there was no difference of stiffness between PEM fibers and PEM GCC condition at relatively low ash content. The elastic properties of PEM GCC condition handsheets became higher along with ash content than those of PEM fibers condition. Lindström and Florén (1984) reported that cationic starch significantly improve elastic properties of only filled paper while improve tensile index of both unfilled paper and filled paper. It was interpreted that effect
of starch on elastic properties showed greatly in relatively weak bonding such as fiber to filler bonding or filler to filler bonding than relatively strong bonding between fibers. In other words, improvement of bonding strength between GCC particles was related to higher tensile and bending stiffness of PEM GCC condition handsheets than PEM fibers condition handsheets at high ash content.
Fig. 3-16. Strain of the filled handsheets as a function of ash content.

Fig. 3-17. Tensile energy absorption (TEA) index of the filled handsheets as a function of ash content.
Fig. 3-18. Tensile stiffness index of the filled handsheets as a function of ash content.

Fig. 3-19. Bending stiffness index of the filled handsheets as a function of ash content.
3.2.4 Optical properties of filled handsheets

Fig. 3-20 and 3-21 showed opacity and light scattering coefficient of the filled handsheet. Opacity of all conditions increased with an increase in ash content. Control condition showed higher opacity than other conditions. This was related to apparent density (Fig. 3-9) and light scattering coefficient (Fig. 3-21) of the filled handsheets. Because Control condition showed relatively low density and high light scattering coefficient compared to other three conditions, the opacity of Control condition was higher than that of other conditions. PEM fibers and PEM GCC condition showed similar opacity at same ash content. There was also no difference between opacity of these two PEM conditions and opacity of Control w/ C-starch condition. In other words, PEM treatment on fibers and fillers did not affect opacity compared to opacity of filled paper prepared with a dry strength agent. This meant that PEM treatment enabled to improve strength of filled paper without change in opacity.
Fig. 3-20. Opacity of the filled handsheets as a function of ash content.

Fig. 3-21. Light scattering coefficient of the filled handsheets as a function of ash content.
Fig. 3-22 and 3-23 showed brightness and light absorption coefficient of the filled handsheets. Only PEM GCC condition showed relatively low brightness compared to other conditions. This was associated to the higher light absorption coefficient at 457 nm of PEM GCC condition. Unlike Control, Control w/ C-starch, and PEM fibers conditions that untreated GCC was used to prepare, PEM GCC conditions were prepared with PEM treated GCC. It was considered that the formation of multilayer on surface of GCC affected reflectance of the GCC. However, the brightness loss for PEM GCC condition was not a big problem for filler high loading because the brightness can be increased with an increase in the filler content without losing strength of filled paper.
Fig. 3-22. Brightness of the filled handsheets as a function of ash content.

Fig. 3-23. Light absorption coefficient of the filled handsheets as a function of ash content.
3.3 Mechanism for improvement on strength of filled paper by PEM treatment

3.3.1 Determination of bonding strength between fiber and filler

To determine contribution of PEM to bonding strength between fiber and filler, delamination peel force of semi-empirical model introduced by Li et al. (2002) was evaluated. This model consisted of model substrates for fibers at top and bottom layers and fillers at the middle layer. This laminate simulates contact zone between fibers, and contact zone between fiber and filler. From the images of filler-laminated surface of fiber model layer (Fig. 3-24), it seemed that a layer of fillers was monolayer, i.e. there was no filler to filler contact in the laminates. The differences from the previous model was that model substrate for fibers were made of mixture of cellulose nanofibrills (CNF) and fibers. This modified model layers had very smooth surfaces to prevent particles buried in valley that originated from thickness of fibers. Thus, it seemed that all of filler particles can participate in bonding.
Fig. 3-24. Surface images of fillers-laminated fiber model layer. Filler content is (a) 0.04 g/m² and (b) 0.10 g/m².
Fig. 3-25 showed delamination peel force as a function of filler content for the laminate. Applied fillers were two types, one was untreated GCC and the other was C-starch/A-PAM 3 layers GCC. The delamination force without a fillers layer was 320 N/m, which was a much higher value than around 45 N/m in the previous report (Li et al. 2002). This large difference was related to the fibers model containing CNF resulting from larger bonded area due to smooth surface, and higher surface area of nanofibrils.

Delamination force with a fillers layer of the PEM treated GCC was higher at same filler loading compared to untreated GCC condition. The dotted curves were exponentially fit to the data as like Eq. [3-2].

\[
\text{Peel force (N/m)} = \alpha \times e^{-\Gamma \beta} \quad [3-2]
\]

where, \(\alpha\) is a coefficient indicating peel force without fillers, \(\Gamma\) is filler loading (g/m\(^2\)), \(\beta\) is the specific debonding factor (m\(^2\)/g), introduced by Li et al. (2002). The authors suggested that \(\beta\) is a measure of the tendency of filler to weaken paper. These \(\alpha\) and \(\beta\) values were represented in Table 3-3. \(\beta\) was 18.0 m\(^2\)/g and 21.6 m\(^2\)/g for C-starch/A-PAM 3 layers GCC and untreated GCC, respectively. The \(\beta\) is correlated with specific surface area of fillers if filler particles have similar morphology (Li et al. 2002). Thus, fillers with the higher \(\beta\) values more reduce strength of filled paper (Li et al. 2002). However, the C-starch/A-PAM 3 layers GCC had lower \(\beta\) than untreated GCC in spite of same average particle size and distribution. This indicated that multilayer gave bonding ability between fiber and filler. Cationic starch in the outermost layer produced
more hydrogen bonds and gave more interdiffusion at the interfaces between fiber and filler.

At the low filler loading less than 0.05 g/m², there was no difference of the average peel force between C-starch/A-PAM 3 layers GCC and untreated GCC. On the other hands, the average peel forces calculated from fit data C-starch/A-PAM 3 layers GCC was 45.6 N/m at GCC at 0.10 g/m² filler loading, which was 36% increased value compared to 33.5 N/m for untreated GCC at 0.10 g/m² filler loading. In addition, this increase ratio became higher along with filler loading (Table 3-4). The effect of PEM on improvement of the average peel force became greater as filler loading increased. This trend was similar with mechanical properties as a function of ash content presented in Fig. 3-11 – 3-19. As a results, PEM improved bonding strength between fiber and filler, and this improvement of the bonding strength contributed to increase the strength of the filled paper.
Fig. 3-25. Delamination peel force of the laminate depending on filler loading.
Table 3-3. The coefficients obtained from empirical equation of peel force versus filler loading

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated GCC</td>
<td>290.0</td>
<td>21.6</td>
<td>0.995</td>
</tr>
<tr>
<td>C-starch/A-PAM 3 layers GCC</td>
<td>277.6</td>
<td>18.0</td>
<td>0.989</td>
</tr>
</tbody>
</table>

Table 3-4. Estimated average peel force calculated from empirical equation

<table>
<thead>
<tr>
<th>Filler loading, g/m²</th>
<th>0.10</th>
<th>0.15</th>
<th>0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated GCC</td>
<td>33.5</td>
<td>11.4</td>
<td>3.9</td>
</tr>
<tr>
<td>C-starch/A-PAM 3 layers GCC</td>
<td>45.7</td>
<td>18.5</td>
<td>7.5</td>
</tr>
</tbody>
</table>

| Ratio of increase based on untreated GCC | 36% | 63% | 94% |


3.3.2 Bonding ability between PEM treated fillers

Surface of filler particles such as GCC is so coarse that the particles cannot adhere each other. Fig. 3-26 showed flexure strength of the dense film composed of fillers determined using three point bending setup. The film composed of untreated GCC showed very low flexure strength at break, less than 1 MPa. It was very difficult to handle the untreated GCC structure because it was fragile structure even at slight impact. This means that there was few bonding between untreated GCC particles, only weak van der Waals forces worked. The film composed of C-starch/A-PAM 3 layers showed 7.0 MPa of flexure strength at break, which was more than 7 times greater for the flexure strength of the untreated GCC structure. Multilayer can be formed onto GCC due to electrostatic attraction forces between negative surface of GCC and first layer, i.e. cationic starch. This multilayer provide additional bonding such as hydrogen bonding and van der Waals bonding between PEM treated GCC particles. In addition, It has been suggested that multilayer with cationic starch was soft and adaptable (Lundström-Hämälä et al. 2010). Thus, it was considered that PEM treatment on GCC turned from the rigid surface of untreated GCC into soft surface, resulting in more conformability between PEM treated GCC particles. Therefore, PEM treatment gave greater bonding strength between filler particles.
Fig. 3-26. Flexure stress of untreated GCC and PEM treated GCC.
The flexure strength of C-starch/A-PAM 3 layers GCC was still lower than tensile strength of unfilled handsheets made of PEM treated fibers around 30 MPa calculated from tensile index and apparent density in Table 3-2. Porosity calculated from apparent density was 36% for the dense film composed of fillers and 64% for the unfilled handsheets. Although the porosity and specific bonded area were not considered, it was obvious that bonding strength between PEM treated fillers was weaker than fiber to fiber bonding strength. However, the great improvement on the flexure strength of C-starch/A-PAM 3 layers GCC compared to untreated GCC had positive impact for highly filled paper. Fig. 3-27 showed cross section images of PEM GCC conditions handsheets which were made of untreated fibers and C-starch/A-PAM 3 layers GCC. At the relatively low level of filler content (9.9% ash content in this case), there was little contact area between fillers, while most bonding occurred between fibers and between fiber and filler. (white arrows in Fig. 3-27 (a)). On the other hands, clusters of GCC particles were observed inside the highly filled handsheets (white arrows in Fig 3-27 (b)). In this case, polyelectrolytes multilayer improved bonding strength of the clusters. As a results, PEM treatment on fillers contributed to enhance not only fiber to filler bonding but also filler to filler bonding.
Fig. 3-27. Cross section images of the filled handsheets made of untreated fibers and C-starch/A-PAM 3 layers GCC. Ash content was (a) 9.9% and (b) 27.9%.
4. Summary

In this chapter, the effect of PEM treatment on either fibers or fillers on the strength of filled paper was investigated to determine more effective approach for highly filled paper with high strength. Multilayering system of cationic starch and anionic polyacrylamide was conducted on fibers and fillers, respectively. Mechanism for improvement on strength of filled paper by PEM treatment was also investigated.

PEM treatment improved the strength of the filled paper in both cases, PEM treatment on pulp fibers and PEM treatment on fillers. PEM treatment on pulp fibers was more effective to improve the strength of the filled paper at relatively low level of fillers loading. This was due to enhancement of joint strength of PEM treated fibers. This improvement of fibers joint strength enabled to maintain high strength of the filled paper. On the other hands, PEM treatment on fillers was effective for the strength of highly filled paper. This effect on enhancement of paper strength became greater as ash content was increased. This was due to influences of PEM on the bonding strength between fiber and filler as well as the bonding strength between fillers.

The influence of PEM on fillers was investigated in two aspects of fiber-filler bonding and filler-filler bonding. The specific debonding factor of PEM treated GCC became lower than untreated GCC, indicating less weakening bonding between fiber and filler. The breaking
strength of PEM treated GCC was more than 7 times greater than that of untreated GCC. It was proposed that multilayer on GCC played a role of adhesive at contact zone between fiber and filler, and contact zone between fillers.
Chapter 4.

Factors affecting properties of PEM fillers and strength of filled paper
1. Introduction

Since the concept of multilayering is introduced by Decher and Hong (1991), numbers of studies have been published for process of multilayering and characteristics of multilayer. The characteristics of polyelectrolytes multilayer (PEM) such as thickness and viscoelastic properties are affected by nature of polyelectrolytes such as molecular weight and charge density, and operating conditions such as ionic strength, pH, temperature, and rising protocol (Schönhoff 2003b). The multilayer characteristics controlled by those factors are also related to degree of improvement on joint strength between PEM treated surfaces such as PEM treated fibers (Eriksson et al. 2005a, Ryu et al. 2011, Chin et al. 2012).

Many researchers have found that ionic strength, i.e. salt concentration of the polyelectrolyte solution is a dominant factor for the growth of multilayer and properties of the multilayer in comparison with concentration of the polymer solution, adsorption time, and molecular weight of polyelectrolytes (Dubas and Schlenoff 1999, Schlenoff and Dubas 2001, Voigt et al. 2003). Configuration of polyelectrolyte chains as like stretched-up or coiling-up is determined by salt concentration (Dobrynin et al. 1995, Liu et al. 2003). Charged particles are also affected by so called “charge screening effect” (Terao and Nakayama 2001). It is important to identify interaction between polyelectrolyte and filler particles, and characteristics of multilayering growth on filler
particles by controlling salt concentration.

Nature of polyelectrolytes is also one of factors to affect characteristics of multilayer as well as effect of polyelectrolytes multilayering on the joint strength between PEM treated fibers. It has been demonstrated that cationic starch provides greater strength improvement then other polyelectrolytes at the same layer number when they are used for polyelectrolytes multilayering on pulp fibers (Johansson et al. 2009, Chin et al. 2012). In addition, cationic starch gives outstanding strengthening effect on filled paper in the both cases of single treatment as a dry strength agent and polyelectrolytes multilayering on ground calcium carbonate (Lindström et al. 1985, Ahn 2014). Mechanism for strengthening effect of multilayer containing cationic starch on filled paper was also demonstrated in chapter 3. Polydiallyldimethylammonium chloride (PDADMAC) is barely used for strength agents in papermaking industry. In spite of this fact, there are some advantages of investigation on characteristics of multilayer consisting of PDADMAC. PDADMAC is such a standard polyelectrolyte due to quite simple polymer structure and numerous basic researches for properties of PDADMAC (Guzmán et al. 2009, Adamczyk et al. 2014, Michna et al. 2015). It was considered that understanding properties of multilayer containing PDADMAC depending on salt concentration and its effect on paper strength was important to construct appropriate multilayer on fillers for great strengthening effect on filled paper. Therefore, influences of salt
concentration during polyelectrolytes multilayering and nature of polyelectrolytes on strength of filled paper was investigated through comparison between multilayer with cationic starch and multilayer with PDADMAC under different salt concentration.

In chapter 3, strengthening effect of PEM on GCC was proven. GCC is widely used as fillers in Korea as well as other countries, thus PEM treatment was expected for useful technique for high filler loading. However, other types of inorganic particles such as precipitated calcium carbonate (PCC) and kaolin are also widely used as fillers. Not only irregular types of GCC but also scalenohedral type of PCC is one of the most widely used fillers to achieve high bulk and high opacity. Platy type of clay is also sometimes used as fillers in some countries. It was important to examine the strengthening effect of PEM depending on the morphology of fillers in order to apply PEM technique to various types of fillers. Therefore, it was necessary to investigate the effect of polyelectrolytes multilayering on properties of fillers depending on their morphology, and to compare their strengthening effect on filled paper.
2. Materials & methods

2.1 Materials

Polyelectrolytes used for polyelectrolytes multilayering treatment were polydiallyldimethylammonium chloride (PDADMAC, Mw 100,000 – 200,000 g/mol, Sigma Aldrich) and cationic starch (C-starch, DS 0.06, Samyang) as cationic polyelectrolytes, and poly(sodium 4-styrene sulfonate) (PSS, Mw ~200,000 g/mol, Sigma Aldrich) and anionic polyacrylamide (A-PAM, Mw ~70,000 g/mol, OCI-SNF) as anionic polyelectrolytes. Chemical structure of the polyelectrolytes for PEM treatment was shown in the Fig. 4-1. Cationic polyacrylamide (C-PAM, Percol 63, BASF) and anionic micropolymer (Telioform M300, BASF) were used as retention aids. Sodium chloride (NaCl) was used to control salt concentration. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust pH.

Ground calcium carbonate (GCC, Hydrocarb 75K, Omya), Precipitated calcium carbonate (PCC, Syncarb F0474, Omya), kaolin (Sigma Aldrich) were used as inorganic filler particles. Morphology and size distribution of fillers, and characteristic of fillers were presented in Fig. 4-2, and Table 4-1, respectively. Mixed hardwood bleached pulp fibers (Hw-BKP, Moorim P&P) were used after beating to 400 mL Canadian Standard Freeness (CSF, TAPPI methods 227 om-99) using a
laboratory beater.

Fig. 4-1. Chemical structure of polyelectrolytes used for PEM treatment, (a) polydiallyldimethylammonium chloride (PDADMAC), (b) cationic starch (C-starch), (c) poly(sodium 4-styrene sulfonate) (PSS), and anionic polyacrylamide (A-PAM).
Fig. 4-2. Morphology of (a) GCC, (b) PCC, (c) kaolin and (d) size distribution.

Table 4-1. Characteristics of fillers

<table>
<thead>
<tr>
<th>Types</th>
<th>GCC</th>
<th>PCC</th>
<th>Kaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shapes</td>
<td>Irregular (blocky)</td>
<td>Scalenoahedral</td>
<td>Platy</td>
</tr>
<tr>
<td>Charge*</td>
<td>Negative (-44 mV)</td>
<td>Negative (-45 mV)</td>
<td>Negative (-63 mV)</td>
</tr>
<tr>
<td>Size**</td>
<td>2.0 μm</td>
<td>2.6 μm</td>
<td>2.6 μm</td>
</tr>
<tr>
<td>Specific area</td>
<td>8.8±0.1 m²/g ¹</td>
<td>7.0±0.1 m²/g ¹</td>
<td>20 m²/g ¹</td>
</tr>
</tbody>
</table>

* Measured at pH 9.0 using Zetasizer Nano (Malvern)
** Measured at pH 9.0 using Mastersizer 2000 (Malvern)
¹ BET method
² Supplier information
2.2 Formation of polyelectrolytes multilayer on filler particles

Polyelectrolytes multilayering (PEM) treatment on fillers was followed as described in chapter 3. GCC and PCC were consecutively treated by PDADMAC/PSS system or C-starch/A-PAM system. For PDADMAC/PSS system, addition level of the PDADMAC and PSS was 1 wt% based on oven dried weight of fillers. Salt concentration during PEM treatment on GCC was 0 M NaCl (using fresh deionized water), 0.01 M NaCl, and 0.1 M NaCl. Salt concentration in the case of PCC was only 0.1 M NaCl. The pH was kept at pH 9.0±0.5. For C-starch/A-PAM system, addition level of C-starch and A-PAM was 3.5 wt% and 1 wt% based on oven dried weight of fillers, respectively. Salt concentration and pH were 0.01 M NaCl and pH 9.0±0.5, respectively.

Kaolin was consecutively treated by PDADMAC/PSS system. Addition level of the PDADMAC and PSS was 2 wt% based on oven dried weight of kaolin. Salt concentration and pH were 0.1 M NaCl and pH 9.0±0.5, respectively.
2.3 Properties of PEM fillers

2.3.1 Zeta potential and particle size of PEM filler

Zeta potential of PEM fillers was measured by using Zetasizer Nano ZS (Malvern, UK). PEM fillers were diluted to 0.1 g/L using 0.01 M NaCl at pH 9. Particle size was measured by using Mastersizer 2000 (Malvern, UK). In the measurement, PEM fillers were diluted to 0.01 g/L using 0.01 M NaCl at pH 9. The average particle size was represented as volumetric average particle size.

2.3.2 Adsorbed amount of polyelectrolytes

Adsorbed amount of PDADMAC was evaluated by analysis of nitrogen content using Kjeldahl Protein/Nitrogen Analyzer (Kjeltec Auto 1035/1038 System, Tecator AB, Sweden). As only PDADMAC contains nitrogen in the system of PDADMAC/PSS, adsorbed amount of PDADMAC can be calculated using calibration line of polyelectrolyte concentration-nitrogen content.

Adsorbed amount of PSS was quantified by sulfur content analysis. The PEM fillers (about 0.5 g) were added in mixture of HNO₃ 8 mL, HCl 1 mL, and H₂O₂ 1 mL. The mixture was digested using a microwave
(Multiwave 3000, Anton-paar, Austria) for 70 min, and then sulfur content in the mixture was analyzed by using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-730 ES, Varian, Australia). Adsorbed amount of PSS was calculated using calibration line of PSS concentration-sulfur content.

2.3.3 Charge demand of PEM GCC

Charge demand of PEM GCC was evaluated by using particle charge detector (PCD, PCD-03pH, Mütek, Germany) with back titration method. Titrants used in this study were cationic PDADMAC (0.001 N, BTG) and anionic poly(sodium ethersulfone) (PES-Na, 0.001 N, BTG). It was used to dilute the titrants to 0.0001 N. 0.3 g of PEM GCC was suspended in 30 mL of oppositely charged titrant solution, e.g. positively charged PEM GCC in PES-Na, and negatively charged PEM GCC in PDADMAC. After shaking the suspension slowly for 30 min, the suspension was centrifuged for 20 min at 3000 G. Charge demand of supernatant was measured by using PCD, and charge demand of PEM GCC was evaluated using Eq. [4-1].

\[
\text{Charge demand of PEM GCC (μeq/g) = } \frac{(A - B \times V)}{C} \cdots [4-1]
\]

Where, \( A \) is total charges of titrant (μeq), \( B \) is measured charge demand of supernatant (μeq/mL), \( V \) is volume of supernatant in measurement (mL), and \( C \) is dried weight of PEM GCC.
2.3.4 Monitoring of growth of PDADMAC/PSS multilayer using Quartz Crystal Microbalance with Dissipation

The formation of PDADMAC/PSS multilayer was monitored using Quartz Crystal Microbalance with Dissipation (QCM-D, E-100, Q-Sense, Sweden). The QCM-D crystals were AT-cut silicon-dioxide-coated crystals (Q-Sense AB, Sweden) with a fundamental resonance frequency of $f_0 \approx 4.95$ MHz and a sensitivity constant of $C \approx 18.06$ ng/m$^2$·Hz. The sensors were cleaned in an RCA solution at 65 °C for 10 min (Kern and Puotinen 1970) before QCM-D monitoring. Formation of the multilayer was performed by alternately passing 1 g/L in 0 M NaCl or 0.1 M NaCl polyelectrolytes solution using a peristaltic pulp. For washing steps, 0M or 0.1 M NaCl was passed. QCM-D data, change in frequency ($\Delta f$) and change in dissipation ($\Delta D$) were measured by simultaneously at the fundamental resonance frequency 5 MHz, and at 15, 25, and 35 MHz (overtone number = 1, 3, 5, and 7). According to Ramos et al. (2010), Sauerbrey thickness can be obtained using Sauerbrey equation Eq. [4-2] (Sauerbrey 1959) and Eq. [4-3] because ratio of $\Delta D$/-$\Delta f$ was less than $0.2 \times 10^{-6}$/Hz,

$$m_{QCM} = -C \times \Delta f_i/i \quad [4-2]$$

$$d_{QCM} = m_{Qcm}/\rho_{Qcm} \quad [4-3]$$

Where, $m_{QCM}$ is mass per unit area, $C = 18.06 \pm$ ng/m$^2$·Hz for sensors with a resonance frequency of $4.95 \pm 0.02$ MHz, $d_{QCM}$ is thickness, and
\[
\rho_{QCM} = 1.0 \text{ g/cm}^3
\]
being the density of the solvated polymer film. The normalized frequency changes, \(\Delta f = \Delta f_i\) of 7 overtone were employed for the Eq. [4-2]. It is known that the density of PDADMAC and PSS are between 1.0 – 1.2 g/cm\(^3\) while the density of water and salt solution is 1.0 g/cm\(^3\) (Ramos et al. 2010). Thus, the thickness calculated from QCM-D data can be overestimated by at most 20%.

2.4 Preparation and properties of filled handsheets

2.4.1 Handsheets preparation

Filled handsheets were prepared with various types of PEM fillers. The types of PEM fillers were described in Table 4-2. Retention system was micropolymer system. Fillers, C-PAM, and micropolymer were added into pulp stock in sequence. Addition level of C-PAM and micropolymer was 0.04% and 0.06% based on dried weight of fibers and fillers, respectively. Target grammage and filler content of the filled handsheets was controlled to 80±4 g/m\(^2\), and 15-35%, respectively.

Filled handsheets were prepared by using the square handsheets former. After making wet sheets, 5 times couching, pressing at 3.5 bar using a laboratory press machine, and drying at 120\(^\circ\)C using a cylinder dryer were conducted. The dried handsheets was pre-conditioned at
23±1°C and 50±2%RH more than 24 hr.

Table 4-2. Description of PEM fillers used for handsheets preparation

<table>
<thead>
<tr>
<th>Notation</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un GCC</td>
<td>Untreated GCC</td>
</tr>
<tr>
<td>Un PCC</td>
<td>Untreated PCC</td>
</tr>
<tr>
<td>Un kaolin</td>
<td>Untreated kaolin</td>
</tr>
<tr>
<td>PD3 (0M) GCC</td>
<td>PDADMAC/PSS 3 layers (0 M NaCl) GCC</td>
</tr>
<tr>
<td>PD7 (0M) GCC</td>
<td>PDADMAC/PSS 7 layers (0 M NaCl) GCC</td>
</tr>
<tr>
<td>PD3 (0.1M) GCC</td>
<td>PDADMAC/PSS 3 layers (0.1 M NaCl) GCC</td>
</tr>
<tr>
<td>PD7 (0.1M) GCC</td>
<td>PDADMAC/PSS 7 layers (0.1 M NaCl) GCC</td>
</tr>
<tr>
<td>CS3 GCC</td>
<td>C-starch/A-PAM 3 layers GCC</td>
</tr>
<tr>
<td>PD7 PCC</td>
<td>PDADMAC/PSS 7 layers (0.1 M NaCl) PCC</td>
</tr>
<tr>
<td>CS3 PCC</td>
<td>C-starch/A-PAM 3 layers PCC</td>
</tr>
<tr>
<td>PD7 kaolin</td>
<td>PDADMAC/PSS 7 layers (0.1 M NaCl) kaolin</td>
</tr>
</tbody>
</table>
2.4.2 Properties of filled handsheets

Grammage and apparent thickness of filled handsheets were measured in accordance with TAPPI test methods T410 om-98 and T410 om-97, respectively. The apparent thickness was measured by using micrometer (L&W Co., Sweden). Apparent density of filled handsheets was calculated using the grammage and thickness values.

Fillers content in filled handsheets was evaluated by measurement of ash content using furnace in accordance with TAPPI test method T211 om-93. Filler distribution was observed by using Field Emission Scanning Electron Microscope (FE-SEM, SUPRA 55VP, Sweden).

Tensile strength of filled handsheets were measured by using tensile tester (L&W Co., Sweden) in accordance with TAPPI test method T494 om-96. Tensile index was calculated with measured grammage. Internal bond strength of filled handsheets was measured in accordance with TAPPI test method T569 pm-00 (Scott type internal bond strength).
2.5 Bonding ability of PEM fillers

2.5.1 Measurement of bonding force between fiber and filler

Bonding force between fibers and fillers was evaluated by measuring delamination force of laminate for fiber-filler bonding. Experiment process in detail was described in section 2.6.1 in chapter 3.

2.5.2 Measurement of bonding strength between fillers

Bonding strength between fillers was evaluated by measurement of flexure strength of the dense film composed of fillers as described in section 2.6.2 in chapter 3.
3. Results & Discussion

3.1 Effect of multilayer characteristics on properties of PEM GCC and strength of filled paper

3.1.1 Effect on properties of PEM GCC depending on salt concentration

PDADMAC and PSS are known as strong polyelectrolytes of which characteristics are affected by ionic strength, i.e. salt concentration. In the presence of salt in polyelectrolyte solution, counter ions screen charges of polyelectrolyte, thus the polyelectrolyte chain is changed from fully extended rod like configuration into random coil configuration due to charge screening effect (Dobrynin et al. 1995). As well as the strong polyelectrolytes, counter ions also screen charges of inorganic particles such as GCC. Thus, influences of salt concentration on charges of GCC and formation of first layer with PDADMAC were investigated before PDADMAC/PSS multilayering on GCC.

Fig. 4-3 showed zeta potential of GCC depending on salt concentration of the GCC suspension. The zeta potential of GCC was not changed until 0.01 M NaCl, but the zeta potential became the weaker with the higher salt concentration more than 0.01 M NaCl. Fig. 4-4 showed zeta potential of GCC with a PDAMAC layer formed at different
salt concentration. Formation of a PDADMAC layer at up to 0.1 M NaCl turned the zeta potential of GCC from the negative to the positive. In this range of salt concentration, the zeta potential of GCC with a PDADMAC layer showed similar values. At more than 0.1 M NaCl, however, the zeta potential of GCC with a PDADMAC layer was on the decrease. The zeta potential was turned into the negative again at more than 0.3 M NaCl. It seemed that the PDADMAC layer was not formed on the surface of GCC at more than 0.3 M NaCl. This phenomenon was related to charge characteristic of PDADMAC affected by ionic strength. It has been suggested that effective ionization degree of PDADMAC keep a constant value up to 0.01 M NaCl, but the effective charges decrease above the salt concentration (Adamczyk et al. 2014). The PDADMAC shows still relatively high values of the effective charges and positive mobility at the NaCl concentration from 0.01 M to 0.15M resulting in slender body (extended chain) of the PDADMAC (Adamczyk et al. 2014). However, this chain configuration is changed to coil configuration above the salt concentration, which is caused by weak effective charges (Adamczyk et al. 2014). In other words, the stable PDADMAC layer can be formed with strong charges characteristic at less than 0.15 M NaCl, but the PDADMAC layer formed above the salt concentration would be unstable. Therefore, it was considered that appropriate salt concentration for PDADMAC/PSS multilayering was up to 0.15 M NaCl.
Fig. 4-3. Zeta potential of GCC depending on salt concentration of GCC suspension.

Fig. 4-4. Zeta potential of GCC with a PDADMAC layer formed at different salt concentration.
Fig. 4-5 presented zeta potential of PDADMAC/PSS GCC depending on salt concentration during PEM treatment. The zeta potential showed the positive at the odd layers in which PDADMAC was the outermost layer, whereas the negative at the even layers in which PSS was the outermost layer. This changes in the zeta potential indicated PDADMAC/PSS multilayer was successfully formed. There were differences of zeta potential depending on salt concentration, especially at the odd layers. The zeta potential slightly rose with an increase in salt concentration. This charges characteristics were shown in more detail in Fig. 4-6 presenting charge demand of PDADMAC/PSS GCC. The charge demand of PDADMAC/PSS GCC formed at 0 M NaCl and 0.01 M NaCl kept constant values at each of the odd layers and the even layers. On the other hands, PDADMAC/PSS GCC formed at 0.1 M NaCl showed much higher charge demand compared to the PDADMAC/PSS GCC formed at relatively low salt concentration. Furthermore, the charge demand of PDADMAC/PSS GCC formed at 0.1 M NaCl on the increase along with an increase in layer number.

These phenomenon seemed to be related to charge compensation when the multiayer was constructed. There are two different mechanism related with the charge compensation (electrical neutralization) (Schlenoff et al. 1998). Intrinsic mechanism is that the polyelectrolytes charges are compensated by charges of the opposite polyelectrolytes implying a stoichiometric 1:1 ratio (cationic polymer : anionic polymer) in the multilayer. In the alternate mechanism, extrinsic mechanism is that
much of charges are compensated by counter ions during built of the multilayer. Guzmán et al. (2009) reported that charge compensation is strongly related to salt concentration, and main mechanism for charge compensation turns from intrinsic compensation into extrinsic compensation at 0.3 M NaCl in the case of PDADMAC/PSS multilayer. According to the suggestion of Guzmán et al. (2009), in this results, 0.1 M NaCl condition was closer to extrinsic charge compensation than 0 M and 0.01 M NaCl condition for construction of PDADMAC/PSS multilayer on GCC, although the three salt concentration belongs to intrinsic charge compensation regime. It might be that PDADMAC and PSS were compensated by a stoichiometric 1:1 ratio at the relatively low level of salt concentration such as 0 M and 0.01 M NaCl, while there were partial extrinsic charge compensation at 0.1 M NaCl. Thus, the charges of PDADMAC/PSS GCC at 0 M and 0.01 M NaCl kept constant values, whereas the charges of PDADMAC/PSS GCC at 0.1 M NaCl showed the trend of an increase.
Fig. 4-5. Zeta potential of PDADMAC/PSS GCC depending on salt concentration during PEM treatment.
Fig. 4-6. Charge demand of PDADMAC/PSS GCC depending on salt concentration.
Adsorbed amount of PDADMAC and PSS was shown in Fig. 4-7. The adsorbed amount of PDADMAC and PSS was lineally increased along with an increase in layer number. This is also evidence of growth of the multilayer by intrinsic charge compensation (McAloney et al. 2001). There was no difference between adsorbed amounts at 0 M NaCl and 0.01 M NaCl, but the adsorbed amount at 0.1 M NaCl showed much higher. This indicated that much thicker multilayer was formed on GCC in the case of 0.1 M NaCl resulting from more adsorption of PDADMAC and PSS.

The characteristics of PDADMAC/PSS multilayer can be estimated by QCM-D model experiment. Fig. 4-8 (a) showed frequency changes ($\Delta f$) and dissipation changes ($\Delta D$) during growth of PDADMAC/PSS multilayer onto oxidized silicon surface. The $\Delta f$ and $\Delta D$ were increased with an increase in layer number. The $\Delta f$ and $\Delta D$ for 0.1 M NaCl condition were higher than those for 0 M NaCl. According to Ramos et al. (2010), if $\Delta D/(-\Delta f)$ is less than $0.2 \times 10^{-6}$/Hz, adsorbed amount and thickness are related to only the frequency changes ($\Delta f$), which is defined as rigid surface. Thus, the change in frequency ($\Delta f$) was proportional to adsorbed amount of PDADMAC and PSS like Fig. 4-7. The thickness obtained from the change in frequency ($\Delta f$) was shown in Fig. 4-8 (b). Thickness of the PDADMAC/PSS multilayer was proportional with layer number. The thickness of the 7 layers GCC was 6 nm for 0 M NaCl, and 16 nm for 0.1 M NaCl. Therefore, this QCM-D data supported that
PDADMAC/PSS multilayer built at 0.1 M NaCl was thicker than the multilayer built at 0 M and 0.01 M NaCl.

The dissipation data depends on rigidity of the polyelectrolytes adsorbed onto surface (Tammelin et al. 2004, Lingström and Wågberg 2008). It is known that strong polyelectrolytes such as PDADMAC and PSS form thin multilayer due to the strong electrostatic interaction (Schönhoff 2003b, Lingström and Wågberg 2008). The dissipation data in this study showed very low values compared to dissipation values such as starches (Lundström-Hämälä et al. 2010). This low dissipation values indicated that strong interaction inside the multilayer and a small number of loops and tail at the outermost layer (Enarsson and Wågberg 2008). However, an increase of salt concentration gave higher dissipation, and this meant that the multilayer formed at 0.1 M NaCl became less rigid structure. This changes at 0.1 M NaCl would result in more mobility of polyelectrolytes at the outermost layer. As a result, it was considered that PDADMAC/PSS multilayer on GCC formed at 0.1 M NaCl showed relatively thick and less rigid properties, while the others showed thin and more rigid properties.
Fig. 4-7. Adsorbed amount of (a) PDADMAC and (b) PSS per gram of GCC.
Fig. 4-8. QCM-D data of the fifth overtone (25 MHz), (a) change in frequency and dissipation as a function of time and (b) thickness obtained from the change in frequency.
Fig. 4-9 and Fig. 4-10 showed average particle size of PDADMAC/PSS GCC and size distribution, respectively. The particle size of PDADMAC/PSS GCC kept constant with around 2 μm until 7 layers regardless of salt concentration. This unchanged particle size with an increase in layer number meant that PDADMAC/PSS multilayer was formed at individual particles without any flocculation. This interpretation was supported by the size distribution result in Fig. 4-10, which showed similar distribution between untreated GCC and PDADMAC/PSS 7 layers GCC. As a result, PDADMAC/PSS multilayer was constructed on surface of individual GCC particles regardless of salt concentration, but the characteristics of the multilayer became different depending on the salt concentration as described in Fig. 4-5 to Fig. 4-8.
3.1.2 Effect on strength of filled paper

Fig. 4-11 and Fig. 4-12 showed tensile index and internal bond strength of filled handsheets with untreated GCC, PD3 (0M) GCC, PD3 (0.1M) GCC, PD7 (0M) GCC, or PD7 (0.1M) GCC. PD3 (0M) and PD7 (0M) GCC were prepared at relatively low salt concentration until 3 layers and 7 layers, respectively. On the other hands, PD3 (0.1M) and PD7 (0.1M) GCC were prepared at relatively high salt concentration until 3 layers and 7 layers, respectively. Filled handsheets with PDADMAC/PSS GCC with 3 layers showed a small increase in the strength at the same ash content compared to filled handsheets with untreated GCC. On the other hands, there was a great improvement of the strength in the case of filled handsheets with PDADMAC/PSS 7 layers GCC. In addition, PD7 (0.1M) GCC showed greater ability to improve paper strength than PD7 (0M) GCC. In other words, PDADMAC/PSS multilayer showed strengthening effect on filled paper.

PDADMAC is more widely used for a fixing agent rather than a dry strength agent in papermaking. Because PDADMAC does not have hydrogen bonding sites, and is adsorbed onto surface of fibers like flat conformation, PDADMAC is not as efficient as other dry strength agents for improvement of paper strength. In spite of this general view, the multilayering of PDADMAC and PSS showed quite good ability to improve strength of filled paper in this result. There are some previous studies for PDADMAC/PSS multilayer resulting in improvement of
paper strength. It has been suggested that the increased smoothness resulted from formation of PDADMAC/PSS multilayer increase molecular contact area between fibers, thus joint strength between adjacent fibers is increased (Lingström et al. 2006). It has been proposed that an increase in molecular mobility and strong interaction inside multilayer contribute to strength improvement of paper (Lingström and Wågberg 2008). The bonding between fibers can be produced from not only hydrogen bonding but also van der Waals forces, interdiffusion, Coulomb forces, capillary forces, and interlocking mechanisms (Wågberg 2009, Hirn and Schennach 2015). Therefore, it was considered that the PDADMAC/PSS multilayer contributed to improve paper strength with mechanisms such as interdiffusion that refers migration of polymer chains in the outermost layer into cellulose molecules at surface of fibers, van der Waals force at interfaces between cellulose surface and polymer chains at the multilayer, and Coulomb interaction between cationic charges of PDADMAC and anionic charges of fibers, e.g. carboxyl groups.
Fig. 4-11. Tensile index of filled handsheets.

Fig. 4-12. Internal bond strength of filled handsheets.
To determine the different degree of strength improvement, relationship between adsorbed amount of PDADMAC and paper strength was investigated in Fig. 4-13 for tensile index and Fig. 4-14 for internal bond strength. These two strength was proportional to the amount of PDADMAC in the multilayer, and PD7 (0.1M) GCC showed the highest strength values with 16.6 mg/g of PDADMAC. It was considered that these phenomenon was related to thickness and characteristics of multilayer. Structure of the PDADMAC/PSS multilayer was illustrated in Fig. 4-15. This structure was based on growth model during the initial step for multilayer with strong polyelectrolytes in (Guzmán et al. 2009). According to Guzmán et al. (2009), the adsorbed polyelectrolytes (PDADMAC in this case) in the first layer would not fill the whole surface due to the Coulombic repulsion between them as described in Fig. 4-15. The next PSS would fill onto the PDADMAC layers. This might enable the next PDADMAC to fill the empty surface as well as to adsorb on the PSS layers of the second layer. According to this growth model for multilayer, 3 layers of PDADMAC/PSS would not be enough to create strong interaction at interfaces between fibers and PEM treated GCC, or interfaces between PEM treated GCC. On the other hands, it was likely that the thicker 7 layers than 3 layers were more appropriate to create the strong interaction. In addition, the higher strength improvement would be given by the thicker multilayer resulting from high adsorption amount and higher mobility of PDADMAC in the outermost layer like 0.1 M NaCl condition. As a result, adsorbed amount in multilayer and mobility were dominant.
factors to improve strength of filled paper with PEM GCC.

Fig. 4-13. Relationship between adsorbed amount of PDADMAC and tensile index at 25±1% ash content.

Fig. 4-14. Relationship between adsorbed amount of PDADMAC and internal bond strength at 25±1% ash content.
Fig. 4-15. Schemes of multilayer structure with (a) PDADMAC/PSS 0 M and (b) PDADMAC/PSS 0.1 M.
3.2 Effect of nature of polyelectrolytes on strength of filled paper

Influence of polyelectrolyte nature in multilayer on strength of filled paper with PEM fillers were investigated. Table 4-3 summarized characteristics of untreated GCC and three types of PEM GCC. CS3 GCC denoted C-starch/A-PAM 3 layers GCC. PD3 (0.1M) GCC and PD7 (0.1M) GCC were PDADMAC/PSS 3 layers GCC and PDADMAC/PSS 7 layers GCC prepared at 0.1 M NaCl, respectively. Particle size of untreated GCC and three types of PEM GCC were similar. CS3 GCC showed weak positive charges but PD3 and PD7 GCC showed strong positive charges. Total amount of polyelectrolytes in multilayer of CS3 GCC was higher compared to PD3 (0.1M) GCC whereas it was similar with that of PD7 (0.1M) GCC. However, the amount of CS in multilayer estimated by combustion method and nitrogen content in chapter 2 was higher than the amount of PDADMAC in PD7 (0.1M) GCC.

Table 4-3. Characteristics of untreated GCC and PEM GCC applied to filled paper

<table>
<thead>
<tr>
<th>Zeta potential</th>
<th>Particle size</th>
<th>Adsorbed amount of PEs</th>
<th>Total PE</th>
<th>Cationic PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated GCC</td>
<td>-44 mV</td>
<td>2.0 μm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CS3 GCC</td>
<td>3.3 mV</td>
<td>2.1 μm</td>
<td>32.3 mg/g</td>
<td>~30.0 mg/g</td>
</tr>
<tr>
<td>PD3 (0.1M) GCC</td>
<td>45.8 mV</td>
<td>2.1 μm</td>
<td>8.4 mg/g</td>
<td>5.2 mg/g</td>
</tr>
<tr>
<td>PD7 (0.1M) GCC</td>
<td>43.4 mV</td>
<td>2.1 μm</td>
<td>32.1 mg/g</td>
<td>16.9 mg/g</td>
</tr>
</tbody>
</table>

PE denotes polyelectrolyte.
Fig. 4-16 showed delamination peel force of model laminates including interfaces between fibers and interfaces between fibers and fillers. The dots were experiment data, and the curves were trend obtained from exponential fits of the data as described in chapter 2. Debonding factors (β, m$^2$/g), related with bonding ability of fillers and other coefficients were presented in table 4-4. In chapter 2, it was already proven that CS3 GCC showed improved bonding ability with fibers resulted from lower debonding factor than untreated GCC. Debonding factor of PD3 (0.1M) GCC was 21 m$^2$/g, which was similar with untreated GCC but was higher than CS3 GCC. This meant that PDADMAC/PSS 3 layers barely contributed to improve the bonding strength between fibers and fillers, and thus there was no different delamination forces between PD3 (0.1M) GCC and untreated GCC. On the other hands, PD7 (0.1M) GCC showed the lowest debonding factors indicating the greatest bonding ability with fibers.

Table. 4-4. Summary of coefficients fitting peel force versus filler loading obtained from Microsoft excel trend line function

<table>
<thead>
<tr>
<th></th>
<th>α</th>
<th>β</th>
<th>R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un GCC</td>
<td>290</td>
<td>21.6</td>
<td>0.995</td>
</tr>
<tr>
<td>CS3 GCC</td>
<td>277.6</td>
<td>18</td>
<td>0.989</td>
</tr>
<tr>
<td>PD3 (0.1M) GCC</td>
<td>307.2</td>
<td>21</td>
<td>0.944</td>
</tr>
<tr>
<td>PD7 (0.1M) GCC</td>
<td>299.8</td>
<td>15.9</td>
<td>0.993</td>
</tr>
</tbody>
</table>
Fig. 4-16. Delamination peel force of the laminate. The curves are trend lines from exponential fit of data, black dotted line for untreated GCC, gray dashed line for CS3 GCC, black dashed line for PD3 (0.1M) GCC, and black solid line for PD3 (0.1M) GCC.
Fig. 4-17 presented flexure strength of the dense film composed of fillers determined by three point bending setup. As described in chapter 2, CS3 GCC showed much higher flexure strength than untreated GCC. PD3 (0.1M) GCC showed also higher flexure strength than untreated GCC, but PD3 (0.1M) GCC was weaker than CS3 GCC. On the other hands, the PD7 (0.1M) GCC showed the strongest flexure strength. This flexure strength results had similar trend with the delamination results in Fig. 4-17, indicating that the multilayer such as C-starch/A-PAM and PDADMAC/PSS contributed to improvement of specific bonding strength between fillers as well as that between fibers and fillers.

![Flexure strength graph](image)

**Fig. 4-17. Flexure strength of the dense film composed of fillers.**
It was considered that the different strengthening effect originated from nature of polyelectrolytes used and characteristics of the multilayer. It has been reported that C-starch/A-PAM 3 layers shows around -80 Hz for change in frequency (Δf), and around 15×10⁻⁶ for change in dissipation (ΔD) in QCM-D model experiment (Ahn 2014). According to Johansson et al. (2009), Thickness of 3 layers with cationic starch and anionic starch is around 15 nm obtained from viscoelastic model with QCM-D data. This was the reason that C-starch/A-PAM multilayer showed strengthening effect with the thick and bulky properties resulting in better deformability and interdiffusion of polymer chains (Schönhoff 2003b, Notley et al. 2005, Chin et al. 2012) as well as ability to form numerous hydrogen bonding. On the other hands, it is known that PDADMAC is usually adsorbed onto substrate with flat conformation (Chin 2010). This polymer chains conformation can be controlled with salt concentration, thus relatively thicker multilayer was constructed at high salt concentration as described in Fig. 4-8 and Fig. 4-15. Although the PDADMAC/PSS 3 layers showed strengthening effect in Fig. 4-16 and Fig. 4-17, this was not as effective as C-starch/A-PAM 3 layers. This was due to still thin thickness of the PDADMAC/PSS (0.1 M) 3 layers as presented in Fig. 4-8 (b). Thickness of PDADMAC/PSS (0.1 M) 7 layers was reached to 15 nm with -85 Hz for Δf and 3.5 ×10⁻⁶ for ΔD. With this growth of the multilayer, PDADMAC/PSS (0.1 M) 7 layers showed greater performance for the bonding ability than C-starch/A-PAM 3 layers. C-starch/A-PAM 3 layers showed similar thickness, but bulkier properties than the PDADMAC/PSS 7 layers. This bulkier
properties implied the polymer chains were more mobile, thus such polymer chains could be more prone to be diffused into cellulose surface and entangle across the interface between PEM treated fillers (Johansson et al. 2009). In spite of this higher mobility, CS3 GCC showed weaker bonding ability than PD7 (0.1M) GCC. There were two possible interpretations for this phenomenon. One was relationship of surface charges between PD7 (0.1M) GCC and CS3 GCC. PD7 (0.1M) GCC showed higher zeta potential that CS3 GCC. This higher zeta potential resulted from numbers of cationic charges in the outermost layer would enable to produce coulombic forces with anionic charges at surface of fibers, e.g. carboxyl groups. The other was characteristics of the multilayer. It is known that polyelectrolytes such as PDADMAC and PSS shows strong interaction each other during construction of multilayer resulting in compacted structure (Lingström and Wågberg 2008). It was considered that this compacted structure enabled to give strong intra-bonding inside the multilayer, and thus this affected to improve bonding strength at interfaces between fibers and fillers and interfaces between fillers. In other words, it seemed that bulky characteristics were positive on the mobility related to inter-bonding between two surfaces, but negative on the intra-bonding inside the multilayer like both sides of a coin.

Fig. 4-18 – 4-20 presented tensile index, internal bond strength, and wet tensile index of filled handsheets, respectively. Handsheets filled with CS3 GCC and PD7 (0.1M) GCC showed great improvement of the
strength at same ash content in comparison with untreated GCC. The mechanism for strength improvement depending on polyelectrolytes can be explained by wet tensile index of the filled handsheets presented in Fig. 4-20. It is known that hydrogen bond forces can hold adjacent surfaces when the surfaces are very close to contact within 0.5 nm (Wågberg 2009). When the paper is saturated with water, the hydrogen bonds are cleaved within a few seconds. Even though CS3 GCC condition showed stronger mechanical properties than untreated GCC condition, CS3 GCC conditions showed similar wet tensile index compared to untreated GCC conditions. This implied that strength improvement of C-starch/A-PAM multilayer originated from creation of hydrogen bonds by c-starch in the outermost layer. However, wet tensile index of PD7 (0.1M) GCC condition handsheets was higher than that of other conditions at given ash content. In addition, the wet tensile index of PD7 (0.1M) GCC condition increased as the ash content was increased. This indicated that the outermost layer of PDADMAC/PSS multilayer provided strong interaction due to more interdiffusion and different strengthening effect rather than creation of hydrogen bonds. Contrary to hydrogen bonds, van der Waals bonds have a range of at least 10 nm (Wågberg 2009). Thus, some of van der Waals bonds can be present when the paper was saturated with water. In addition, it was considered that those van der Waals bonds can be more closed due to coulombic forces between negatively charged fibers and strong positive PDADMAC in the outermost layer. These indicated that PDADMAC/PSS multilayer formed on GCC can produce van der Waals
forces and columbiaf forces. As a results, both of C-starch/A-PAM multilayer and PDADMAC/PSS multilayer can improve strength of filled paper despite different mechanism for strength improvement.

Fig. 4-18. Tensile index of the filled handsheets.

Fig. 4-19. Internal bond strength of the filled handsheets.
Fig. 4-20. Wet tensile index of the filled handsheets.
3.3 Effect of filler morphology on strength of filled paper

3.3.1 Properties of PEM fillers

Fig. 4-21 showed zeta potential of PEM fillers. Zeta potential of PDADMAC/PSS GCC, PCC, and kaolin was presented in Fig. 4-21 (a). Regardless of types of fillers, the zeta potential showed charge inversion patterns indicating that PDADMAC/PSS multilayer was successfully formed onto the three types of fillers until 7 layers. Formation of C-starch/A-PAM multilayer onto GCC and PCC until 3 layers was also determined by zeta potential patterns in Fig. 4-21 (b).

Surface charges were mainly affected by nature of polyelectrolytes rather than types of fillers. Both of the negative and positive charges of C-starch/A-PAM layers was weak in comparison those of PDADMAC/PSS layers in the both cases of GCC and PCC. This was likely that PDADMAC and PSS with higher charge density than cationic starch and A-PAM gave strong zeta potential. There was no differences of zeta potential between PEM GCC and PEM PCC in the same polyelectrolytes system, but zeta potential of PDADMAC/PSS kaolin was slightly higher than that of other PEM fillers. This difference was related to adsorbed amount of the polyelectrolytes to form the multilayer.
Fig. 4-21. Zeta potential of (a) PDADMAC/PSS GCC, PCC, and kaolin, and (b) C-starch/A-PAM GCC and PCC.
Fig. 4-22 showed amount of PDADMAC and PSS in the outermost layer of PDADMAC/PSS multilayer, and total amount of polyelectrolytes in PDADMAC/PSS 7 layers and C-starch/A-PAM 3 layers, respectively. Addition amount of PDADMAC and PSS to construct each layer was 10 mg per gram of fillers for GCC and PCC, and 20 mg per gram of fillers for kaolin. The empty space in the sticks meant the amount of polyelectrolytes which were removed during washing process. Because kaolin particles have larger specific surface area than GCC and PCC (Table 4-1), it was needed to add more polyelectrolytes for charge inversion for kaolin, and finally the more polyelectrolytes was adsorbed to form multilayer (Table 4-5). The PDADMAC and PSS were more adsorbed onto PCC to construct multilayer than onto GCC even though the addition amount of the polyelectrolytes was same. Cationic starch and A-PAM were also more adsorbed onto PCC like PDADMAC and PSS. This was likely due to pore structure of PCC particles (Fig. 4-2 (b)) resulting in some of polyelectrolytes were penetrated into the pores.

<table>
<thead>
<tr>
<th>PDADMAC/PSS 7 layers</th>
<th>GCC</th>
<th>PCC</th>
<th>Kaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDADMAC</td>
<td>17.8</td>
<td>24.4</td>
<td>59.9</td>
</tr>
<tr>
<td>PSS</td>
<td>15.9</td>
<td>20.9</td>
<td>50.5</td>
</tr>
<tr>
<td>Total</td>
<td>33.7</td>
<td>45.3</td>
<td>110.4</td>
</tr>
</tbody>
</table>

Table 4-5. Polyelectrolyte amount adsorbed in multilayer (mg/g)
Fig. 4-22. Adsorbed amount of (a) PDADMAC and (b) PSS in the outermost layer of PDADMAC/PSS multilayer.
Fig. 4-23 and Fig. 4-24 showed average particle size and size distribution of PEM fillers. During formation of PDADMAC/PSS, a little change in the average particle size was detected in the case of PCC and kaolin (Fig. 4-23 (a)). In the size distribution of PDADMAC/PSS 7 layers PCC (Fig. 4-24 (b)), volume fraction of small particles less than 0.7 μm was decreased, and the peak of distribution was shifted to left with decreasing fraction of the large sized particles. PDADMAC/PSS 7 layers kaolin showed narrow distribution by decreasing fraction of both particles shorter than 1 μm and longer than 5 μm compared to untreated kaolin. This indicated that there would be aggregation for some small particles due to polymeric bridge mechanism although charges of particles are inversed (Rojas and Hubbe 2004, Gesenhues 2011). Because PDADMAC has around 40 nm of hydrodynamic diameter (Adamczyk et al. 2014), it could make the bridges between the small particles. This might change untreated PCC into less open structure of PDADMAC/PSS 7 layers PCC (Fig. 4-25 (d)), and untreated kaolin into more sphere-like shape of PDADMAC/PSS 7 layers kaolin (Fig. 4-25 (f)). Meanwhile, there would be breakage of some large particles such as bundles of PCC particles (Fig. 4-1 (b) and kaolin stacks (Fig. 4-1 (c)). It was possible to disperse the bundles of PCC and kaolin stacks due to very strong power of ultrasonic during washing step. In spite of these changes in the size distribution, PDADMAC/PSS 7 layer PCC and kaolin
were mostly dispersed like Fig. 4-25 due to electrostatic repulsion with strong positive charges.

During formation of C-starch/A-PAM on GCC and PCC, there was aggregation in 2 layers step, which A-PAM was in the outermost layer. In this 2 layers, the zeta potential was quite weak in comparison with even layers of PDADMAC/PSS fillers, thus some aggregation would be possible due to not enough electrostatic repulsion. However, odd layers of C-starch/A-PAM GCC and PCC almost maintained their own particle size in spite of very weak positive charges. It was considered that this dispersive distribution originate form steric stabilization mechanism due to steric hindrance of branched chains of cationic starch.

As a result, polyelectrolytes multilayer can be successfully formed on GCC as well as PCC and kaolin. The characteristics of PEM fillers were dependent on nature of polyelectrolytes used rather than types of fillers. Although there were some changes in particle distribution, quite well dispersed PEM fillers could be obtained.
Fig. 4-23. Average particle size of (a) PDADMAC/PSS GCC, PCC, and kaolin, and (b) C-starch/A-PAM GCC.
Fig. 4-24. Size distribution of PEM fillers. (a) PDADMAC/PSS 7 layers GCC, (b) PDADMAC/PSS 7 layers PCC, (c) PDADMAC/PSS 7 layers kaolin, (d) C-starch/A-PAM 3 layers GCC, and (e) C-starch/A-PAM 3 layers PCC.
Fig. 4-25. Morphology of (a) untreated GCC, (b) PDADMAC/PSS 7 layers GCC, (c) untreated PCC, (d) PDADMAC/PSS 7 layers PCC (e) untreated kaolin, (f) PDADMAC/PSS 7 layers kaolin, (g) C-starch/A-PAM 3 layers GCC, and (h) C-starch/A-PAM 3 layers PCC.
3.3.2 Effect of types of fillers on handsheets properties

Fig. 4-26 - 28 showed apparent density and light scattering coefficient (LSC) at 457 nm, surface images of filled handsheets, respectively. The apparent density of handsheets filled with untreated GCC and untreated kaolin was similar at given filler content. On the other hands, handsheets filled with untreated PCC showed higher apparent density. This was due to “open” structured scalenohedral particles as presented in Fig 4-28 (c). It is known that the open structured fillers such as scalenohedral types of PCC give more opened and bulkier structure of sheets. This was the reason that PCC resulted in lower density, i.e. higher bulk (Gill 1989) and higher LSC in comparison with GCC and kaolin. Kaolin particles gave similar density but high LSC in comparison with GCC. It was likely due to nature of fillers rather than pore volumes inside sheets.

PDADMAC/PSS 7 layers PCC and kaolin gave higher density and lower LSC in same filler content. This was due to a decrease in volume fraction of relatively small particles after formation of the multilayer (Fig. 4-24). In addition, the PDADMAC/PSS 7 layers PCC showed less open structure (Fig. 4-25 (e) and Fig. 4-28 (e)) than untreated PCC, and PDADMAC/PSS 7 layers kaolin showed more sphere-like shapes (Fig. 4-25 (f) and Fig. 4-28 (f). It was considered that these two facts less interfered in fibers bonding resulting in higher density with untreated PCC and kaolin.
Fig. 4-26. Apparent density of filled handsheets. Dotted lines are for untreated fillers and solid lines are for PDADMAC/PSS 7 layers fillers.

Fig. 4-27. Light scattering coefficient at 457 nm of filled handsheets. Dotted lines are for untreated fillers and solid lines are for PDADMAC/PSS 7 layers fillers.
Fig. 4-28. Surface images of handsheets filled with (a) untreated GCC, (b) PD7 (0.1M) GCC, (c) untreated PCC, (d) PD7 (0.1M) PCC, (e) untreated kaolin, and (f) PD7 (0.1M) kaolin at 25% ash content.
Fig. 4-29 and Fig. 4-30 showed tensile index and internal bond strength of handsheets filled with untreated fillers and PDADMAC/PSS 7 layers fillers. The tensile index and internal bond strength of handsheets filled with untreated kaolin was lower than those of handsheets filled with untreated GCC and PCC at same ash content. Untreated kaolin had much larger specific surface area than untreated GCC and PCC (Table 4-1), therefore handsheets filled with kaolin particles became more weakened because of more interference in inter-fiber bonding. The untreated PCC provided similar strength values at same ash content in comparison with untreated GCC even though PCC had open structure (Fig. 4-2 (b)) and provided bulkier properties than GCC (Fig. 4-26). This might be related to small specific surface area and large average size of PCC compared to GCC. It is known that scalenohedral types of PCC typically give higher bulk but lower mechanical properties than solid types of filler such as GCC (Hubbe and Gill 2016). However, Gill (1989) reported that scalenohedral fillers exhibit better opacity/tensile performance than solid types of fillers such as GCC and chalk. In this reference, some PCC give high bulk but similar tensile properties at same ash content in comparison with solid types of fillers. Laufmann et al. (2000) also suggested that PCC with coarse distribution and large average size provides slight decrease in tensile strength but relatively high bulk in comparison with GCC with fine distribution and small average size. These two previous results agreed that large particle size of PCC gave high bulk but similar mechanical strength in comparison with GCC.
PDADMAC/PSS 7 layers provided strengthening effect on GCC as well as PCC and kaolin as presented in Fig. 4-29 and Fig. 4-30. However, the degree of improvement was quite different depending on types of fillers. PDADMAC/PSS 7 layers PCC exhibited somewhat low strengthening effect in comparison with PDADMAC/PSS 7 layers GCC. This was due to more open area inside filled handsheets with PCC. It is known that scalenohedral particles do not pack as tightly together when aggregates are formed causing the sheet to be much more open and bulkier than a similar sheet formed from more solid particles such as GCC (Gill 1989). This situation was detected in this results (Fig. 4-28 (b) and (d)). In addition, surface of GCC particles was smoother than that of PCC particles (Fig. 4-2 and Fig. 4-28). It seemed that these two facts gave more chance for the multilayer to interact with surface of fibers or surface of fillers. PDADMAC/PSS 7 layers kaolin showed the greatest improvement of strength. Kaolin had the smoothness surface indicating the greatest chance to interact with surface of fibers or other particles surface. In addition, it seemed that the most amount of PDADMAC in the multilayer on kaolin (Table 4-5) also gave the greatest performance to improve strength of filled paper.
Fig. 4-29. Tensile index of filled handsheets.

Fig. 4-30. Internal bond strength of filled handsheets
The strengthening effect of C-starch/A-PAM 3 layers was similar with that of PDADMAC/PSS 7 layers. Fig. 4-31 and Fig 4-32 showed tensile index and internal bond strength of handsheets filled with C-starch/A-PAM 3 layers GCC and PCC. C-starch/A-PAM 3 layers GCC showed slightly higher strength than C-starch/A-PAM 3 layers PCC like the results with PDADMAC/PSS 7 layers.

As a result, the performance of multilayer to improve strength of filled paper was dependent on types of fillers, i.e. their morphology. Smooth and flat surface of fillers provided great performance for strengthening effect.

Fig. 4-31. Tensile index (a) and internal bond strength (b) of handsheets filled with C-starch/A-PAM 3 layers GCC and C-starch/A-PAM 3 layers PCC.
3.4 Summary

In this chapter, factors to affect strength of filled paper were investigated with respect to multilayer characteristics controlled by salt concentration, nature of polyelectrolytes, and morphology of fillers.

For the salt concentration effect, multilayering of PDADMAC and PSS on GCC was performed. Because GCC is charged particle as well as PDADMAC and PSS, charges of GCC was also affected by salt concentration. Even though the zeta potential of GCC became weakened with increasing salt concentration, PDADMAC can be stably adsorbed onto GCC particles up to 0.15 M NaCl. At relatively low salt concentration like 0 M NaCl and 0.01 M NaCl, there was no differences with respect to adsorbed amount of polyelectrolytes and charges of PEM GCC. However, relatively high salt concentration like 0.1 M NaCl gave much higher charges to GCC, and thick and bulky multilayer resulted from more amount of polyelectrolytes in the multilayer in comparison with the low salt concentration. This thick and bulky multilayer properties led to greater improvement on the strength of handsheets filled with PEM GCC.

Multilayer with cationic starches provided greater strengthening effect on filled paper than multilayer with PDADMAC at given layer number. However, the PDADMAC/PSS 7 layers at 0.1 M NaCl showed similar strengthening effect with C-starch/A-PAM 3 layers. The multilayer
containing cationic starch can produce numerous hydrogen bonding. In addition, it had bulkier properties, thus this led to higher molecular interdiffusion. On the other hands, it was considered that the PDADMAC/PSS multilayer can produce strong Coulombic interaction with anionic charges at surface of fibers when the PDADMAC was in the outermost layer, and had stronger intra-bonding inside the multilayer than C-starch/A-PAM multilayer.

Multilayering effect depending on morphology of fillers was also investigated. PEM can be successfully formed on irregular types of GCC as well as scalenohedral types of PCC and platy types of kaolin. Open structured fillers like the scalenohedral PCC gave less strengthening effect on filled paper than solid types of fillers such as GCC and kaolin. For the GCC and kaolin, PEM treatment on kaolin was better for strength improvement of filled paper than PEM treatment on kaolin. It was considered that more amount of polyelectrolytes in the multilayer and PEM on the smoother surface of fillers provided the greater chance to interact with surface of fibers or surface of other particles.
Chapter 5.

Application of polyelectrolytes multilayering:

Washless polyelectrolytes multilayering for mill application

and antibacterial effect of PEM fillers
1. Introduction

Strengthening effects of polyelectrolytes multilayering on fillers and its mechanism for the strengthening were discussed in chapter 3 and 4. Polyelectrolytes multilayering (PEM) can provide excellent improvement of strength of filled paper. This PEM process consists of adsorption step with massive addition of polyelectrolytes. To form regular and pure multilayer, washing steps for rinsing excess polyelectrolytes should be followed after the adsorption step. This ideal PEM process was economically unattractive to install and run in papermaking industry. Hubbe (2006) suggested that the ideal PEM process is not truly important relative to practical goal of increasing strength of paper. There is alternate PEM process excluding the washing step (Hubbe 2006). This PEM process is usually called as washless PEM. The concept of this washless PEM is a series of consecutive addition of polyelectrolytes to a continuous stream for fiber stocks or filler suspension. This concept requires that polyelectrolytes should be added for enough charge inversion to adsorb polyelectrolytes added in the next step, but too much excess of unadsorbed polyelectrolytes are not allowed due to uncontrolled complexation with the next added oppositely charged polyelectrolyte (Hubbe 2006). In this study, therefore, the appropriate washless PEM process was designed.

Fig. 5-1 showed the designed washless PEM process, called as inline washless PEM system. This inline washless PEM system consisted of
three inline homogenizers and peristaltic pumps. Main stream was GCC suspension, and multilayering can be achieved up to 3 layers. Addition level of polyelectrolytes can be controlled by flow rate of the polyelectrolytes solution. Shear rate can be controlled by rotation speed of the homogenizer. Polyelectrolytes system for the multilayering was cationic starch (C-starch) and anionic acrylamide (A-PAM). This C-starch/A-PAM multilayering system was the most effective combination for strength improvement at the given layer number. Therefore, appropriate treatment condition was investigated for successful washless multilayering in terms of control of addition level of polyelectrolytes and shear effect on the properties of inline washless PEM fillers.

Fig. 5-1. Scheme of laboratory inline system for inline washless polyelectrolytes multilayering.
Polyelectrolytes multilayering can provide strengthening effect as well as various functionality such as electrical conductivity and antibacterial activity (Agarwal et al. 2006, Wistrand et al. 2007, Westman et al. 2009b, Imani et al. 2011, Illergård et al. 2012, Lee et al. 2012, Illergård et al. 2015). It has been demonstrated that cationic polyelectrolytes such as polyvinylamine show antibacterial activity (Westman et al. 2009a). As PVAm can also improve adhesion between fibers (Pelton and Hong 2002, Pelton 2014), paper with PEM treated cellulose fibers using PVAm could have great potential to show not only antibacterial activity but also high strength. However, fabrication of antibacterial paper using the treated cellulose fibers may lead to reduce antibacterial activity when inorganic particles are used to make paper such as filled paper and coated paper. If PEM treatment using PVAm on inorganic particles is possible to show antibacterial properties, it is expected that types of antibacterial paper is enlarged such as filled paper and coated paper grades. Therefore, this study was to investigate PEM treatment using PVAm on inorganic particles and to suggest appropriate strategy to apply PEM treated inorganic particles to fabricate antibacterial paper.

In this chapter, two different application of PEM were discussed, washless polyelectrolytes multilayering for mill application and fabrication of antibacterial paper using PEM treated fillers.
2. Materials & methods

2.1 Materials

2.1.1 Pulp fibers

Mixed hardwood bleached pulp fibers (Hw-BKP) were supplied by Moorim P&P in South Korea. The Hw-BKP was beaten to 400 mL Canadian Standard Freeness (TAPPI methods 227 om-99) using a laboratory beater.

2.1.2 Fillers

Ground calcium carbonate (GCC, Hydrocarb 75K, Omya) was used for inline washless PEM process. Kaolin particles (Sigma Aldrich) were used for preparation of antibacterial filler.

2.1.3 Polyelectrolytes

Cationic starch (C-starch, DS 0.06, Samyang), and anionic polyacrylamide (A-PAM, Mw ~70,000 g/mol, OCI-SNF) were used for
inline washless PEM process. Cationic polyvinylamine (PVAm, Xerlex 1300, BASF) and anionic polyacrylic acid (PAA, Mw ~100 kDa, Sigma Aldrich) were used for polyelectrolytes multilayering to prepare antibacterial filler.

Cationic polyacrylamide (C-PAM, Percol 63, BASF) and anionic micropolymer (Teloform M300, BASF) were used as retention aids, and alkyl keton dimer (AKD, Hercules) was used as internal sizing agent. Polyvinyl alcohol (PVOH, Mw 13,000 – 23,000 g/mol, 98% hydrolyzed, Sigma Aldrich) was used as surface sizing agent.

2.1.4 Bacteria

Strains of *Escherichia coli* (E. coli) O157:H7 (ATCC 35150, ATCC 43889, and ATCC 43890) and *Listeria monocytogenes* (*L. monocytogenes*) (ATCC 15313, ATCC 19111, and ATCC 19115) were obtained from the bacterial culture collection of Seoul National University in South Korea and used in this experiment. Stock cultures were stored at -80°C in tryptic soy broth (TSB, Difco, Becton Dickinson, Sparks, MD, USA) supplemented with 15% glycerol. Working culture were streaked onto tryptic soy agar (TSA, Difco) plate, incubated at 37°C for 24 hr, and stored at 4°C. Each strain of *E. coli* O157:H7 and *L. monocytogenes* was grown in 5 mL of TSB at 37°C for 24 hr. Cells of each strain were collected by centrifugation at 4000 rpm at 4°C for 20
min and washed two times with 0.2% peptone water (PW, Bacto, Sparks, MD). The final pellets were resuspended in sterile PW, corresponding to approximately $10^8$-$10^9$ colony-forming units (CFU)/mL for fraction of *E. coli* O157:H7 and $10^7$-$10^8$ CFU/mL for fraction of *L. monocytogenes*.

2.2 Washless polyelectrolytes multilayering

2.2.1 Inline washless polyelectrolytes multilayering

Polyelectrolytes system for the washless multilayering was cationic starch (CS) and anionic acrylamide (A-PAM). GCC suspension was diluted to 50 wt%, and the polyelectrolytes were diluted to 2 wt% for CS and 1 wt% for A-PAM. Inline washless polyelectrolytes multilayering was performed using the laboratory inline system presented in Fig. 5-1. This system consisted of three inline homogenizers (KT-30-KFC 30, Korea Process Technology Co., Ltd., Korea) and peristaltic pumps (EMP-2000S, E.M.S. Tech., Korea). There were two inlet and an outlet in each inline homogenizers. GCC suspension and CS solution were injected into the first homogenizer, and then the CS-treated GCC suspension was emitted from the outlet. Like this process, washless multilayering can be performed up to 3 layers. Main stream was GCC suspension, and addition level of polyelectrolytes based on dried weight of GCC can be controlled by flow rate of the polyelectrolytes solution at
the given flow rate of GCC suspension. Shear rate can be controlled by rotation speed of the homogenizer.

2.2.2 Handsheets preparation

Filled handsheets were prepared using a handsheet former (Square type). Target grammage of filled handsheets was 150 g/m² and target filler content was 20-30%. Fillers in this section were untreated GCC, C-starch/A-PAM 3 layers GCC prepared by conventional method in chapter 2, and washless C-starch/A-PAM 3 layers GCC. Retention system was micropolymer system. Fillers, C-PAM, and micropolymer were added into pulp stock in sequence. Addition level of C-PAM and micropolymer was 0.03% and 0.02% based on dried weight of fibers and fillers, respectively. In the case of untreated GCC condition, 1% of CS based on dried weight of fibers was an added as dry strength agent.

Filled hadnsheets were prepared by using the square handsheets former. After making wet sheets, 5 times couching, pressing at 3.5 bar using a laboratory press machine, and drying at 120°C using a cylinder dryer were conducted. The dried hadnsheets was pre-conditioned at 23±1°C and 50±2%RH more than 24 hr.
2.2.3 Measurement

2.2.3.1 Properties of inline washless PEM GCC

Zeta potential of PEM fillers was measured by using Zetasizer Nano ZS (Malvern, UK). PEM fillers were diluted to 0.1 g/L using 0.01 M NaCl at pH 9. Particle size was measured by using Mastersizer 2000 (Malvern, UK). In the measurement, PEM fillers were diluted to 0.01 g/L using 0.01M NaCl at pH 9. The average particle size was represented as volumetric average particle size.

Adsorbed amount of CS and A-PAM was evaluated by measuring concentration of unadsorbed polyelectrolytes in supernatant after centrifugation. The centrifugation condition was 20 min at 3000 G. The concentration of the unadsorbed polyelectrolytes in supernatant was estimated by measurement of chemical oxygen demand (COD) through colorimetric method kit (Test method 8000, HACH, USA) using spectrophotometer (DR 2800, HACH, USA). The concentration of the unadsorbed polyelectrolytes was calculated from calibration line of COD-polyelectrolytes concentration. Total adsorbed amount of polyelectrolytes was finally obtained using relationship between input-polyelectrolytes concentration and the concentration of unadsorbed polyelectrolytes in the supernatant.
2.2.3.2 Handsheets properties

Grammage and apparent thickness of filled handsheets were measured in accordance with TAPPI test methods T410 om-98 and T410 om-97, respectively. The apparent thickness was measured by using micrometer (L&W Co., Sweden). Apparent density of filled hadnsheets was calculated using the grammage and thickness values.

Fillers content in filled handsheets was evaluated by measurement of ash content using furnace in accordance with TAPPI test method T211 om-93. Filler distribution was observed by using Field Emission Scanning Electron Microscope (FE-SEM, SUPRA 55VP, Sweden).

Tensile strength of filled hadnsheets were measured by using tensile tester (L&W Co., Sweden) in accordance with TAPPI test method T494 om-96. Tensile index was calculated with measured grammage. Internal bond strength of filled handsheets was measured in accordance with TAPPI test method T569 pm-00 (Scott type internal bond strength).
2.3 Antibacterial PEM fillers

2.3.1 Formation of PVAm/PAA multilayer on kaolin

Kaolin particles was suspended to 30 wt% using 0.01 M NaCl solution. PVAm and PAA were diluted to 50 g/L using 0.01 M NaCl solution. Polyelectrolytes multilayering was performed as described in chapter 2. Addition level of PVAm and PAA was 3wt% based on oven dried kaolin weight. A first layer on negatively charged surface of kaolin particles was formed by adding cationic PVAm, and then anionic PAA was added to form a next second layer. Finally, PVAm/PAA multilayer on kaolin particle was formed with the repetitive laying process until 7 layers. The pH during polyelectrolytes multilayer (PEM) treatment was adjusted at pH 3.5 for adsorption steps of PVAm and pH 9.0 for adsorption steps for PAA.

Zeta potential and Particle size of the PEM kaolin were measured by using Zetasizer Nano ZS (Malvern, UK), and Malvern Mastersizer 2000 (Malvern, UK), respectively. The measurement was followed as described in chapter 2. Adsorbed amount of PVAm on kaolin particles was evaluated by analysis of nitrogen content using Kjeldahl Protein/Nitrogen Analyzer (Kjeltec Auto 1035/1038 System, Tecator AB, Sweden). As only PVAm contained nitrogen in this system, adsorbed amount of PVAm was calculated using PVAm concentration-
nitrogen content calibration line.

### 2.3.2 Preparation of antibacterial paper

Filled handsheets were prepared using a handsheet former (Square type). Target grammage of filled handsheets was 150 g/m² and target filler content was 20% for antibacterial test. Fillers used in this experiment were untreated kaolin, 3 layers PEM kaolin, and 7 layers PEM kaolin. Retention system was micropolymer system using C-PAM and micropolymer, and AKD was added for internal sizing effect. Addition levels of C-PAM, micropolymer, and AKD were 0.03%, 0.05%, and 0.1% based on dried fibers and fillers in pulp stock.

Surface treatment of PEM kaolin on filled handsheets was conducted through pigmentizing technique. Pigmentizing agent was prepared by mixing the 3 layers PEM kaolin and PVOH solution. Solids content of the pigmentizing agent was 24%, and mixing ratio was 1:1 based on dried weight of the 3 layers PEM kaolin particles and PVOH. There were two types of base paper: one was handsheets with untreated kaolin, and the other was handsheets filled with 3 layers PEM kaolin. The pigmentizing agent was coated on double sides of the base paper using rod coater, and the pigmentized handsheets were dried in a hot-air dryer at 120°C. Pick up weight of the mixture of the PEM kaolin and PVOH was 14.1±1.3 g/m² for low pick up weight condition and 27.5±0.4 g/m²
for high pick up weight condition. Surface images of the filled handsheets and the pigmentized handsheets were obtained from a field emission scanning electron microscope (FE-SEM, SUPRA 55VP, Sweden). Kaolin content in the filled handsheets and pigmentized handsheets were evaluated by measurement of ash content based on TAPPI test methods T 211 om-p93.

2.3.3 Antibacterial test

Antibacterial performance of three types of handsheets, control, filled handsheets, and pigmentized handsheets was compared. There were two controls: a bacteria suspension without handsheets (D.W.) and handsheets prepared made of only fibers (Pulp); three filled handshseets: handsheets filled with untreated kaolin (FU), handsheets filled with 3 layers PEM kaolin (F3L), and handsheets filled with 7 layers PEM kaolin (F7L); and three pigmentized handsheets: low pick up weight on F3L (PL_F3L), high pick up weight on F3L (PH_F3L), and high pick up weight on FU (PH_FU).

Antibacterial test of the filled handsheets and pigmentized handsheets was evaluated by measuring ratio of bacteria reduction in bacteria suspension in which the handsheets were soaked. Each handsheets were cut into approximately 0.5×0.5 cm square pieces. The accurately weighted 0.4 g of handsheets samples were soaked in 10 mL of deionized
water, and then 100 µL of the mixed culture of *E.coli* O157:H7 and *L. monocytogenes* was added. The initial bacteria fraction in the bacteria-added suspension was 10⁶-10⁷ CFU/mL for *E. coli* O157:H7 and 10⁵-10⁶ CFU/mL for *L. monocytogenes*. This bacteria suspension was incubated in D.W. with or without handsheets under shaking slowly for 18 hr at 23°C. After 18 hr incubation, 100 µL of the suspension was spread-plated onto selective media. Sorbitol MacConkey agar (SMAC; Difco) and Oxford agar base (OAB; Difco) with antimicrobial supplement (Bacto Oxford antimicrobial supplement; Difco) were used as selective media for enumeration of *E. coli* O157:H7 and *L. monocytogenes*, respectively. All plates were incubated at 37°C for 24 to 48 h before counting colonies characteristic of the pathogens.

2.3.4 Evaluation of cell membrane integrity after exposure onto antibacterial paper

A square handsheet of 1 cm × 1 cm was fixed on slide glass using double-side adhesive tape, and then 10 µL of *E.coli* O157:H7 culture (10⁷ – 10⁸ CFU/mL) was dropped onto the handsheet. This sample was placed in a closed chamber at 37°C and 99% relative humidity for 2 hr. Thereafter, 10 µL of a bacteria Live/Dead bacterial viability kit (L-7012, Molecular Probes, USA) solution was applied to the sample and the sample was stained for 30 min in the dark. The stained images were
obtained using confocal microscope (SP8 X, Leica, Germany). Emission light from viable cells and damaged cells was observed as green and red range, respectively.
3. Results & Discussion

3.1 Inline washless polyelectrolytes multilayering

3.1.1 Investigation on treatment conditions for inline washless process

Table 5-1 showed variables of treatment conditions for inline washless polyelectrolytes multilayering (PEM). Addition level of polyelectrolytes, flow rate of GCC suspension, and mixing speed were investigate to determine appropriate treatment condition for preparation of inline washless PEM GCC.

Table 5-1. Variables of treatment conditions for inline washless PEM

<table>
<thead>
<tr>
<th>Variables</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition level of polyelectrolytes</td>
<td>Cationic starch : 0.5 – 2.0%</td>
</tr>
<tr>
<td></td>
<td>A-PAM : 0.2 – 0.6%</td>
</tr>
<tr>
<td>Flow rate</td>
<td>Flow rate of GCC suspension :</td>
</tr>
<tr>
<td></td>
<td>1.0 - 2.5 L/min</td>
</tr>
<tr>
<td>Mixing speed</td>
<td>Peripheral speed : 12.5 - 36.1 m/sec</td>
</tr>
</tbody>
</table>
Effect of addition level of cationic starch on the first layering was shown in Fig. 5-2. Addition level of cationic starch was controlled by flow rate of cationic starch solution with maintaining flow rate of GCC suspension. As the addition level of cationic starch was increased, zeta potential and average particle size of the treated GCC were also increased (Fig. 5-2 (a) and (b)). Isoelectric point for the zeta potential was 1.5% of addition level of cationic starch based on dried weight of GCC. Even though the zeta potential changed to the positive at 2.0% addition level, the particle size increased (Fig. 5-2 (b) and (d)). This flocculation behavior was similar with polymeric bridge mechanism (Rojas and Hubbe 2004). This flocculation was mostly due to charge and structure properties of cationic starch, which was weak cationic and branched type. Flocs due to the bridge mechanism can be easily broken with higher shear and longer mixing time (Asselman and Garnier 2001, Hubbe 2005). It was necessary for dispersion of the treated GCC to control the time for exposure of the particles to hydrodynamic shear or induced shear rate in the inline washless PEM system. In addition, zeta potential would maintain its positive properties with redistribution onto surface of GCC although the flocculation was broken (Asselman and Garnier 2001). Adsorbed level of cationic starch was more than 90% regardless of addition level of cationic starch. This meant most cationic starch was associated with formation of the polymeric layer onto GCC. In spite of the flocculation, charges of GCC was inversed to the positive. This indicated that A-PAM added in next step can be adsorbed onto the
positively charged GCC. Therefore, addition level of cationic starch for the first layering was determined as 2.0%.

Fig. 5-2. Effect of addition level of cationic starch on (a) zeta potential, (b) adsorbed level of cationic starch, (c) average particle size, and (d) size distribution of treated GCC.
Fig. 5-3 showed effect of addition level of A-PAM onto cationic starch-treated GCC. The zeta potential results (Fig. 5-3 (a)) indicated that isoelectric point for the zeta potential was less than 0.2% addition level of A-PAM. It was estimated that adsorbed level of A-PAM was 100 % up to 0.2% addition level (Fig. 5-3 (b)). With addition of A-PAM more than 0.2%, however, numbers of A-PAM were not adsorbed onto the particles, thus these excess A-PAM would interfere that cationic starch added in next step (the third step) is adsorbed onto the particles. The particle size was decreased as addition level of A-PAM was increased (Fig. 5-3 (c) and (d)). This indicated that the flocculation from addition of cationic starch was reversible. As a result, addition level of A-PAM in the second step was determined as 0.2%.
Fig. 5-3. Effect of addition level of A-PAM onto cationic starch-treated GCC on (a) zeta potential, (b) adsorbed level of cationic starch, (c) average particle size, and (d) size distribution.
Addition level of cationic starch and A-PAM was determined as 2.0% for cationic starch in the first and third steps, and 0.2% for A-PAM in the second step. With this addition level of polyelectrolytes, influences of exposure time to shear and shear rate on properties of inline washless 3 layers GCC were investigated. Fig. 5-4 presented the effect of exposure time to shear by controlling flow rate of GCC suspension at given shear rate. The exposure time to shear becomes short as fast as flow rate of GCC suspension. Zeta potential of the inline washless 3 layers GCC was finally the positive, but independent on the flow rate of GCC suspension. However, particle size and total adsorbed amount of cationic starch and A-PAM were affected by the flow rate of GCC suspension. As the flow rate of GCC suspension was decreased, the average particle size of the inline washless 3 layers GCC and adsorbed amount of cationic starch and A-PAM were decreased. These indicated that flocs of the treated GCC can be broken with increasing the exposure time to shear, and some of polyelectrolytes were detached. These phenomenon were agreed with polymer transfer mechanism due to shear (Asselman and Garnier 2001). According to Asselman and Garnier (2001), flocs of fibers and fines with polymeric bridge are broken with shear, and then the polymers onto surface of fibers and fines are redistributed onto the surfaces. In other words, the polyelectrolytes onto the surface of GCC were redistributed, thus zeta potential was still positive even though some of polyelectrolytes were detached.
Fig. 5-4. Properties of inline washless 3 layers GCC as a function of flow rate of GCC suspension, (a) zeta potential, (b) total adsorbed amount of cationic starch and A-PAM, (c) average particle size, and (d) size distribution.
The shear rate during inline washless multilayering was controlled by rotation speed of inline mixer. Fig. 5-5 showed zeta potential of inline washless 3 layers GCC and total adsorbed amount of cationic starch and A-PAM depending on the rotation speed at given flow fate of GCC suspension. The zeta potential was independent on the rotation speed, some of polyelectrolytes were detached as the shear became stronger. However, this detachment of polyelectrolytes did not affect the zeta potential like influence of flow rate of GCC suspension. Average particle size was also decreased up to 11 μm (Fig. 5-7 and Fig 5-8), and the variation of particle size was large in comparison with influence of flow rate of GCC suspension. As a result, particle size of the inline washless PEM GCC can be controlled by shear condition without change in zeta potential.

Fig. 5-9 showed zeta potential and average particle size of cationic starch/A-PAM GCC prepared from conventional PEM treatment in chapter 3 and inline washless C-starch/A-PAM GCC. The treatment condition for the inline washless C-starch/A-PAM GCC in Fig. 5-9 was that flow rate of GCC suspension was 2.0 L/min, and rotation speed of the inline mixer was 18.7 m/sec. The zeta potential pattern of the inline washless C-starch/A-PAM GCC was similar with that of the C-starch/A-PAM GCC (conventional treatment). Therefore, this continuous inline washless system can be appropriate PEM process for field application.
Fig. 5-5. Zeta potential of inline washless 3 layers GCC (a) and adsorbed amount of cationic starch and A-PAM (b) depending on rotation speed.
Fig. 5-6. Particle size of inline washless 3 layers GCC.

Fig. 5-7. Optical microscopic images of inline washless 3 layers GCC prepared at (a) 12.5 m/sec, (b) 18.7 m/sec, (c) 27.4 m/sec, and (d) 36.1 m/sec.
Fig. 5-8. Patterns of (a) zeta potential and (b) average particle size of C-starch/A-PAM GCC (conventional treatment) and inline washless C-starch/A-PAM GCC.
### 3.1.2 Effect of inline washless PEM GCC on strength of filled paper

Table 5-2 showed properties of untreated GCC and two types of PEM GCC used for preparation of filled handsheets. PEM GCC was prepared from conventional multilayering of C-starch/A-PAM 3 layers. Inline PEM GCC was prepared from inline washless polyelectrolytes multilayering of C-starch/A-PAM 3 layers. These two PEM GCC had positive charges, and the inline PEM GCC showed larger particle size due to flocculation during washless PEM treatment than PEM GCC. Unlike chapter 2 and 3, cationic starches were used as a dry strength agent for handsheets filled with untreated GCC. The addition level of cationic starch was 1 wt% based on oven dried (O.D) weight of fibers.

<table>
<thead>
<tr>
<th>Addition level of polyelectrolytes, %</th>
<th>Untreated GCC</th>
<th>PEM GCC</th>
<th>Inline PEM GCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>cationic starch</td>
<td>-</td>
<td>3.5×2</td>
<td>2.0×2</td>
</tr>
<tr>
<td>A-PAM</td>
<td>-</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Average particle size, μm</td>
<td>2.0</td>
<td>3.3</td>
<td>11.0</td>
</tr>
<tr>
<td>Zeta potential, mV</td>
<td>-32.3</td>
<td>+3.5</td>
<td>+9.6</td>
</tr>
</tbody>
</table>

Table 5-2. Properties of untreated GCC and two types of PEM GCC
Fig. 5-9 presented surface images of filled handsheets with around 25% ash content. Untreated GCC particles were relatively well distributed on the surface of handsheet (Fig. 5-9 (a)). This was due to addition of cationic starch used as a dry strength agent before addition of untreated GCC to pulp stock when handsheets were made. The added cationic starch gave partially positive charges to fibers, thus some of negatively charged untreated GCC deposited onto the partially positive surface of fibers. This provided relatively good distribution of untreated GCC in spite of very strong flocculation ability of the micropolymer retention system. On the other hands, there were more fillers aggregates in the both cases of PEM GCC (Fig. 5-9 (b) and (c)). However, it seemed that there was no difference between PEM GCC and inline PEM GCC for the degree of aggregates.

Fig. 5-10 showed apparent bulk of filled handsheets. Handsheets filled with untreated GCC showed higher bulk than handsheets filled with two types of PEM GCC. It was considered that the better distribution of untreated GCC particles provided more interference of fibers bonding resulting in the higher bulk. The bulk of handsheets filled with the two types of PEM GCC was similar at the same ash content.
Fig. 5-9. Surface images of handsheets filled with (a) untreated GCC, (b) C-starch/A-PAM 3 layers GCC, and (c) inline washless C-starch/A-PAM 3 layers GCC at around 25% ash content.

Fig. 5-10. Apparent bulk of filled handheets.
Fig. 5-11 presented tensile index and internal bond strength of filled handsheets. PEM GCC gave higher mechanical properties than untreated GCC with using dry strength agent at given ash content. Even though the influence of dry strength agent was somewhat offset due to higher bulk properties, the results for mechanical properties implied that PEM was more effective for strength improvement of filled paper than conventional treatment of dry strength agent. Inline PEM GCC gave higher strengthening effect than PEM GCC, especially for the internal bond strength. Even though inline PEM GCC had larger particle size, distribution of filler particles was similar between PEM GCC condition and inline PEM GCC condition (Fig. 5-9). Thus, higher strength properties of inline PEM GCC condition was related to amount of polyelectrolytes in the multilayer rather than aggregation of particles during washless PEM process. Total amount of cationic starch and A-PAM in the C-starch/A-PAM 3 layers were around 32 mg per gram of GCC, implying more than 50% of added polyelectrolytes were removed during washing step. On the other hands, all polyelectrolytes added to GCC suspension remained in the GCC suspension in the case of inline PEM GCC. Even though total amount of polyelectrolytes added for 3 layers of inline PEM GCC were less than those for 3 layers of PEM GCC, more than 80% of polyelectrolytes were adsorbed on GCC (around 35 mg per gram of GCC in this case). In addition, the excess polyelectrolytes, i.e. unadsorbed polyelectrolytes might act like strength agent. Therefore, inline washless PEM treatment had economically advantages of not only installation of PEM process to papermaking
industry but also consumption of polyelectrolytes.

Fig. 5-11. Tensile index (a) and internal bond strength (b) of filled handsheets.
3.2 Antibacterial effect of PEM fillers

3.2.1 Properties of PVAm/PAA kaolin and its effect on paper strength

Zeta potential of the PEM kaolin showed the positive at odd layers in which cationic PVAm was outermost layer, and the negative at even layers in which anionic PAA was outermost layer (Fig. 5-12 (a)). During polyelectrolytes multilayering, there was no aggregates of particles (Fig. 5-12 (b)). The cumulative adsorbed amount of PVAm at 7 layers was higher than that at 3 layers (Fig. 5-12 (c)). These facts indicated alternate formation of PVAm and PAA onto individual kaolin particles.

PVAm is also known to be used for dry strength agent (Lindström et al. 2005, Pelton 2014). This strengthening effect worked on also filled paper. Fig. 5-13 showed tensile index and internal bond strength of handsheets filled with PVAm/PAA kaolin. PVAm/PAA multilayering provided strength improvement of filled paper like other multilayering system, e.g. PDADMAC/PSS and C-starch/A-PAM as described in chapter 3. The more PVAm was in the multilayer, the higher strength was given. As a result, PVAm/PAA kaolin can provide strong mechanical properties as well as antibacterial activity.
Fig. 5-12. Properties of PVAm/PAA kaolin, (a) zeta potential, (b) average particle size, and (c) amount of PVAm in the multilayer.
Fig. 5-13. Tensile index (a) and internal bond strength (b) of handsheets filled with PVAm/PAA kaolin.
3.2.2 Antibacterial effect

Conditions of paper fabricated for evaluation of antibacterial activity was presented in Table 5-3. There were three groups, control, filled handsheets, and pigmentized handsheets. Antibacterial activity was compared depending on layer number and application way of PEM kaolin, i.e. internal addition or surface treatment.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Notation</th>
<th>Condition</th>
<th>Ash content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>Blank</td>
<td>A bacteria suspension without handsheets</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Pulp</td>
<td>Handsheets prepared made of only fibers</td>
<td>-</td>
</tr>
<tr>
<td>Filled handsheets</td>
<td>FU</td>
<td>Handsheet with untreated kaolin</td>
<td>20.4</td>
</tr>
<tr>
<td></td>
<td>F3L</td>
<td>Handsheet with 3 layers PEM kaolin</td>
<td>22.3</td>
</tr>
<tr>
<td></td>
<td>F7L</td>
<td>Handsheet with 7 layers PEM kaolin</td>
<td>20.1</td>
</tr>
<tr>
<td>Pigmentized handsheets</td>
<td>PL_F3L</td>
<td>Low pick up weight on F3L</td>
<td>23.8</td>
</tr>
<tr>
<td></td>
<td>PH_F3L</td>
<td>High pick up weight on F3L</td>
<td>25.7</td>
</tr>
<tr>
<td></td>
<td>PH_FU</td>
<td>High pick up weight on FU</td>
<td>24.8</td>
</tr>
</tbody>
</table>
Fig. 5-14 showed surface images of filled handsheets with untreated kaolin, 3 layers PEM kaolin and 7 layers PEM kaolin, and pigmentized handsheets treated on surface of filled handsheets with 3 layers PEM kaolin. Untreated kaolin, 3 layers PEM kaolin, and 7 layers PEM kaolin particles were seen at the surface of filled handsheets (Fig.5-14 (a), (b), and (c), respectively). Although those filled handsheets contained around 20-22% of kaolin, a little amount of PEM kaolin existed at surface of the filled handsheets. On the other hands, surface of pigmentized handsheets was almost fully covered by 3 layers PEM kaolin (Fig.5-14 (d), (e), and (f)). Increment of 3 layers PEM kaolin content after pigmentizing was 1.5%, 3.4%, and 4.4% for PL_F3L, PH_F3L, and PH_FU, respectively. In other words, coverage of PEM kaolin was much better in the cases of pigmentized handsheets despite of a little increment of kaolin content.
Fig. 5-14. Surface images of (a) FU, (b) F3L, (c) F7L, (d) PL_F3L, (e) PH_F3L, and (f) PH_FU. Parenthesis means kaolin content.
Fig. 5-15 depicted concentration of alive \textit{E.coli} (Fig. 5-15 (a)) and \textit{L. monocytogenes} (Fig.5-15 (b)) in only bacteria suspension (D.W. condition) and handsheets-soaked bacteria suspension (other conditions) without nutrient after incubation for 18 hr. Blank condition maintained its initial bacteria concentration (10^6-10^7 \text{ CFU/mL} for \textit{E. coli O157:H7} and 10^5-10^7 \text{ CFU/mL} for \textit{L. monocytogenes}). Both of \textit{E.coli} and \textit{L. monocytogenes} were still alive after 18 hr incubation without nutrient. Bacteria concentration in Pulp condition and filled handsheets conditions (PU, F3L, F7L) were decreased but the reduction was small. It seemed that almost bacteria were still alive in the conditions of F3L and F7L despite exposure of handsheets filled with 3 layers or 7 layers PEM kaolin. On the other hands, pigmentized handsheets decreased bacteria concentration. Reduced population of the bacteria was more than 10^6 \text{ CFU/mL} for \textit{E.coli O157:H7} and 10^5 \text{ CFU/mL} for \textit{L. monocytogenes}. In addition, PH\_F3L and PH\_FU (high pick up weight condition) more decreased bacteria than PL\_F3L (low pick up weight condition) regardless of types of base handsheets. As a result, pigmentized handsheets gave much reduction of the bacteria population.
Fig. 5-15. Alive bacteria population for (a) *E.coli* O157:H7 and (b) *L. monocytogenes* in handsheets-soaked bacteria suspension after 18 hr incubation.
Table 5-4 showed antibacterial activity of filled handsheets and pigmentized handsheets as a reduction ratio of bacteria population compared to remaining bacteria population of blank condition. Filled handsheets with 3 layers PEM kaolin or 7 layers PEM kaolin had poor antibacterial activity, whereas pigmentized handsheets with surface treatment of 3 layers PEM kaolin provided good antibacterial activity more than 99.9% for *E. coli* and 99% for *L. monocytogenes*.

Table 5-4. Antibacterial activity described as reduction ratio of bacteria population compared to remaining bacteria population of blank condition. Symbols of -, +, ++, and +++ mean less than 90%, 90-99%, 99-99.9%, and more than 99.9%, respectively.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Notation</th>
<th>Condition</th>
<th>Performance</th>
<th>E. coli</th>
<th>L. monocytogenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>Pulp</td>
<td>Only pulp (without fillers)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>PU</td>
<td>Untreated kaolin</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Filled</td>
<td>F3L</td>
<td>3 layers PEM kaolin</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Handsheets</td>
<td>F7L</td>
<td>7 layers PEM kaolin</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pigmentized</td>
<td>PL_F3L</td>
<td>Low pick up weight on F3L</td>
<td>+++</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Handsheets</td>
<td>PH_F3L</td>
<td>High pick up weight on F3L</td>
<td>+++</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>PH_PU</td>
<td>High pick up weight on FU</td>
<td>+++</td>
<td>++</td>
<td>-</td>
</tr>
</tbody>
</table>
Antibacterial mechanism of PVAm is contact active mechanism, which contact active surface kills bacteria directly with physical interaction (Illergård et al. 2015). It was inferred that the reason of poor antibacterial activity for filled hadnsheets was coverage of PEM kaolin on surface of handsheet. Pigmententized handsheets which were fully covered with PEM kaolin had great performance to kill bacteria. It is known that bacteria have amphoteric charge properties due to such a carboxyl, phosphate, or amino groups (van der Wal et al. 1997). van der Wal, et al (1997) reported that isoelectric point of gram-positive bacteria is weak acid condition around pH 3-4. Charge of bacteria in this antibacterial test would be negative because the pH range of the bacteria suspension used in this study was neutral. Therefore, positive surface of the pigmentized handsheet with the 3 layers PEM kaolin was so easy to immobilize bacteria that the pigmentized handsheet had great chance to kill bacteria. On the other hands, PEM kaolin was partially covered on surface of filled handsheets, although more than 20% of PEM kaolin was contained in the filled handsheets. This indicated that bacteria had low possibility to encounter only the PEM kaolin even if all of bacteria was immobilized on surface of filled handsheets. The reduction ratio of bacteria was approximately 30% for \textit{E.coli} and 90% for \textit{L. monocytogenes} in the case of filled handsheets with 3 layers PEM kaolin. It was considered that only bacteria immobilized onto sites of the PEM kaolin particles on surface of the filled handsheet were killed. As a results, surface treatment of PEM kaolin was much more effective for good antibacterial activity than internal addition of PEM kaolin.
It would be possible that decrease in bacteria population in the bacteria suspension was due to not inactivation of bacteria but just immobilization of bacteria onto surface of pigmentized handsheets. Thus, it was necessary to confirm the inactivation of the immobilized bacteria onto the handsheets surface. Fig.5-16 showed the stained *E. coli* O157:H7 immobilized onto surface of filled handsheets with untreated kaolin ((a) and (b)) and pigmentized handsheets with 3 layers PEM kaolin ((c) and (d)) using a bacteria Live/Dead bacterial viability kit. This staining kit is mixture of SYTO9 and propidium iodide (PI). SYTO9 (green color) labels all bacteria with intact membranes or with damaged membranes due to diffusion of SYTO9 into membrane, whereas PI (red color) can penetrate only damaged membranes and label DNA inside bacteria membranes. *E. coli* O157:H7 immobilized onto the surface of filled handsheets with untreated kaolin was stained by only SYTO9 (green color, Fig.5-16 (a)). This meant that all *E. coli* O157:H7 was alive. On the other hands, *E. coli* O157:H7 onto the pigmentized handsheets with 3 layers PEM kaolin was stained by both of SYTO9 (Fig.5-16 (c)) and PI (red color, Fig.5-16 (d)). This indicated that membrane of the *E. coli* O157:H7 onto the pigmentized handsheets was damaged, that is bacteria were dead. Therefore, it was demonstrated that pigmentized handsheets could inactivate pathogens and the antimicrobial mechanism would be the membrane damage.
Fig. 5-16. Bacteria membrane integrity of *E. Coli* O157:H7 on filled handsheets with untreated kaolin ((a) and (b)) and pigmentized handsheets treated with 3 layers PEM kaolin ((c) and (d)) after exposure for 2 hr.
4. Summary

Two different application of polyelectrolytes multilayering (PEM) were discussed in this chapter. One was washless PEM for mill application. Inline system for the washless PEM on fillers was designed, and appropriate treatment condition to operate the inline system was investigated. For the multilayering, cationic starch and A-PAM were used. Zeta potential of the treated GCC at each layers were controlled by addition level of polyelectrolytes. Addition level of cationic starch and A-PAM was 2 wt% and 0.2 wt% based on oven dried weight of GCC, and this addition level gave charge inversion at each layers with more than 80% of adsorption level. The zeta potential patterns was similar with zeta potential of conventional PEM GCC, but there were some flocculation of GCC particles during inline washless PEM. This flocculation can be broken through shear as far as it goes. Inline washless PEM GCC provide a little more effective strength improvement than conventional PEM GCC. Inline washless PEM led to efficient polyelectrolytes usage in the way that all polyelectrolytes would be associated with strength improvement of filled paper, while more than half of polyelectrolytes were removed in the case of conventional PEM treatment. However, these unadsorbed polyelectrolytes should be minimized for mill application of PEM treatment because these excess polyelectrolytes might result in problems such as polyelectrolytes complexes.
The other application of PEM was fabrication of antibacterial paper using PEM fillers. It is known that PVAm is one of the polyelectrolytes that can give antibacterial activity. In this chapter, PEM treatment using PVAm on kaolin particles was performed and appropriate strategy to apply the PEM treated kaolin to fabricate antibacterial paper was investigated. PVAm/PAA multilayer was successfully formed onto kaolin particles, and this PEM kaolin gave antibacterial activity to paper. Surface treatment of kaolin treated with PVAm/PAA multilayer on paper was much better for antibacterial activity than internal addition of the treated kaolin to paper. It seemed that surface coverage of the treated kaolin on paper was important factor for antibacterial effect. It was demonstrated that bacteria immobilized onto surface of the treated kaolin treated paper were inactivated with damaging membrane through bacteria staining method.
Chapter 6.

Overall Conclusions
The objectives of this study was to investigate mechanism for strengthening effect of polyelectrolytes multilayer on filled paper, and to present application of polyelectrolytes multilayering (PEM) technique for mill application and antibacterial activity as functionality. To achieve higher strength of highly filled paper, more effective approach between PEM treatment on fibers and PEM treatment on filler particles was investigated. In addition, influences of PEM treatment on filler particles were examined from bonding ability point of view. Factors affecting strength improvement of paper filled with PEM fillers were investigated with respect to multilayer characteristics controlled by salt concentration, nature of polyelectrolytes, and morphology of fillers. For mill application, inline system for the washless PEM on fillers was designed, and appropriate treatment condition to operate the inline system was investigated. In addition, fabrication of antibacterial paper using PEM treated fillers was presented as one of the application of PEM technique in the papermaking.

Both cases of PEM treatment on fibers and PEM treatment on fillers provided improved strength of filled paper. This improvement of the strength was due to effect of polyelectrolytes multilayer on strength. However, the effect of PEM treatment on the strength was dependent on the filler content and the substrate type in PEM treatment. PEM treatment on pulp fibers was more effective to improve strength of filled paper at relatively low level of fillers loading. This was due to enhancement of joint strength of PEM treated fibers. This strengthening effect on fibers
joint enabled to maintain high strength of filled paper with relatively low filler content. On the other hands, PEM treatment on fillers was more effective for strength of highly filled paper. PEM treatment of fillers affected bonding strength between fiber and filler as well as bonding strength between fillers. PEM treated GCC showed lower specific debonding factor than untreated GCC, indicating less impact on weakening bonds between fiber and filler. PEM treatment on fillers also improved bonding strength between fillers. This was confirmed by measurement of flexure strength of dense film composed of filler particles. As a results, it was expected that PEM treatment on filler particles was more appropriate approach for high filler loading.

Factors affecting strength improvement of filled paper were investigated depending on multilayer characteristics controlled by salt concentration, nature of polyelectrolytes, and morphology of fillers. Control of salt concentration during construction of multilayer affected both of properties of PEM treated fillers and strength of paper filled with PEM treated fillers. Relatively high salt concentration, 0.1 M NaCl, gave higher adsorption amount of PDADMAC and PSS and thicker PDADMAC/PSS multilayer than relatively low salt concentration, 0 M and 0.01 M NaCl. In addition, PDADMAC/PSS multilayer at high salt concentration showed bulkier properties than PDADMAC/PSS multilayer at low salt concentration. Strength of paper filled with PDADMAC/PSS GCC depended on the amount of PDADMAC in the multilayer formed onto GCC. The more adsorbed amount of PDADMAC
gave the high strength improvement of filled paper. It was expected that high salt concentration up to 0.1 M NaCl provided better strengthening effect on filled paper with higher amount of polyelectrolytes in multilayer in the case of strong polyelectrolytes.

C-starch/A-PAM multilayer provided greater strengthening effect on filled paper than PDADMAC/PSS multilayer given layer number. However, the PDADMAC /PSS 7 layers at 0.1 M NaCl showed similar strengthening effect with C-starch/A-PAM 3 layers. These two cases of multilayer showed similar amount of polyelectrolytes in the multilayer and thickness around 15 nm, but it was considered that there were different mechanisms to provide strengthening effect. C-starch/A-PAM multilayer showed bulkier properties resulting in more molecular interdiffusion, and can produce numerous hydrogen bonding. On the other hands, it was considered that PDADMAC /PSS multilayer can produce strong Coulombic interaction with anionic charges at surface of fibers when the PDADMAC was in the outermost layer. In addition, PDADMAC /PSS multilayer had stronger intra-bonding due to strong electrostatic attraction between PDADMAC and PSS inside the multilayer than C-starch/A-PAM multilayer. Characteristics of multilayer as well as adsorbed amount of polyelectrolytes can be dominant factors affecting strength of filled paper.

Influences of PEM treatment depending on morphological characteristics of fillers were investigated. PEM can be successfully formed on irregular types of GCC as well as scalenohedral types of PCC.
and platy types of kaolin. PEM treatment gave strengthening effect to all three different types of fillers. However, degree of the strength improvement was dependent on morphology of fillers. The platy type of kaolin showed the highest strengthening effect of PEM treatment. Open structured fillers like PCC showed less strengthening effect than solid types of fillers such as GCC and kaolin. It was considered that the smoother surface of fillers was the proper for multilayer to interact with surface of fibers or surface of other particles.

Inline washless PEM system was designed as one of applicable process for mill application. This inline washless PEM system consisted of three inline mixer and peristaltic pumps, thus multilayering can be perfomed up to 3 layers. Appropriate treatment condition in laboratory scale was investigated. Zeta potential can be controlled by addition level of polyelectrolytes, and particle size was dependent on control of shear in the inline mixer. 3 layers of multilayer can be formed onto GCC with fast and continuous treatment of polyelectrolytes. Inline washless PEM GCC provided a little more effective strength improvement than conventional PEM GCC. This was because of efficient polyelectrolytes usage in the way that all polyelectrolytes would be associated with strength improvement of filled paper no matter whether polyelectrolytes were adsorbed onto GCC or not.

Fabrication of antibacterial paper using PEM fillers was also suggested as one of application of PEM technique in the papermaking. PVAm/PAA multilayering was performed onto kaolin particles because PVAm is
known to be one of polyelectrolytes that shows antibacterial activity. PVAm/PAA kaolin provided antibacterial activity as well as strength improvement. Surface treatment of the PVAm/PAA kaolin on paper showed much greater antibacterial activity than internal addition of PVAm/PAA kaolin.
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초 록

무기 입자 충전물은 제지분야에서 인쇄용지나 백상지 제조에 사용되는 가장 중요한 원료 중 하나이다. 충전물의 적용은 종이의 강도를 감소시키나, 종이의 광학적 특성, 평활성, 인쇄적성 등을 향상시킬 수 있으며 건조에너지와 종이 제조 원가를 줄일 수 있다. 따라서, 종이의 강도 감소를 최소화하면서 충전물 함량을 늘릴 수 있는 충전물 하이로딩 기술에 대한 연구가 필요한 실정이다. 본 연구에서는 충전물 하이로딩을 위한 고분자전해질 다층박막 형성 (Polyelectrolytes multilayering, PEM) 기술 적용 가능성에 대한 탐색과 더불어 고충전지의 강도 향상 기작에 대해 구명하고, 실제 제지 산업에 적용 가능한 PEM 방안과 PEM 기술을 이용한 항균성 적용 방안에 대해서 제시하고자 하였다.

고충전지에 적합한 PEM 전략을 수립하고, 다층흡착기술에 따른 고충전지 강도 향상 기작을 구명하고자 하였다. 펄프 섬유 또는 충전물에 대한 다층박막 형성은 둘 다 종이의 강도를 향상시킬 수 있었으나, 강도 향상에 대한 효과는 충전물 함량에 따라 달랐다. 펄프 섬유에 대한 다층박막 형성은 충전물 함량이 낮은 조건에서 강도 향상에 더 효과적이었으며, 충전물 함량이 높아질수록 강도 향상 정도는 미비하였다. 반대로 충전물에 대한 다층박막 형성은 충전물 함량이 높은 종이의 강도를 향상시키는 데에 더 효과적이었다. 이는 모델화지의 박리강도 측정을 통한 충전물과 섬유간 결합력 평가와 충전물로만 구성된 필름의 과파강도 측정을 통한 충전물간 결합력 평가를 통해 충전물 표면에 형성된 다층박막에 의해 충전물과 섬유간, 충전물간 결합력이 증가하여 고충전 종이의 강도가 향상된 것으로 밝혀졌다.
충전물 표면에 형성된 다층박막의 특성과 충전물의 종류가 종이의 강도 향상에 미치는 영향에 대해서 살펴보고자 하였다. 농도가 높아질수록 PDADMAC과 PSS의 흡착량을 향상시킬 수 있었으며 이로 인해 다층박막의 두께를 증가시킬 수 있었다. 이러한 다층박막의 두께 증가를 통해 종이의 강도를 더욱 향상시킬 수 있었다. 동일한 충의 다층박막 형성 조건에서는 PDADMAC 보다는 양성전분이 다층박막 최외각층에 존재할 때 종이의 강도 향상에 더욱 효과적이었다. 그러나 PDADMAC/PSS 조합도 0.1 M NaCl 조건에서 7 레이어까지 다층박막을 형성하면 양성전분/A-PAM 조합 3 레이어 조건과 유사한 수준의 강도 향상을 나타낼 수 있었다. 양성전분 조합의 다층박막은 주로 수소결합 생성을 통해 강도를 향상시킨 것으로 판단되며, PDADMAC 조합의 다층박막은 고분자전해질 사슬에 의한 interdiffusion 현상, van der Waals 결합과 coulomb 결합 형성에 의해 강도를 향상시키는 것으로 판단되었다. 표면 형상이 상이한 무정형의 중질탄산칼슘, 침상형의 경질탄산칼슘, 판상형의 카울린 충전물에 각각 다층박막을 형성하였으며, 충전물 형상이 종이 강도에 미치는 영향을 구명하였다. 판상형의 카울린에 다층박막을 형성한 경우 가장 높은 강도 향상을 나타내어, 충전물 입자의 표면이 매끄러워수록 다층박막이 종이의 강도를 향상시키는 데에 더 효과적인 것으로 판단되었다.

PEM 기술의 현장 적용 방안을 위해 세 대의 인라인 미세와 펌프로 구성된 연속식의 무세척 다층박막 형성 시스템 (Inline washless PEM system)을 제안하였다. 본 시스템을 통해 제조한 개질 충전물 역시 종이 적용 시 높은 강도 향상을 나타내었다. 이러한 결과를 토대로 연속식의 무세척 다층박막 형성 시스템은 실제 제조 현장에 적용하기에 적합한 것으로 판단되었다.
PEM 기술의 폭 넓은 활용을 위한 방안으로 항균성 종이 제조 방안을 제시하고자 하였다. PVAm/PAA 다층막막이 형성된 카울린 입자를 내침한 종이의 박테리아 제거 효율은 90% 미만으로 항균 특성을 나타내지 않았지만, 종이에 표면처리 하면 경우 99% 이상의 박테리아 제거효율을 나타내어 우수한 항균 특성을 나타내었다. 이러한 항균 특성을 나타내는 개질 카울린은 종이의 강도 역시 향상시킬 수 있어, 종이의 강도 향상뿐만 아니라 종이에 항균성을 부여할 수 있는 것으로 여겨졌다.

본 연구를 통해 충전물에 대한 고분자전해질 다층막막 형성 특성을 이해하고, 다층막막이 충전지의 강도를 향상시키는 기작에 대해 구명할 수 있었다. 또한 고분자전해질 다층막막 형성 기술을 실제 산업으로 적용하기 위한 처리 방안과 고분자전해질 다층막막 형성 기술을 통해 종이에 항균성과 같은 기능성을 부여할 수 있는 가능성이 제시되었다.

주요어: 고분자전해질, 다층막막, 충전물, 고충전지, 종이 강도, 무세척 고분자전해질 다층흡착처리, 항균성

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