Deposition Behavior of LbL Multilayered GCC Particles on Pulp Fibers

Jegon Lee, Jungeon Ahn, Hak Lae Lee, Hyeyoon Lee, and Hye Jung Youn *

The effects of ground calcium carbonate (GCC) modification through the polyelectrolyte multilayering technique on deposition kinetics were investigated. The surface charge of GCC particles was changed from negative to positive through Layer-by-Layer (LbL) multilayering with polyelectrolytes on GCC particles. The LbL multilayered GCC particles could deposit onto negatively charged cellulose fibers due to electrostatic attraction. Deposition kinetics followed modified Langmuir kinetics, which describe the dynamic equilibrium of deposition and detachment of the particles. The multilayer that had more affinity to the fibers had the higher deposition rate constant. The multilayer with a branched polyelectrolyte showed a low detachment rate constant compared to the linear polyelectrolyte, which led to a high equilibrium deposition amount for the particle. Application of high shear had adverse effects on deposition. However, LbL multilayered GCC particles showed reversible deposition characteristics after lowering the stirring speed.

Keywords: GCC particles; Cellulose fiber; Polyelectrolyte multilayer; Deposition; Langmuir kinetics

Contact information: Department of Forest Sciences, College of Agriculture and Life Sciences, Seoul National University, 1, Gwanak-ro, Gwanak-gu, Seoul, 151-921 (Korea);
** Corresponding author: page94@snu.ac.kr*

INTRODUCTION

Inorganic filler particles such as calcium carbonate and clay are widely used in the papermaking industry. The purpose of adding fillers to fiber suspensions are to improve the optical properties and printability of paper and to save production costs and drying energy by replacing the fibers. For these reasons, it is very important to increase the filler content of the paper in the papermaking process. However, an increase in the inorganic particle content in the filled paper is accompanied by two negative effects. The first is a decrease in the retention level of the particles, and the second is a decrease in strength of the paper due to a very weak bonding between the fiber and particle. Therefore, it has been proposed that, by treatment with suitable water-soluble polymers, the content of the inorganic particles in the filled paper may be increased without deteriorating the retention level (Antunes *et al.* 2008; Bernier and Begin 1994) and mechanical strength of the filled paper (Mabee and Harvey 2000; Shen *et al.* 2009).

The pre-flocculation technique (Blanco *et al.* 2005; Im *et al.* 2013; Lee and Lee 2006; Mabee and Harvey 2000; Seo *et al.* 2012) and the modification of the surface of inorganic particles (Yan *et al.* 2005; Yoon and Deng 2006; Zhao *et al.* 2005) have been considered to overcome the negative effects of filler particles on filled paper. Pre-flocculation secures the fiber-fiber bonding area through the flocculation of inorganic fillers in advance of adding them to the papermaking stock. However, pre-flocculation is limited by the absence of good bonding between the fiber and the agglomerate of particles. The surface modification of particles enables them to bond with the fibers by generating additional bonds such as electrostatic attraction and hydrogen bonds. The surface modification also has the possibility to change the colloidal characteristics of the particles.

Layer-by-Layer (LbL) multilayering (Decher and Hong 1991) provides an alternative way to modify the surface of a substrate. The LbL multilayering technique with polyelectrolytes has been applied to planar substrates (Decher *et al.* 1992; Srivastava *et al.* 2008) and colloidal spheres (Caruso and Gittins 2001; Khopade and Caruso 2003; Radeva *et al.* 2002; Wong *et al.* 2009) to change their surface properties. The application of LbL multilayering to the field of papermaking have been reported (Wågberg *et al.* 2002; Torgnysdotter and Wågberg 2003; Eriksson *et al.* 2005; Ryu *et al.* 2011). LbL multilayering on fibers remarkably increased the mechanical strength of paper in the cited studies. As for the LbL multilayering on filler particles, the surface charge of the inorganic particles could be changed by the type of polyelectrolytes or layer number (Lee *et al.* 2011). Furthermore, the mechanical strength of filled paper with LbL multilayered particles was improved at the same filler levels compared to filled paper with untreated ground calcium carbonate (GCC) particles (Ahn *et al.* 2012). This may be the result of additionally generated bonding between the particle and the fiber. However, previous reports about the application of LbL multilayered GCC were focused on properties of LbL multilayered GCC and their effect on paper strength (Ahn *et al.* 2012). For effective application of the LbL multilayered GCC to papermaking field, it is necessary to comprehend the deposition behavior of the LbL multilayered GCC.

Analyses of the behavior of filler particles have been reported in several studies using a modified Langmuir theory (Alince *et al.* 1991; Alince and van de Ven 1993; Kamiti and van de Ven 1994; Liimatainen *et al.* 2009; Vanerek *et al.* 2000). Alince *et al.* (1991) reported the kinetics for the deposition of clay particles on fibers. However, the detachment of the particles was not considered (Alince *et al.* 1991; Alince and van de Ven 1993). Deposition kinetics of positively charged precipitated calcium carbonate (PCC) particles was investigated by considering deposition and detachment (Kamiti and van de Ven 1994; Liimatainen *et al.* 2009; Vanerek *et al.* 2000). However, the deposition phenomenon of LbL multilayered filler was not investigated. The deposition kinetics of the LbL multilayered particles is expected to be determined by the multilayer characteristics on the particles and process variables such as shear. Therefore, the effects of polyelectrolyte types, molecular weight, layer number, and shear on deposition behavior of the LbL multilayered particles on fibers were investigated using a modified Langmuir theory in this study. Results of the study will contribute to a better understanding of the deposition mechanism of LbL multilayered GCC and the establishment of effective application strategy, including a retention system for filler high-loading of paper.

The Modified Langmuir Theory

The Langmuir theory was developed for the adsorption of gases onto solid surfaces (Langmuir 1918) and has been modified for reversible deposition of particles on fibers in an aqueous system (Alince *et al.* 1991). The modified Langmuir theory is a suitable model for deposition kinetics of filler particles onto a fiber surface. In a shear-induced aqueous system, bonds between the particles and fiber are not always maintained because the behavior of small filler particles and fibers is influenced by their colloidal characteristics and shear rate. In other words, the deposition kinetics is related to the competition between deposition and detachment of filler particles. Therefore, the modified Langmuir kinetics is expressed as Eq. (1) (Kamiti and van de Ven 1994),

$$\frac{d\theta}{dt} = k_1(n_0 - \theta)(1 - \theta) - k_2\theta \tag{1}$$

where θ is the fractional coverage of the fibers by filler particles, defined as $\theta = \Gamma/\Gamma_{max}$. The quantity Γ is the deposition amount of filler particles on the fibers (g/g), and Γ_{max} is the maximum amount that can be deposited on the fibers (g/g). The variable n_0 is the initial concentration of filler particles divided by Γ_{max}. k_1 is the deposition rate constant, and k_2 is the detachment rate constant. The deposition rate constant for shear induced interactions is expressed in Eq. 2 (Petlicki and van de Ven 1992; Vanerek *et al.* 2000),

$$k_1 = \alpha k_0 N_f \approx \frac{\alpha}{\pi} G \emptyset_F \tag{2}$$

where α is the collision efficiency and k_0 is the Smoluchowski rate constant for collisions between particles and fibers: $k_0 = GV_F/\pi$. The quantity G is the shear rate, V_F is single fiber volume, N_F is the fiber number per unit volume, and Φ_F is the volume fraction of the fibers (Vanerek *et al.* 2000). The collision efficiency is related to the particle radius, shear rate, and colloidal forces between the particles and fibers. The detachment rate constant related to bond strength and hydrodynamic shear is expressed in Eq. 3 (Kamiti and van de Ven 1994; van de Ven 1993),

$$k_2 = k_2{}^0(G)e^{-E/kT} \tag{3}$$

where $k_2{}^0(G)$ is dependent on the shear rate, E is bond strength, and kT is the thermal energy. The value of k_2 is affected by bond strength under the same shear rate condition. Here, colloidal forces are interaction forces between two particles (Liang *et al.* 2007), and bond strength implies the depth of the energy minimum in which particle is captured (van de Ven 1993).

At a steady state ($t \rightarrow \infty$) for the deposition of the particles, $d\theta/dt = 0$. Therefore,

$$\frac{1}{\Gamma_\infty} = \frac{K}{C_\infty} + \frac{1}{\Gamma_{max}} \tag{4}$$

where Γ_∞ and C_∞ are the deposition amount and un-deposition amount at the steady state, respectively, and K is the equilibrium constant, defined as $K = k_2/k_1$. The values of K and Γ_{max} can be obtained by plotting $1/\Gamma_\infty$ versus $1/C_\infty$ using experimental data. From Eq. 1, the analytical solution is,

$$\theta = \frac{2n_0(\lambda - 1) + \theta_0[A(1-\lambda) + B(\lambda + 1)]}{A(\lambda - 1) + B(\lambda + 1) + \theta_0(1 - \lambda)} \tag{5}$$

where θ_0 is the value of θ when time is zero.

$$\lambda = e^{Bk_1t} \tag{6}$$

$$A = K + n_0 + 1 \tag{7}$$

$$B = \sqrt{(n_0 - 1)^2 + 2K(n_0 + 1) + K^2} \tag{8}$$

The value of k_1 was obtained from a best fit of Eq. 5, and the value of k_2 was obtained from the relationship between K and k_1.

EXPERIMENTAL

Materials

Bleached *Eucalyptus* kraft pulp fibers were disintegrated and beaten to 450 mL Canadian Standard Freeness (TAPPI methods 227 om-99) using a laboratory Hollander beater. Short fibers and fines were removed using a vibration screen (Sweco Co., USA) equipped with a 100-mesh wire so that only the beaten long fibers were used for the experiment. The length weighted average fiber length of the long fiber fraction was 0.73 mm, as detected by fiber analyzer (Kajaani FiberLab V.3, Metso Automation, Finland). Ground calcium carbonate (GCC, Hydrocarb 75K, Omya) was used as a filler particle. Polyethylenimine (PEI, M_w 750,000 g/mol) and poly(diallyldimethylammonium chloride) with different molecular weights (M_w) (PD_{150k} with M_w 150,000 g/mol and PD_{450k} with M_w 450,000 g/mol) from Sigma Aldrich were used as cationic polyelectrolytes. Poly(sodium 4-styrenesulfonate) with different M_w (PSS_{70k} with M_w 70,000 g/mol and $PSS_{1,000k}$ with M_w 1,000,000 g/mol) from Sigma Aldrich were used as anionic polyelectrolytes. Charge densities were measured by titration method using a streaming current detector (Mütek PCD 03 pH, BTG, Germany) with 0.001N of PD or sodium polyethylene sulfonate (PES-Na). The measured charge densities of used polyelectrolytes were 5.9 meq/g for PD, 6.3 meq/g for PEI at pH 9, -4.3 meq/g for PSS. All polyelectrolytes were diluted to 1 wt% solution with deionized water. For confocal fluorescence microscopy (CLSM), fluorescein isothiocyanate (FITC) from Sigma Aldrich was used.

LbL Multilayering on GCC Particles

A GCC slurry of 30 wt% was stirred at 1400 rpm. To form a multilayer on GCC particles, cationic polyelectrolyte was added to the GCC slurry. The GCC slurry was stirred for 1 min and was then centrifuged for 20 min at 3000 G. The supernatant was replaced by fresh deionized water, and the GCC particles were re-dispersed by an ultrasonicator (VCX 750, frequency: 20 kHz; amplitude: 124 μm; generating power: 750 W; probe diameter: 13 mm, Sonics, USA). Then, the first layer with a cationic polyelectrolyte was formed. Successively, an anionic polyelectrolyte and a cationic polyelectrolyte were alternatively adsorbed until the target layer number was reached. The pH and salt concentration were not adjusted. The conductivity of the GCC slurry was 400 μS/cm, and the pH was around 9. Three multilayer systems of 3, 7, and 11 layers of $PD_{450k}/PSS_{1,000k}$, 3 layers of PD_{150k}/PSS_{70k}, and 3 layers of PEI/PSS_{70k} were adopted. The 3 layers of PD_{150k}/PSS_{70k} means the GCC which was successively treated with PD_{150k}, PSS_{70k}, and PD_{150k}. Table 1 represents the zeta-potential and average particle size of the LbL multilayered GCC. The zeta-potential of the particles was measured using a Zeta-meter (Zeta-metar 3.0+, Zeta-meter, USA) with the electrophoresis principle. The particle size was measured by a Malvern Mastersizer 2000 (Malvern, UK) and was represented by the volumetric average size. The 3 layers of particles were labeled with FITC. The FITC molecules that were not adsorbed on the 3 layers of particles were removed through centrifugation. Images of the FITC-labeled particles were obtained using a confocal laser scanning microscope (LSM 710, Carl Zeiss, Germany). The surfaces of the fibers after deposition of the GCC particles were observed using a field emission scanning electron microscope (FE-SEM, SUPRA 55VP, Sweden).

Table 1. The Zeta-Potential of the LbL Multilayered GCC Particles

Multilayer system	Layer number	Zeta potential, mV	Particle size, µm
Untreated	-	-25.0 ± 1.8	2.4
PD_{150k} /PSS_{70k}	3 layer	+22.7 ± 1.2	2.6
PEI/PSS_{70k}	3 layer	+19.1 ± 1.5	6.2
PD_{450k}/$PSS_{1,000k}$	3 layer	+14.1 ± 1.5	2.6
	7 layer	+14.8 ± 1.5	2.5
	11 layer	+9.3 ± 1.7	2.5

Deposition of LbL Multilayered GCC on the Fibers

A fiber suspension (0.2%) was stirred in a dynamic drainage jar (DDJ) equipped with a 200-mesh wire. The accurately weighed LbL multilayered GCC slurry was added to the fiber suspension to evaluate the deposition of the particles on the fibers. The addition amount of the LbL multilayered GCC particles was 0.2 g to 0.5 g based on grams of oven-dried fibers. The mixing rate was 200 to 700 rpm. The deposition was carried out for 300 s for the PD/PSS system and for 480 s for the PEI/PSS system. After the deposition process, the suspension was filtered through the wire screen of the DDJ while being stirred. Because the opening size of the 200-mesh wire was smaller than the long fibers but larger than the particles, only un-deposited particles could pass the wire, *i.e.*, only un-deposited particles were withdrawn from the suspension. The withdrawn suspension was re-dispersed by an ultrasonicator, and turbidity was measured with a turbidimeter (2100AN, Hach, USA). The amount of un-deposited particles in the withdrawn suspension was determined using a calibration curve of turbidity-particle concentration. The amount of deposited particles on the fibers was calculated by subtracting the un-deposited amount from the added amount of the particles. The filtered fibers were diluted with deionized water. Then, the fibers were taken and observed using scanning electron microscope (SEM) to confirm the deposition of GCC onto fiber.

RESULTS AND DISCUSSION

Effect of Polyelectrolyte Type on Deposition of GCC

The FITC did not react with untreated GCC particles (Fig. 1a) because the surfaces of the GCC particles did not have nucleophiles. In contrast, the GCC particles with three layers of PD_{150k} /PSS_{70k} and GCC particles with three layers of PEI/PSS_{70k} could be labeled with green FITC due to the presence of ammonium or amine groups (Fig. 1b and 1c). This indicated that the negative charge of the untreated GCC particles changed to positive through LbL multilayering (Table 1). It was also confirmed from SEM images on fibers. Untreated GCC was hardly deposited onto pulp fibers (Fig. 2a). On the other hand, the LbL multilayered GCC particles could be deposited onto the surface of the fibers with a negative charge (Fig. 2b). Figure 3 shows the change in the amount of the LbL multilayered GCC particles deposited on the fibers as a function of time.

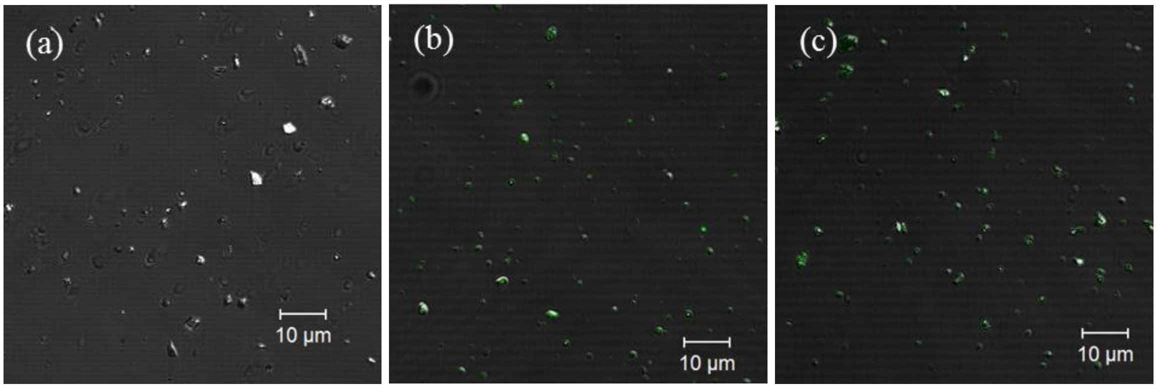

Fig. 1. CLSM images of (a) untreated GCC particles, (b) particles with three layers of PD_{150k}/PSS_{70k}, and (c) particles with three layers of PEI/ PSS_{70k}

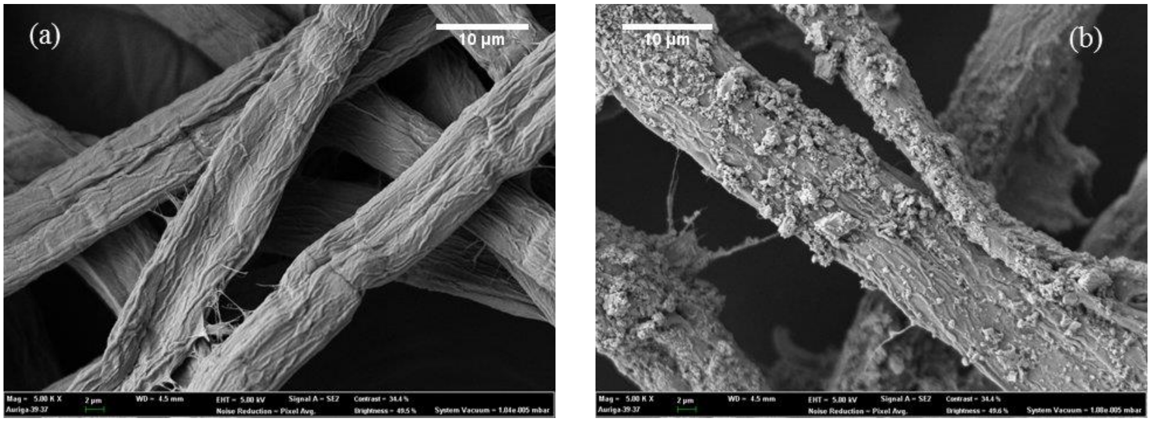

Fig. 2. Images of (a) fibers on which the particles are not deposited and (b) fibers on which the particles with three layers of PD_{150k}/PSS_{70k} are deposited at steady state

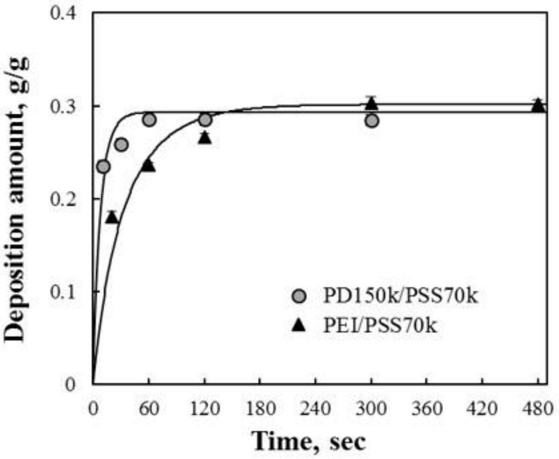

Fig. 3. Amount of particles with different LbL systems (3 layers) deposited on fibers as a function of time depending on polyelectrolyte types (addition amount is 0.5 $g_{particles}/g_{fibers}$). The dots represent experimental results, and the lines are theoretical results that were fit from Eq. 5 and divided by Γ_{max}.

The deposition behavior of the LbL multilayered GCC fit well with the Langmuir deposition theory. The maximum deposition amount was around 0.3 g/g. However, deposition behavior was affected by the polyelectrolyte type used in the multilayer. The particles with three layers of PD_{150k}/PSS_{70k} showed fast deposition. On the other hand, the particles with three layers of PEI/PSS_{70k} had a lower initial deposition rate.

The deposition rate constant and detachment rate constant were obtained from the modified Langmuir theory to evaluate the deposition behavior. They are represented in Fig. 4. The k_1 of the particles with three layers of PD_{150k}/PSS_{70k} (0.096 sec^{-1}) was higher than the k_1 of the particles with three layers of PEI/PSS_{70k} (0.026 sec^{-1}). The deposition rate constant, k_1, is affected by the shear rate, the particle radius, and colloidal forces between fibers and particles (van de Ven 1993). The shear rate for two cases was considered to be the same because mixing speed was identical. The value of k_1 increases along with particle size (Petlicki and van de Ven 1992; van de Ven 1993). The average particle size was 2.6 μm for the particles with three layers of PD_{150k}/PSS_{70k} and 6.2 μm for the particles with three layers of PEI/PSS_{70k} (Table 1). In the case of PEI/PSS_{70k}, k_1 decreased despite the larger particle size. Therefore, it is suggested that the k_1 was strongly affected by colloidal forces between the fibers and the particles. The colloidal force is the net interaction force between two particles, which is composed of van der Waals forces, electrostatic attraction or repulsion forces, hydration forces, hydrophobic forces, and steric forces (Liang *et al.* 2007). These colloidal forces of the multilayer surface are related to the polyelectrolyte type that exists at the surface. The zeta-potential for the two cases was almost the same (Table 1), which means that there are similar electrostatic attraction forces between the fibers. However, PEI was previously shown to have a low affinity with a fiber (Kamiti and van de Ven 1994) because weak polyelectrolytes such as PEI and poly-(allylamine hydrochloride) are more hydrophobic than strong polyelectrolytes such as PD (Chen *et al.* 2001). Thus, the overall colloidal forces between the particles with three layers of PEI/PSS_{70k} and the fibers may be low because of the more hydrophobic characteristic of PEI that induced the particles with three layers of PEI/PSS_{70k} to interact with each other. As a result, the particles with three layers of PD_{150k}/PSS_{70k} were rapidly deposited onto the fibers at the initial state compared to the particles with three layers of PEI/PSS_{70k} (Fig. 3).

The detachment rate constant, k_2, is related to the bond strength and shear force (Kamiti and van de Ven 1994; van de Ven 1993). There is an exponential inverse relationship between k_2 and the bond strength from Eq. 3. That is, lower k_2 means higher bond strength. The k_2 of the particles with three layers of PEI/PSS_{70k} was much lower than that of the particles with the PD/PSS system (Fig. 4). This implies that the bond strength between the fibers and the particles was much higher in the case of LbL multilayering with a PEI. Lee (2011) has described similar results, where the adhesion forces of a PEI layer were stronger than those of a PD layer. This is related to the properties of a polyelectrolyte layer. In a low salt concentration, a thin and flat multilayer can be constructed with a strong linear polyelectrolyte, such as the PD/PSS system (McAloney *et al.* 2001). On the other hand, the structure of the PEI/PSS multilayer was likely to be bulkier because some branches were extending into the water phase. Because the conductivity of the GCC slurry during LbL multilayering process was 400 μS/cm, which is below that of 0.005 M NaCl solution, it was considered that PD/PSS multilayer had a compact-like structure. Moreover, the pH-dependent PEI would be more adsorbed in a coil-up structure because the formation of a PEI/PSS_{70k} multilayer was conducted at pH 9. Because the charge of the PEI was so much lower than the charge of PD above pH

8, the adsorption amount and thickness of the PEI were much higher than that of the PD (Lee 2011; Mészáros *et al.* 2002). Therefore, the branched and more bulky PEI layer was advantageous to bond with fiber surfaces compared to the linear and flat PD layer, although the zeta-potentials of each particle were similar.

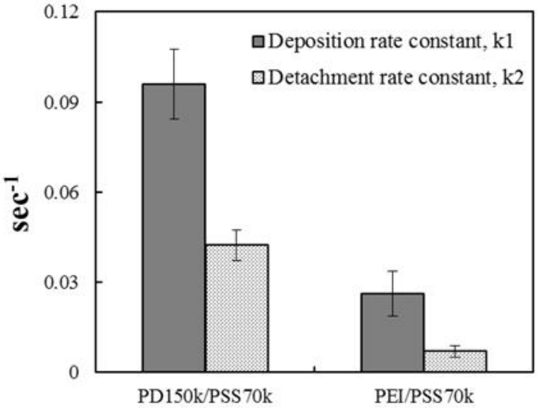

Fig. 4. Effect of different LbL systems on the deposition kinetic parameters

Figure 5 and Table 2 show the effect of the layer number on the deposition amount and the kinetics. The deposition behavior of the particles was almost the same, regardless of the layer number. The kinetic parameters were similar. In addition, there was an insignificant effect of molecular weight on the deposition of the particles (Fig. 3 and 5). The PD/PSS system formed a thin and flat multilayer at a very low salt concentration, similar to the results of a previous study (McAloney *et al.* 2001). Thus, the PD/PSS multilayers would not have structural differences with different molecular weights or layer numbers. Furthermore, the nature of polyelectrolytes is maintained regardless of the molecular weight. In other words, the colloidal forces and bonding strength were not affected by the molecular weight or layer numbers at low salt concentrations.

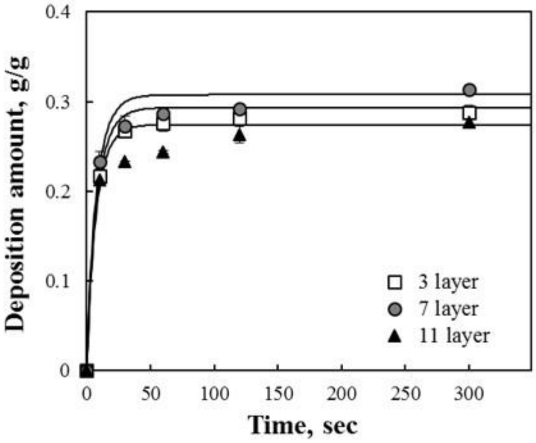

Fig. 5. Amount of particles with the $PD_{450k}/PSS_{1,000k}$ multilayer deposited as a function of time depending on the layer number (addition amount is 0.5 $g_{particles}/g_{fibers}$). The dots are experimental results, and the lines are theoretical results that were fit from Eq. [5] and divided by Γ_{max}.

Table 2. Deposition Kinetics Depending on Layer Number of $PD_{450k}/PSS_{1,000k}$ Multilayer

LbL system	Layer number	k_1, 10^{-2} sec^{-1}	k_2, 10^{-2} sec^{-1}	K
$PD_{450k}/PSS_{1,000k}$	3	8.9±0.9	3.8±0.4	0.43
	7	8.0±1.6	2.8±0.6	0.35
	11	8.1±1.1	4.2±0.6	0.52

The initial deposition rate of the particles with three layers of PD_{150k}/PSS_{70k} was 4 to 5 times faster than that of the particles with three layers of PEI/PSS_{70k} (Table 3). Consequently, the deposition of the particles with the PD/PSS multilayer was almost completed in 30 s. However, only 60% of the particles with three layers of PEI/PSS_{70k} were deposited for 30 s, compared to the total deposition amount at a steady state (Table 3). At a steady state, the deposition amount of both cases was similar due to a low k_2 value of the particles with three layers of PEI/PSS_{70k}. This is very important for the application of the LbL multilayered particles in the papermaking process. The deposition of the particles is allowed only for tens of seconds from the addition point to the headbox. During this period, the particles have to be deposited onto the fibers as much as possible to increase total retention of the particles. Consequentially, the higher positive surface charge and the higher affinity with fibers would be effective in fast papermaking. Particles with the PD/PSS multilayer possess such qualities.

Table 3. Deposition Kinetics of the LbL Multilayered Particles

LbL system	PD_{150k}/PSS_{70k} 3 layer	$PD_{450k}/PSS_{1,000k}$ 3 layer	PEI/PSS_{70k} 3 layer
K	0.44	0.43	0.26
Initial deposition rate, g/g·sec^{-1}	0.053	0.042	0.01
Deposition amount for 30 sec, g/g	0.28 (99)	0.29 (97)	0.18 (60)

The number in parentheses means the relative deposition amount percentage on total deposition amount at steady state

The results from previous studies on kinetics (Kamiti and van de Ven 1994; Liimatainen *et al.* 2009) are compared with the results of the present study in Table 4. The experimental designs for those references were very similar to those in the present study, but the type of particles and shear rate were slightly different. GCC particles were used in our study, while precipitated calcium carbonate (PCC) was used in the reference studies. PCC has a positive charge in deionized water because of the Ca^{2+} on the surface of the particles. The shear in the reference studies was also slightly lower than in our study (Table 4). However, these slight differences may not affect remarkably the k_1 and k_2 values. Regardless of polyelectrolyte type, the multilayered GCC showed a higher k_1

than both of the PCC without polyelectrolyte treatment and the PCC treated by PEI (Table 4). This indicates that interaction between particles and fibers was improved because positive surface of the GCC particle because of the multilayer. In absence of the polyelectrolyte, equilibrium constant, K, was higher than cases of multilayer (our work) or PEI-treated PCC (Kamiti and van de Ven 1994). This means a relatively higher k_2 compared to k_1, which indicates weak bond strength. However, the K value was not significantly different among cases of the multilayer (our work) and PEI treatment (Kamiti and van de Ven 1994). It appeared that there was little effect of multilayer on bond strength under dynamic condition. As a result, polyelectrolytes multilayering on filler particles contributed to improve collision efficiency, which results in faster deposition.

Table 4. Kinetics Results from the Present Work and Previously Reported Works

	rpm	k_1, 10^{-2} sec^{-1}	k_2, 10^{-2} sec^{-1}	K	References
GCC with 3 layer of PD_{150k}/PSS_{70k}	200	9.6±1.2	4.2±0.5	0.44	Our work
GCC with 3 layer of PEI/PSS_{70k}	200	2.6±0.7	0.7±0.2	0.26	
PCC (no treatment)	175	1.4	1.4	1	Liimatainen *et al.* (2009)
PCC (no treatment)	160	0.6±0.2	0.8±0.2	1.33	Kamiti and Van de ven (1994)
PCC treated with PEI	160	1.1±0.5	0.4±0.1	0.34	

Effect of Shear on Deposition Dynamics

Figure 6 shows the deposition kinetics parameters depending on shear. The k_1 and k_2 of the particles with three layers of PD_{150k}/PSS_{70k} were higher than the corresponding values for the particles with three layers of PEI/PSS_{70k}. The k_1 of the particles with three layers of PD_{150k}/PSS_{70k} seemed independent of shear. It was obvious that the collision efficiency from Eq. 2 decreased with increasing shear force (Petlicki and van de Ven 1992), but k_1 involved the collision efficiency and the shear rate. These factors compensated each other, so that the k_1 of the particles with the PD/PSS multilayer were not affected by the shear. However, the k_1 of the particles with three layers of PEI/PSS_{70k} decreased as the shear increased. This was likely due to a drastic decrease in the collision efficiency of the particles with three layers of PEI/PSS_{70k}. The rate constant k_2 had a different behavior from k_1 in that k_2 had a linear relationship with shear, according to Eq. [3]. In the case of the three layers of PD_{150k}/PSS_{70k}, k_2 increased linearly. This indicated that the bonding ability of the particles with the PD/PSS multilayer decreased with the shear.

The deposition amount at a steady state decreased due to the reduced bonding ability as the shear increased (Fig. 7). In the case of the three layers of PEI/PSS_{70k}, k_2 seemed independent of the shear. This was likely due to the very low k_1 of particles with three layers of PEI/PSS_{70k}. The increased K value implied that the detachment of the particles was greater than the deposition of the particles as the shear increased (Table 5). As a result, the deposition amount of the particles with three layers of PEI/PSS_{70k} and the particles with three layers of PD_{150k}/PSS_{70k} at steady state decreased with increasing of the shear.

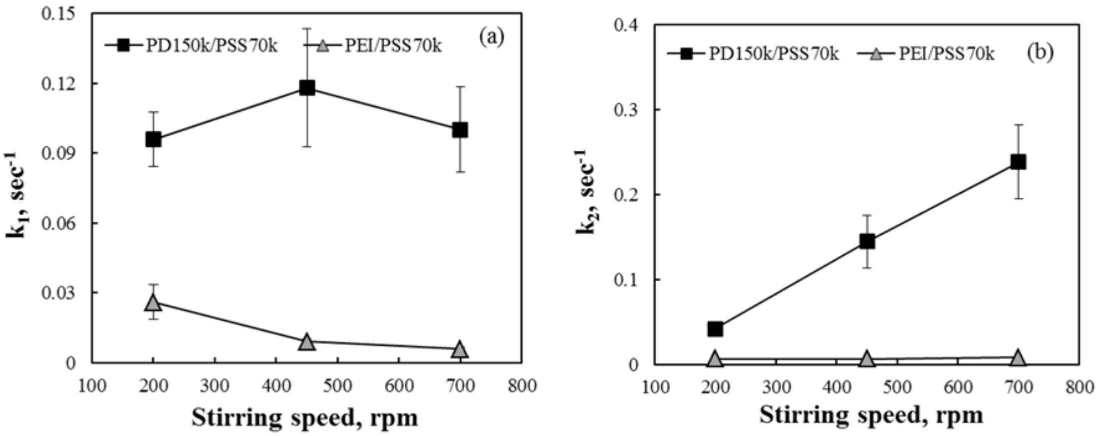

Fig. 6. Deposition kinetics (a) k_1 and (b) k_2 depending on shear force

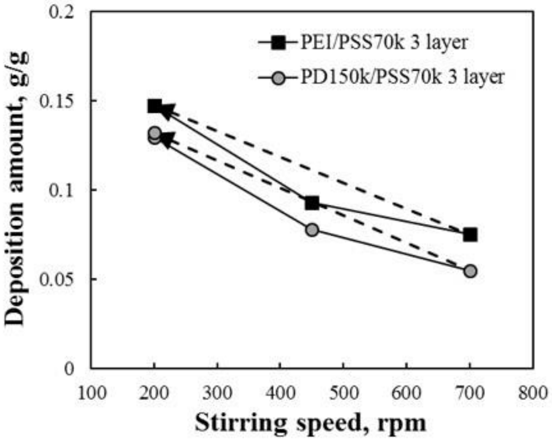

Fig. 7. Deposition amount depending on shear (addition amount is 0.2 $g_{particles}/g_{fibers}$). The dashed lines mean reducing the stirring speed to 200 rpm after pre-stirring at 700 rpm.

Table 5. The K Value as a Function of Shear

rpm	K	
	PD_{150k}/PSS_{70k}	PEI/PSS_{70k}
200	0.44	0.26
450	1.22	0.71
700	2.38	1.41

The decrease of the shear force from high to low affected the deposition amount of the particles. The dashed line in Fig. 7 represents the change in deposition amount during the decrease in the mixing rate from 700 rpm to 200 rpm. When the shear decreased, the detached particles were deposited again on the fibers. This implied that the detached particles did not lose their charge property.

In the papermaking process, pulp slurry experiences very high shear at the fan pump and screens during the transportation of the pulp slurry to the headbox. High shear often decreases the retention level of filler particles because of their irreversible detachment from the fibers in the retention system. However, the deposition of the LbL multilayered particles was reversible, depending on the shear force. Therefore, the LbL multilayered particles would be deposited again after experiencing high shear in the papermaking process.

CONCLUSIONS

1. The surface characteristics of the GCC particles could be controlled by LbL multi-layering with polyelectrolytes. The surface charge of the GCC particles, originally negatively charged, could be changed to positive by LbL multilayering. Its positive charge caused the treated GCC particles to spontaneously deposit onto the fibers.
2. The deposition of all LbL multilayered GCC particles followed the modified Langmuir kinetics, implying that deposition was determined by a dynamic equilibrium of deposition and detachment of the particles.
3. The deposition of the LbL multilayered particles was dependent on multilayer characteristics. The particles with the PD/PSS multilayer had a much higher k_1 than the particles with PEI/PSS multilayer, which resulted from high surface charge and relatively higher affinity to fiber. This caused the particles to have a fast deposition at an initial state. The molecular weight and layer number of the PD/PSS system did not seem to affect the kinetics of the deposition.
4. The particles with the PEI/PSS multilayer had a lower k_1 and k_2. Their hydrophobic characteristics led to slow deposition, but their branched structure and hydrogen bonds seemed to increase the bonding strength between the particle and the fiber.
5. When the shear increased, deposition amount at a steady state was reduced due to a relative increase of detachment compared to deposition. However, deposition of LbL multilayered particles was reversible so that the detached particles could be deposited onto pulp fibers again when the shear decreased.

ACKNOWLEDGMENTS

This work was supported by the Energy Efficiency & Resources of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Ministry of Knowledge Economy, Republic of Korea (No.2010201010037A).

REFERENCES CITED

Ahn, J., Lee, J., Lee, H. Y., Youn, H. J., and Lee, H. L. (2012). "Modification of GCC with Poly-DADMAC and PSS with different molecular weights and its effect on the paper properties," *Journal of Korea TAPPI* 44(5), 21-31.

Alince, B., Petlicki, J., and van de Ven, T. G. M. (1991). "Kinetics of colloidal particle deposition on pulp fibers.1. Deposition of clay on fibers of opposite charge," *Colloid Surface* 59, 265-277.

Alince, B., and van de Ven, T. G. M. (1993). "Kinetics of colloidal particle deposition on pulp fibers .2. Deposition of clay on fibers in the presence of poly(ethylenimine)," *Colloid Surface A* 71(1), 105-114.

Antunes, E., Garcia, F. A. P., Ferreira, P., Blanco, A., Negro, C., and Rasteiro, M. G. (2008). "Use of new branched cationic polyacrylamides to improve retention and drainage in papermaking," *Ind. Eng. Chem. Res.* 47(23), 9370-9375.

Bernier, J. F., and Begin, B. (1994). "Experience of a microparticle retention aid system," *Tappi J* 77(11), 217-224.

Blanco, A., Negro, C., Fuente, E., and Tijero, J. (2005). "Effect of shearing forces and flocculant overdose on filler flocculation mechanisms and floc properties," *Ind. Eng. Chem. Res.* 44(24), 9105-9112.

Caruso, F., and Gittins, D. I. (2001). "Tailoring the polyelectrolyte coating of metal nanoparticles," *J. Phys. Chem. B* 105(29), 6846-6852.

Chen, J. Y., Luo, G. B., and Cao, W. X. (2001). "The study of layer-by-layer ultrathin films by the dynamic contact angle method," *J. Colloid Interf. Sci.* 238(1), 62-69.

Decher, G., and Hong, J. D. (1991). "Buildup of ultrathin multilayer films by a self-assembly process. 1. Consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces," *Makromol. Chem.-M Symp*. 46, 321-327.

Decher, G., Hong, J. D., and Schmitt, J. (1992). "Buildup of ultrathin multilayer films by a self-assembly process. 3. Consecutively alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces," *Thin Solid Films* 210(1-2), 831-835.

Eriksson, M., Notley, S. M., and Wågberg, L. (2005). "The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibres," *J. Colloid Interf. Sci.* 292(1), 38-45.

Im, W., Lee, H. L., Youn, H. J., and Seo, D. (2013). "Structure characterization of ground calcium carbonate flocs by fractal analysis and their effects on handsheet properties," *Tappi J.* 12(3), 17-23.

Kamiti, M., and van de Ven, T. G. M. (1994). "Kinetics of deposition of calcium-carbonate particles onto pulp fibers," *J. Pulp Paper Sci.* 20(7), J199-J205.

Khopade, A. J., and Caruso, F. (2003). "Surface-modification of polyelectrolyte multilayer-coated particles for biological applications," *Langmuir* 19(15), 6219-6225.

Langmuir, I. (1918). "The adsorption of gases on plane surfaces of glass, mica and platinum," *J. Am. Chem. Soc.* 40, 1361-1403.

Lee, J., Ryu, J., Sim, K., Ahn, J., Lee, H. L., and Youn, H. J. (2011). "Preliminary study on properties of Layer-by-Layer assembled GCC with polyelectrolytes," *Journal of Korea TAPPI* 43(3), 35-42.

Lee, K. H., and Lee, H. L. (2006). "Preflocculation of GCC with cationic PAM and cationic starch and the influence of their dosage and shear rate on prefloc size," *Journal of Korea TAPPI* 38(4), 1-9.

Lee, S. H. (2011). "Xylan adsorption on cellulose fibers and its application as paper strength additive," Ph. D. thesis Dept. of Forest Sciences SNU.

Liang, Y., Hilal, N., Langston, P., and Starov, V. (2007). "Interaction forces between colloidal particles in liquid: Theory and experiment," *Adv. Colloid Interfac. Sci.* 134-35, 151-166.

Liimatainen, H., Haapala, A., and Niinimäki, J. (2009). "Retention of PCC and GCC fillers on chemical pulp fines surfaces," *Tappi J* 8(9), 38-42.

Mészáros, R., Thompson, L., Bos, M., and de Groot, P. (2002). "Adsorption and electrokinetic properties of polyethylenimine on silica surfaces," *Langmuir* 18(16), 6164-6169.

Mabee, S., and Harvey, R. (2000). "Filler flocculation technology - Increasing sheet filler content without loss in strength or runnability parameters," *2000 TAPPI Papermakers Conference and Trad Fair*, 797-810.

McAloney, R. A., Sinyor, M., Dudnik, V., and Goh, M. C. (2001). "Atomic force microscopy studies of salt effects on polyelectrolyte multilayer film morphology," *Langmuir* 17(21), 6655-6663.

Petlicki, J., and van de Ven, T. G. M. (1992). "Shear-induced deposition of colloidal particles on spheroids," *J. Colloid Interf. Sci.* 148(1), 14-22.

Radeva, T., Milkova, V., and Petkanchin, I. (2002). "Structure of polyelectrolyte layers on colloidal particles at different ionic strengths," *Colloids Surf. A* 209(2-3), 227-233.

Ryu, J., Youn, H. J., Chin, S. M., and Lee, S. (2011). "Effect of pH and conductivity in weak polyelectrolytes multilayering on paper properties," *Nordic Pulp Paper Res. J.* 26(4), 410-414.

Seo, D., Im, W. H., Youn, H. J., and Lee, H. L. (2012). "The effects of process variables for GCC pre-flocculation on floc and handsheet properties," *Nordic Pulp Paper Res. J.* 27(2), 382-387.

Shen, J., Song, Z. Q., Qian, X. R., and Liu, W. X. (2009). "Modification of papermaking grade fillers: A brief review," *BioResources* 4(3), 1190-1209.

Srivastava, S., Ball, V., Podsiadlo, P., Lee, J., Ho, P., and Kotovlt, N. A. (2008). "Reversible loading and unloading of nanoparticles in "Exponentially" growing polyelectrolyte LBL films," *J. Am. Chem. Soc.* 130(12), 3748-3749.

Torgnysdotter, A., and Wågberg, L. (2003). "Study of the joint strength between regenerated cellulose fibres and its influence on the sheet strength," *Nordic Pulp Paper Res. J.* 18(4), 455-459.

van de Ven, T. G. M. (1993). "Particle deposition on pulp fibers," *Nordic Pulp Paper Res. J* 8(1), 131-134.

Vanerek, A., Alince, B., and van de Ven, T. G. M. (2000). "Interaction of calcium carbonate fillers with pulp fibres: Effect of surface charge and cationic polyelectrolytes," *J. Pulp Paper Sci.* 26(9), 317-322.

Wågberg, L., Forsberg, S., Johansson, A., and Juntti, P. (2002). "Engineering of fibre surface properties by application of the polyelectrolyte multilayer concept. Part I: Modification of paper strength," *J. Pulp Paper Sci.* 28(7), 222-228.

Wong, J. E., Díez-Pascual, A. M., and Richtering, W. (2009). "Layer-by-Layer assembly of polyelectrolyte multilayers on thermoresponsive P(NiPAM-co-MAA) microgel: Effect of ionic strength and molecular weight," *Macromolecules* 42(4), 1229-1238.

Yan, Z. G., Liu, Q. J., Deng, Y. L., and Ragauskas, A. (2005). "Improvement of paper strength with starch modified clay," *J. Appl. Polym Sci*. 97(1), 44-50.

Yoon, S. Y., and Deng, Y. (2006). "Starch-fatty complex modified filler for papermaking," *Tappi J* 5(9), 3-9.

Zhao, Y. L., Hu, Z. S., Ragauskas, A., and Deng, Y. L. (2005). "Improvement of paper properties using starch-modified precipitated calcium carbonate filler," *Tappi J.* 4(2), 3-7.

Article submitted: May 20, 2013; Peer review completed: July 13, 2013; Revised version received and accepted: August 19, 2013; Published: August 20, 2013.