Hydrolysis of Cationic Polyacrylamide and its Effect on Flocculation of Ground Calcium Carbonate

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Cationic polyacrylamides (C-PAMs) have been widely used as flocculating agents to aggregate particles carrying negatively charged surfaces. This study examined the effects of hydrolysis of C-PAM on its adsorption behaviour and flocculation of negatively charged particles, specifically ground calcium carbonate (GCC). C-PAM hydrolysis was examined using polyelectrolyte titration and ion chromatography, while the adsorption behaviour of the polymer was monitored using a quartz crystal microbalance with dissipation (QCM-D). Laser diffraction spectroscopy was used to measure the size of the GCC aggregates under neutral and alkaline conditions. The charge density measurements and ion chromatograms indicated that the hydrolysis of C-PAM was accelerated with increased pH and temperature. The QCM-D measurements of hydrolysed C-PAMs, adsorbed on a substrate with a flat and rigid structure, indicated that hydrolysis of C-PAM suppressed its ability to cause inter-particle bridging flocculation, which reduced the aggregate size of GCC.

Keywords: Cationic polyacrylamide; Hydrolysis; Flocculation; Ground calcium carbonate; QCM-D

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INTRODUCTION

Flocculation of particles induced by water-soluble polymers has attracted great interest in many research fields, including water treatment and papermaking. Understanding the behaviours of polymers in the flocculation process is critical for process control and optimisation. Many types of polyelectrolytes have been used as flocculating agents to aggregate both organic and inorganic materials (Bolto 1995; Nyström *et al.* 2003). Among the various polymers, cationic polyacrylamides (C-PAMs) have been widely applied to aggregate negatively charged particles because C-PAM co-polymers can be manufactured with a wide range of molecular weights and charge densities. Ground calcium carbonate (GCC), which has many applications as an industrial mineral for the production of paper, paint, plastic, and construction materials, is mainly supplied in slurry form. Thus, it is necessary to treat GCC with dispersing agents to stabilise the slurry. However, dispersing agents are not permanently stable, *i.e.*, they dissociate with time, and the rate of dissociation is pH-dependent (Huggenberger *et al.* 2009). This indicates that polyelectrolytes may undergo chemical changes during storage or use, which influences the colloidal stability of the dispersion. It is important, therefore, to understand the changes in the chemical properties of the polyelectrolytes used to control colloidal stability, including dispersion and flocculation.

Flocculating the GCC particles to control their size is a crucial step in the papermaking process because it closely determines the retention efficiency and paper properties. Many variables, including pH, temperature, and ionic strength of the suspension, affect the flocculation of inorganic particles (Badawy *et al.* 2010; Seo *et al.* 2016). The characteristics of the flocculating agent, specifically molecular weight and charge density, are the two most important factors controlling the flocculation process. Seo *et al*. (2016) evaluated the effect of charge density and molecular weight of C-PAMs on the growth and structural characteristics of GCC aggregates under neutral and alkaline conditions. In their study, high charge C-PAM formed larger and denser flocs than low or medium charge C-PAMs both in neutral and alkaline conditions. A flocculating agent with a large molecular weight has an advantage in forming inter-particle bridging bonds (Yu and Somasundaran 1993), thus increasing the floc size. However, Seo *et al*. (2016) showed that molecular weights greater than 8 Mg/mol did not affect GCC flocculation.

The properties of polymeric flocculants may change during storage or use, which influences their efficiency. For instance, C-PAM is hydrolysed under neutral and alkaline conditions, which decreases its cationic charge density. Two pathways have been reported for the hydrolysis of C-PAMs under alkaline conditions (Aksberg and Wågberg 1989; Bolto and Gregory 2007). These pathways involve the hydrolysis of either the amide group or the ester group of C-PAMs, which releases ammonia or choline chloride as hydrolysates, respectively. The change of polymeric characteristics, such as charge density, may influence its adsorption and inter-particle bridge-forming properties. Thus, it is important to understand the mechanism of the hydrolysis of C-PAMs and the factors affecting the hydrolysis to reduce its detrimental aspects in practice. Although the hydrolysis of C-PAMs have been documented in previous studies (Aksberg and Wågberg 1989; Bolto and Gregory 2007), the effect of the degradation of C-PAMs on their flocculation ability, and the corresponding mechanism, have not been thoroughly investigated. This study evaluated the effect of the hydrolysis of C-PAM on the flocculation of GCC by understanding the adsorption behaviour of C-PAM under neural and alkaline conditions.

To investigate the flocculation effect of polymeric flocculants, as well as the corresponding kinetics, the most common approach is to measure the change in the size of the aggregates (Biggs and Lant 2000; Bushell 2005; Rasteiro *et al.* 2008). Among the numerous methods to measure the size, laser diffraction spectroscopy (LDS), which measures the size over time, is among the most widely used (Seo *et al.* 2012; Im *et al.* 2013). In this study, a streaming current detector was used to examine the hydrolysis of C-PAM under neutral and alkaline conditions, by measuring the decrease in charge density caused by hydrolysis. Ion chromatography was used to confirm the dominant hydrolysis pathway by detecting the hydrolysates (Christianson *et al.* 1960; Zhang and Zhu 2007). To understand the adsorption properties of the polyelectrolyte, which affect the flocculation behaviours of particles, a quartz crystal microbalance with dissipation (QCM-D) was used. This device allowed investigation of the adsorption kinetics and mass as well as the viscoelastic properties of the adsorbed polymer layer (Caruso *et al.* 1997; Höök *et al.* 2001; Naderi and Claesson 2006; Notley *et al.* 2004; Alagha *et al.* 2013).

EXPERIMENTAL

Materials

A commercial C-PAM of the ester type, Percol 63, was used. The polymer in powder form was kindly provided by BASF (Seoul, Korea). Its molecular weight was approximately 6 Mg/mol. A stock solution at a concentration of 0.2 wt% was prepared by dissolving the powder-form C-PAM in distilled water (conductivity < 70 µS/cm) for 8 h; the stock was diluted to 0.01 wt% before use. The charge density of the C-PAM measured by polyelectrolyte titration using sodium polyethylene sulfonate and PCD 03 pH (BTG, Herrsching, Germany) was 1.5 meq/g. Three pH buffer solutions of pH 7, 8, and 9 were purchased from Samchun Chemicals (Seoul, Korea).

GCC, Hydrocarb 75F, was supplied by Omya Korea (Seoul, Korea) in slurry form, and its consistency was 60 wt%. The median size of GCC particles measured by LDS was 1.8 µm. A GCC suspension at a consistency of 5 wt% was prepared and continuously stirred to prevent the sedimentation of particles before use. Both 0.1 N and 1 N HCl solutions (Samchun Chemicals) were used to adjust the pH of the GCC suspensions to 7, 8, and 9.

Flocculation of GCC

An experimental set-up to monitor the change of the GCC particle size was used for the flocculation test (Seo *et al.* 2012). The set-up consisted of a particle size analyser (Mastersizer 2000, Malvern Instruments, Worcestershire, UK), circulation pump (Hydro MU, Malvern Instruments), silicon rubber heater (Daihan Scientific, Wonju, Korea), and temperature controller (TC-200P, Mtops, Daejon, Korea). The flocculation test was conducted to investigate the effects of the pH and temperature of the suspension on the aggregation of GCC particles. The zeta potential of the particles was measured using an electrophoretic light scattering device (Zetasizer Nano ZS, Malvern Instruments).

To evaluate the effect of pH, 900 g of distilled water at 25 °C was placed in a 1 L beaker. To this beaker, 2,300 µL of GCC suspension at a consistency of 0.5 wt% was added, making the LDS obscuration equal to 25%. Although the desired obscuration value is less than 20%, the initial value of 25% was used because it decreases with the aggregation of particles. The pH of the suspensions was adjusted to 7, 8, and 9 using either HCl or NaOH solution. The first measurement was carried out immediately before dosing the C-PAM solutions, which gave the size of the GCC particles untreated with polymer. After this measurement, 600 µL of the polymer stock solution, which was equal to 0.1 wt% of the oven-dried GCC, was added to the suspension. The negatively charged particles started to aggregate with the addition of C-PAM, and the floc size was measured every 30 s for 10 min after the C-PAM addition, giving a total of 20 measurements.

Although temperature is a major factor affecting flocculation, most studies on particle aggregation have been conducted at room temperature (Fuente *et al.* 2005; Shen *et al.* 2009). In the papermaking process, however, the stock temperature varies substantially depending on the season and the level of system closure, which causes significant changes in the flocculation of filler particles by polymeric retention aids. In this study, flocculation tests were performed at various temperatures from 25 °C to 45 °C. To investigate the effect of temperature on GCC flocculation, all tests were conducted at pH 9. The polymer addition level was also kept constant at 0.1 wt%. After the termination of the floc size measurements, 40 µL of the suspension was taken and placed on a microscope slide, with a cavity at the centre to prevent the GCC aggregate from being crushed by the cover slip, and a microscopic observation was made (BX-51, Olympus, Tokyo, Japan).

Hydrolysis of the C-PAM

The change in charge density of C-PAM was monitored as previously described (Aksberg and Wågberg 1989). A C-PAM solution of 190 g (0.0105 wt%) was stirred in a beaker using a magnetic stirrer (WiseStir, Daihan Scientific, Wonju, Korea) with a built-in temperature controller at a speed of 300 rpm. The solution temperature was adjusted to 25 °C, 35 °C, and 45 °C, and then 10 g of pH buffer was added. The salt concentration was adjusted to 5 mM with NaCl. The charge densities of the C-PAMs were measured 30 min, 60 min, and 120 min after dosing the buffer solution using a particle charge detector (PCD-03, Mütek, Herrsching , Germany).

Choline chloride and ammonia produced by the hydrolysis reaction were determined using ion chromatography (Dionex ICS 3000, Dionex, Sunnyvale, CA, USA). First, the C-PAMs were hydrolysed with the pH buffer for 30 min, and the mixtures were moved to a stirred ultrafiltration cell (Amicon 8400, Millipore Co., Burlington, MA, USA) to separate the hydrolysates. Ultrafiltration discs (Ultracell, Millipore) with a molecular weight cut-off of 3 kg/mol were used. By supplying a nitrogen gas flow into the ultrafiltration cell, the hydrolysates were passed through the pores of the discs.

Choline chloride standards of analytical grade (Samchun Chemicals, Korea) were used to quantify the amount of choline chloride by the external standard method. Choline chloride was prepared at a concentration of 1,000 ppm, and then diluted to 500 ppm, 100 ppm, and 10 ppm to obtain a calibration curve. Six cation standards (Dionex P/N 43162,) were used to detect the cations Li^+, K^+, NH_4^+, Na^+, Ca^{2+}, and Mg^{2+}. The parameters of the ion chromatography system were as follows: [column: Ionpac CS12A (4 × 250 mm), column oven temperature: 30 °C, flow rate: 1 mL/min, eluent: 20 mM methanesulfonic acid, injection volume: 25 µL, detection: suppressed conductivity (SCRS Ultra, recycle mode), and run time: 15 min].

QCM-D Measurement

QCM-D (Q-Sense E1, Biolin Scientific, Gothenburg, Sweden) was used to examine the adsorption characteristics of the C-PAMs following hydrolysis under neutral and alkaline conditions. A QSX 301 with gold electrodes (AT-cut quartz crystal sensor) was purchased from Biolin Scientific and cleaned in accordance with the cleaning protocol A-1. The sensors were initially treated with UV/ozone for 5 min and immersed in a 5:1:1 mixture of distilled water, ammonia (25%), and hydrogen peroxide (30%) at 75 °C for 10 min. After rinsing with distilled water and drying with nitrogen gas, the sensors were treated with UV/ozone again.

To prepare hydrolysed C-PAMs for QCM-D measurement, 99.5 g of the polymer solution (0.0105 wt%) was poured into a 125 mL Erlenmeyer flask. To the flask, 0.5 g of a buffer solution at pH 7, 8, or 9 was added, and the salt concentration was adjusted to 2 mM by adding NaCl. The mixtures were stirred at 300 rpm for 20 min on a magnetic stirrer.

Changes in frequency (Δf) and dissipation (ΔD) were monitored by QCM-D at 25 °C. These properties are known to describe the mass adsorbed on a quartz crystal sensor and the viscoelastic properties of the polymer layer, respectively. The principle of QCM-D measurement has been described in detail elsewhere (Naderi and Claesson 2006). The Sauerbrey equation accounts for the correlation of Δf with the adsorbed mass per unit area,

$$\Delta m = -\frac{C\,\Delta f}{n} \qquad (1)$$

where n is the vibrational resonance overtone number (1, 3, and 5) and C is a constant describing the sensitivity to changes in mass. The dissipation factor D is defined in Eq. 2,

$$D = \frac{E_{dis}}{2\pi E_{st}} \tag{2}$$

where E_{dis} is the dissipated energy and E_{st} is the stored energy during an oscillation cycle.

RESULTS AND DISCUSSION

Effects of pH and Temperature on the GCC Flocculation

Flocculation of particles induced by polymeric flocculants involves sequential stages of mixing, adsorption, re-conformation, collision, and break-up (Gregory 1988). Therefore, the size of the aggregates continually changes throughout the process, but reaches a steady-state at a given shear condition (Jarvis *et al.* 2005). The equilibrium size is considered as a balance between floc formation and breakage. Thus, a polymer that forms large aggregates in the equilibrium state is judged to have a superior flocculation ability.

The median particle sizes of GCC aggregates formed at various pH levels are shown in Fig. 1.

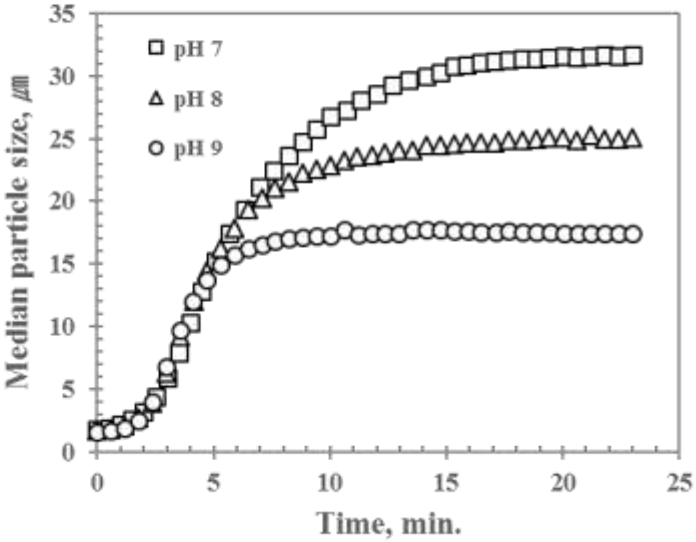

Fig. 1. Median particle sizes of GCC aggregates formed at pH levels of 7, 8, and 9 at 25 °C

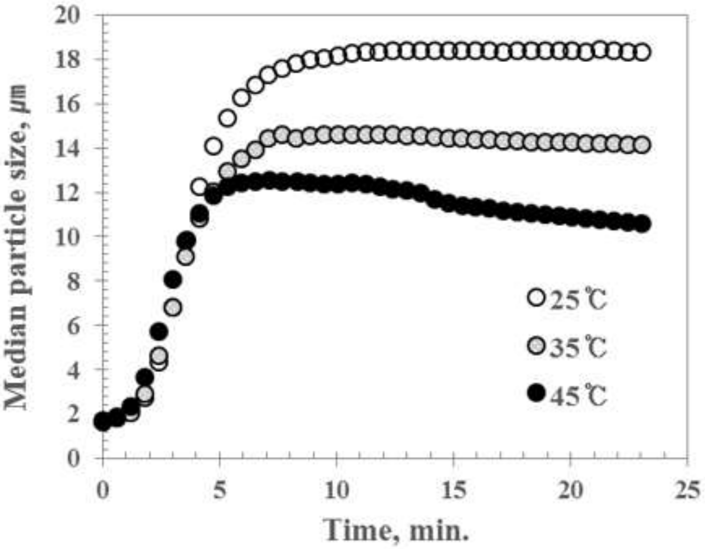

Fig. 2. Median particle sizes of GCC aggregates formed at temperatures of 25 °C, 35 °C, and 45 °C at a pH of 9

The median particle size increased very rapidly in the early stage and then stabilised after *ca*. 5, 10, and 15 min at pH 9, pH 8, and pH 7, respectively. The flocculation rates of GCC particles at the three pH levels were almost identical in the early stage, but a difference in the equilibrium size was observed after 5 min of flocculation. Larger aggregates were formed at pH 7 than at pH 8 and pH 9, *i.e.* the equilibrium size increased with a decrease in pH level. The flocculation test to examine the effect of temperature was performed at pH 9, at which the smallest aggregates were formed, as can be seen in Fig. 1. The test confirmed that GCC flocculation was sensitive to temperature as well as pH (Fig. 2). The equilibrium size decreased as the temperature increased. Interestingly, at 45 °C the median size gradually decreased after reaching a maximum value indicating that cPAM started to lose some of its power of flocculating GCC probably due to hydrolysis. Figure 3 shows images of the GCC flocs taken after the flocculation test at different pH and temperature conditions. These images visually confirm that larger aggregates were formed when the pH and temperature were low.

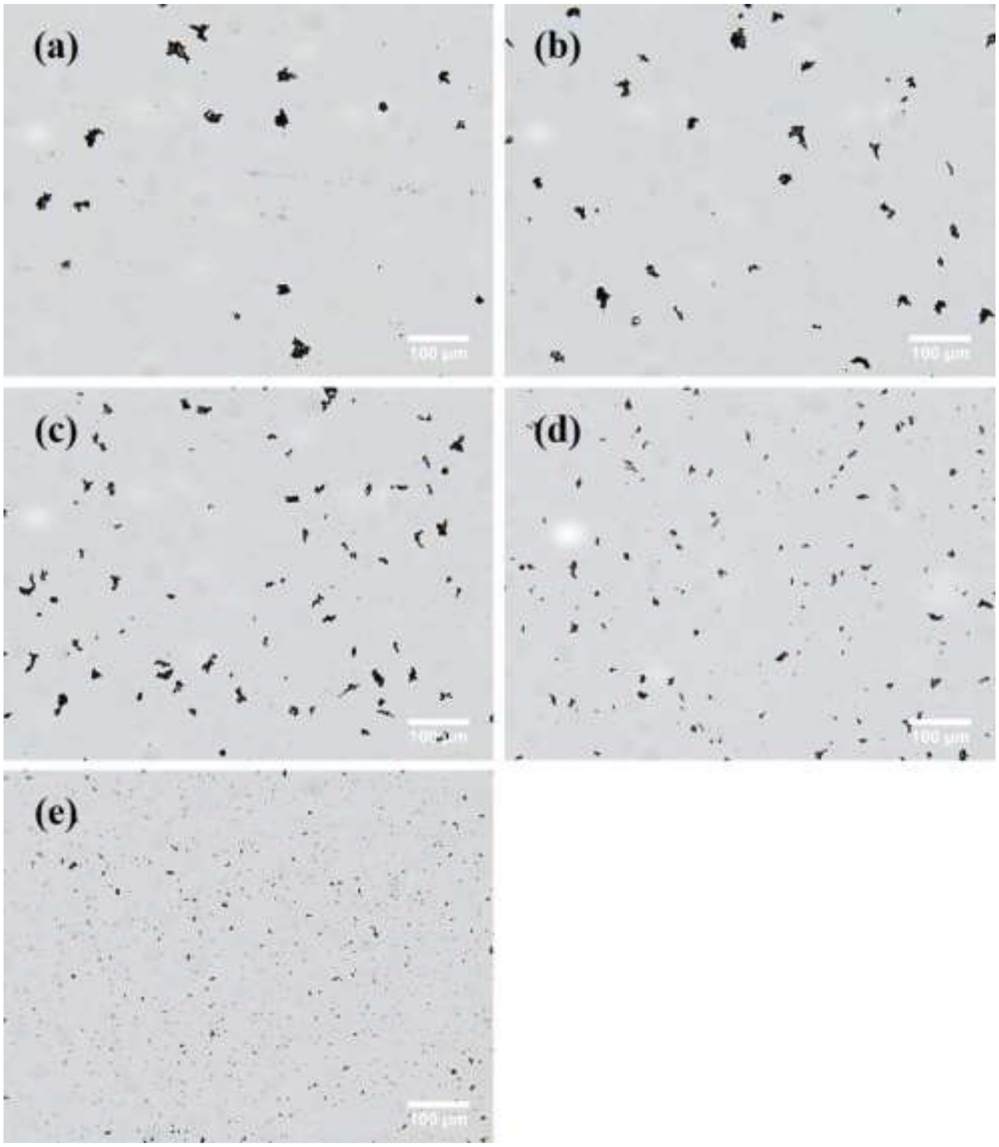

Fig. 3. Images of GCC aggregates formed at various pH levels and temperatures: (a) pH 7; 25 °C, (b) pH 8; 25 °C, (c) pH 9; 25 °C, (d) pH 9; 35 °C, and (e) pH 9; 45 °C

The zeta potential of the GCC flocs was negative at all pH levels examined, but a less negative zeta potential was obtained at pH 7 than at pH 8 and 9 (Fig. 4). Due to the presence of dispersing agents in GCC slurry, the zeta potential of GCC particles varies depending on the pH of the suspension. Anionic dispersing agents, such as polyacrylate, are partly neutralised, *i.e.*, less dissociated, at low and intermediate pH values compared with high pH values. Particles with low zeta potential are unstable and easily form inter-particle aggregations. The zeta potential at pH 7 was the least negative because of the less complete dissociation of the dispersing agent. As the pH increased, the zeta potential became increasingly negative, which implied that flocculation was more favourable at pH 7 than at pH 9. This result is therefore in good accordance with the results in Fig.1. The zeta potential did not change as a function of the temperature at pH 9 (Fig. 4). However, the particle size of the GCC flocs decreased substantially with increasing temperature at this pH (Fig. 3). This indicates that the change in floc size of the GCC could not be solely explained by the dependence of the zeta potential on the temperature.

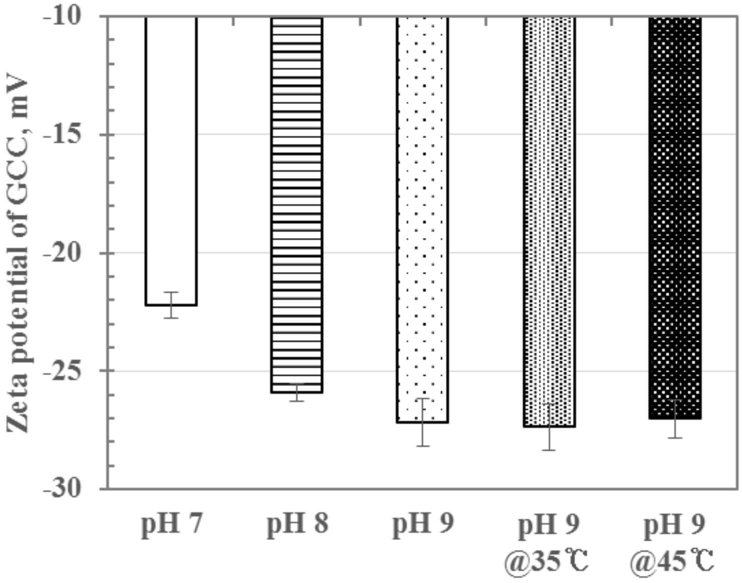

Fig. 4. Zeta potentials of GCC particles measured at pH levels of 7, 8, and 9 at 25 °C, and temperatures of 25 °C, 35 °C, and 45 °C at a pH of 9. The GCC particles were untreated with C-PAM

Hydrolysis of the C-PAM

C-PAMs are susceptible to hydrolysis in alkaline suspensions and that this occurs by two pathways (Aksberg and Wågberg 1989; Caulfield *et al.* 2002). One pathway involves the addition of a hydroxide ion to the amide carbonyl group of C-PAM, followed by the elimination of the amide ion, leaving an acrylic acid residue. The amide ion removes a proton from the acrylic acid residue to form a carboxylate and ammonia (Fig. 5). The other reaction pathway involves the hydrolysis of the ester group in the cationic copolymer, as shown in Fig. 6. This reaction also forms negative charges on the polymer chain, while eliminating choline chloride. Both reaction pathways can greatly influence the GCC flocculation induced by C-PAM; both the formation of negative charges on the main chain and the elimination of cationic groups from the polymer inhibit the induction of bridging flocculation by C-PAM.

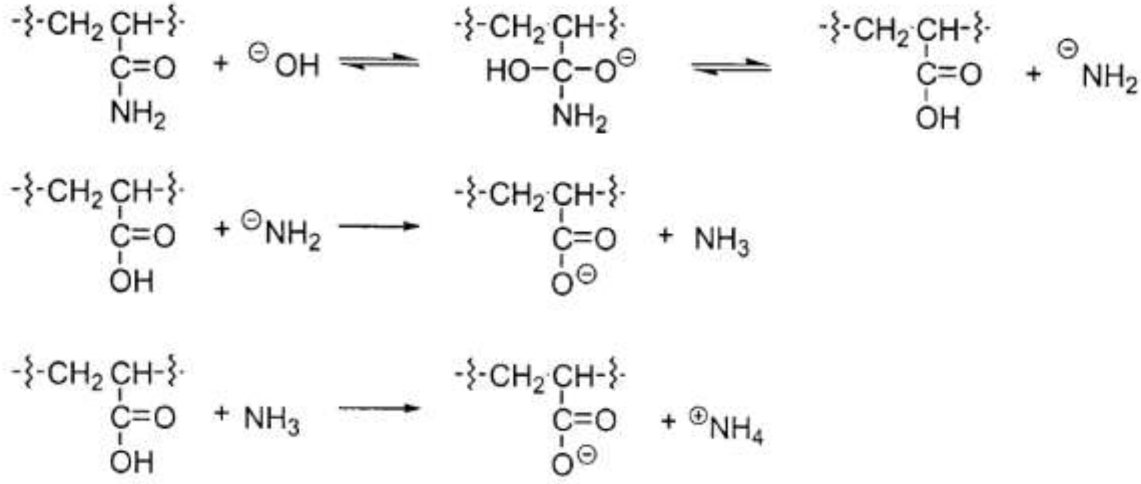

Fig. 5. Hydrolysis of amide group on C-PAM (Caulfield *et al.* 2002)

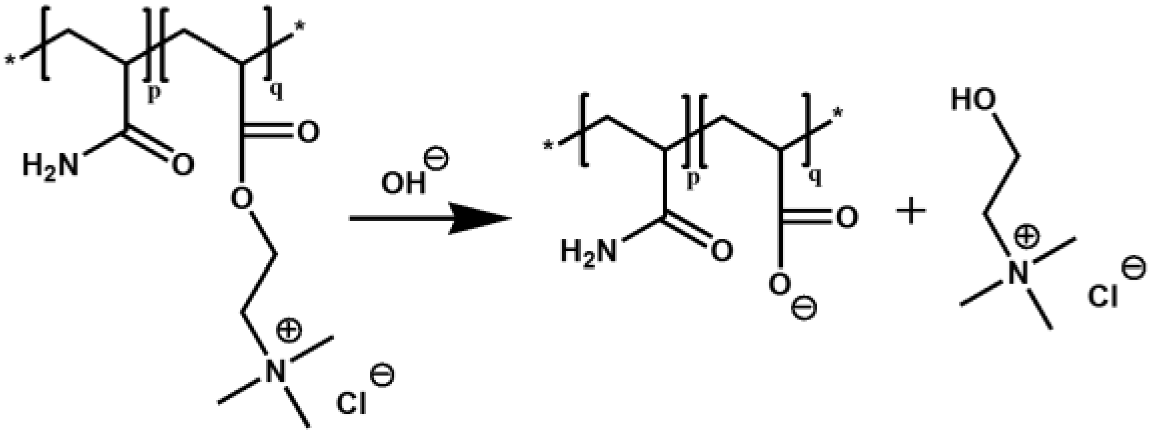

Fig. 6. Hydrolysis of ester group on C-PAM (Aksberg and Wågberg 1989)

To examine the changes in electrostatic properties of the cationic polymer, the charge densities of C-PAMs were measured at various pH levels and temperatures, as depicted in Figs. 7 and 8, respectively. C-PAM was barely hydrolysed at pH 7, thereby keeping its initial charge density at 25 °C. However, the hydrolysis progressed much more rapidly with an increase in pH. Almost complete loss of the charge density of C-PAM was observed after 120 min at pH 9. Furthermore, the temperature also strongly affected the charge density at pH 9. As the temperature increased, the reduction in charge density was accelerated. The intensified hydrolysis reaction at 35 °C and 45 °C resulted in negative charge densities (Fig. 8). These responses of the charge density of C-PAM to the change of pH and temperature are in close agreement with previous studies (Aksberg and Wågberg 1989; Maxwell *et al*. 2012).

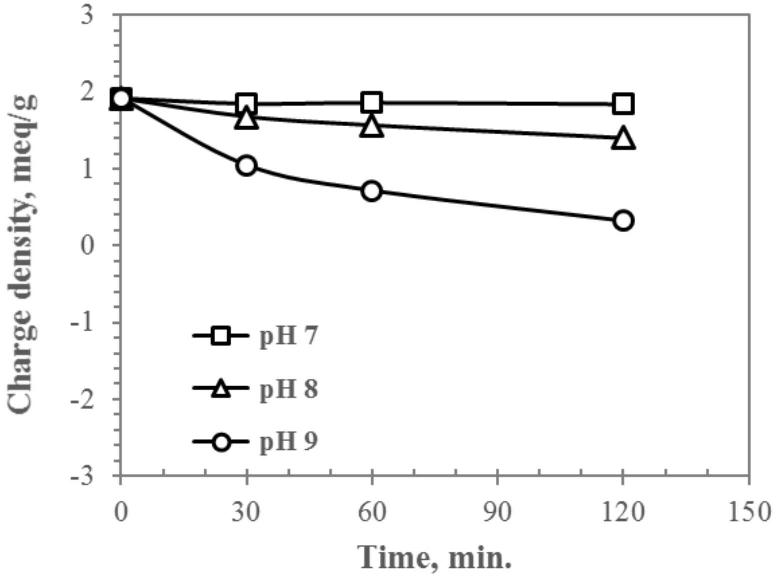

Fig. 7. Changes in the charge density of C-PAM hydrolysed at pH levels of 7, 8, and 9 at 25 °C

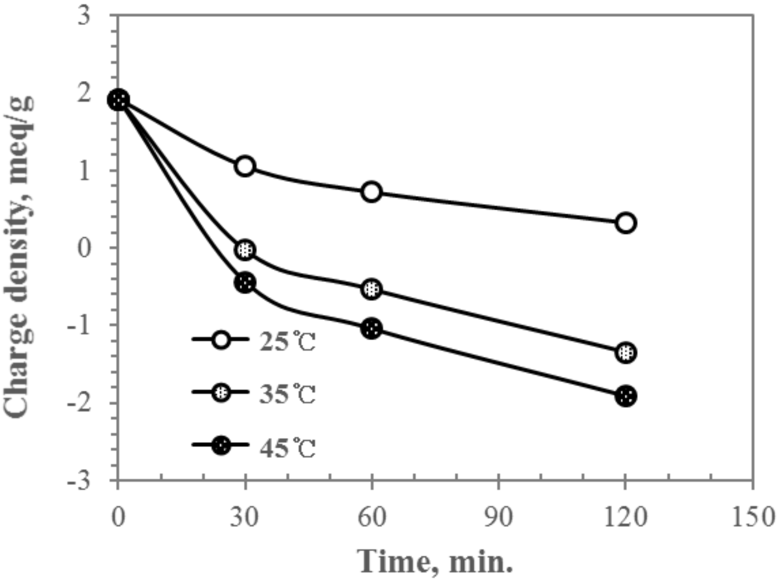

Fig. 8. Changes in the charge density of C-PAM hydrolysed at temperatures of 25 °C, 35 °C, and 45 °C at a pH of 9.

The two pathways of C-PAM hydrolysis give different hydrolysates (Figs. 5 and 6). To confirm which pathway was dominant in the hydrolysis reaction of C-PAM, ion chromatography was used to determine the amounts of choline chloride and ammonia, *i.e.* hydrolysates of the ester group and amide group, respectively. In the chromatograms, the choline peaks appeared after *ca*. 8 min of elution time, but ammonia peaks failed to appear. This result indicated that hydrolysis of ester groups was the dominant process. The amounts of choline formed under various conditions are shown in Table 1. The increase of pH and temperature clearly enhanced the formation of choline chlorides, which would be expected to decrease the charge density of C-PAM.

Table 1. Amounts of Choline Chloride Detected by Ion Chromatography at Different pH Levels and Temperatures

pH	Temperature (°C)	Peak Time (min)	Peak Height (µS)	Peak Area (µS•min)	Amount of Choline (mg/L)
7	25	8.39	0.34	0.20	5.1
8	25	8.29	0.67	0.37	9.4
9	25	8.24	1.49	0.70	17.9
9	35	8.22	1.90	0.87	22.1
9	45	8.21	1.94	0.96	24.4

Adsorption behaviour of the hydrolysed C-PAMs

The effect of pH on the adsorption behaviour of the hydrolysed C-PAMs was examined with QCM-D. Figure 9 shows the Δ*f* signals obtained from the fifth overtone for the C-PAMs hydrolysed at pH 7, 8, and 9. The adsorption rates at all three pH levels were similar in the early stage, but then they decreased rapidly and reached different equilibrium levels (Fig. 9). The smallest adsorbed mass was obtained at pH 7, where the C-PAM was less hydrolysed than at pH 8 or 9. Elimination of choline chloride followed by the formation of negative charges on C-PAM is considered to be a key factor causing these changes in the adsorption behaviour. It has been shown that the hydrolysis of C-PAM allows the formation of a C-PAM multilayer, because each successively adsorbed C-PAM layer contains negatively charged carboxylic groups on its backbone as a result of hydrolysis, encouraging the further adsorption of C-PAM (Peng and Garnier 2010). The adsorbed mass is therefore expected to increase when the attraction force between the C-PAMs is stronger.

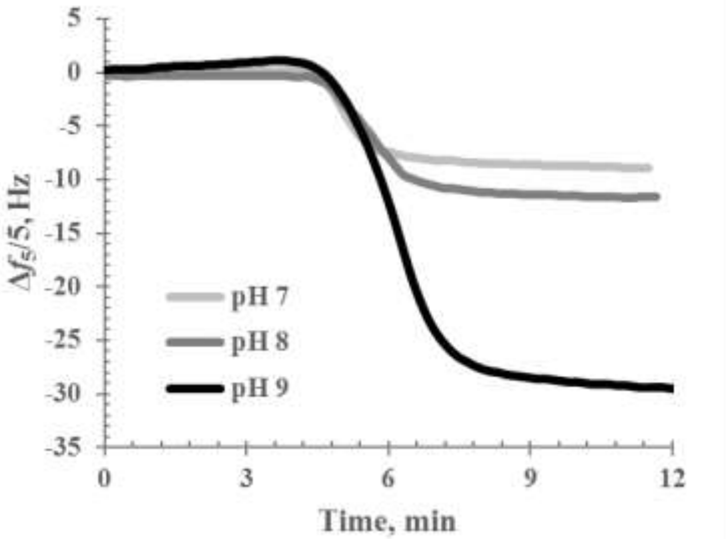

Fig. 9. Changes in the frequency ($\Delta f_5/5$) of C-PAMs hydrolysed at pH levels of 7, 8, and 9 for 30 min

The structure of the adsorbed layers can be inferred from Fig. 10, which shows Δ*D* as a function of Δ*f*. The slope of the plot indicates the rigidity of the adsorbed layer (Tammelin *et al*. 2004). A steep slope indicates that the layer is loose and fluffy, while a gentler slope indicates a rigid and flat structure of the adsorbed polymer. The C-PAM treated at pH 9, *i.e.* the most hydrolysed C-PAM, showed a gentle slope (Fig. 10). In other words, the C-PAMs were adsorbed on the substrate more tightly at pH 9 than at pH 7 and 8. This suggests that for a given amount of C-PAM mixed with GCC slurry, greater hydrolysis of C-PAM allows it to be adsorbed with a flatter configuration on the GCC surfaces, thereby leading to reduced bridging flocculation. Thus, the size of the aggregates decreases as the hydrolysis progresses, as shown in Fig. 2.

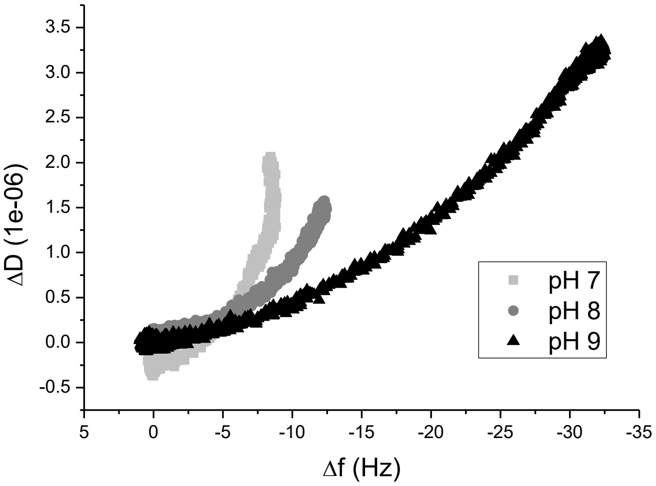

Fig. 10. Changes in the dissipation shift (Δ*D*) as a function of frequency shift (Δ*f*) of C-PAMs hydrolysed at pH 7, 8, and 9

The adsorption behaviour of the hydrolysed C-PAMs was similar to that of the C-PAMs charge-screened by salt. The signals of Δ*f* and Δ*D* obtained from the QCM-D measurement at several salt concentrations are depicted in Figs. 11 and 12, respectively. As the salt concentration increased, the adsorbed mass also increased. An increase of ionic strength decreases the hydrodynamic diameter of a polymer, and thereby increases the adsorption, because it allows the adsorbed polymer to form a tighter and more rigid layer on the adsorbate (Höök *et al.* 1998; Solberg and Wågberg 2003).

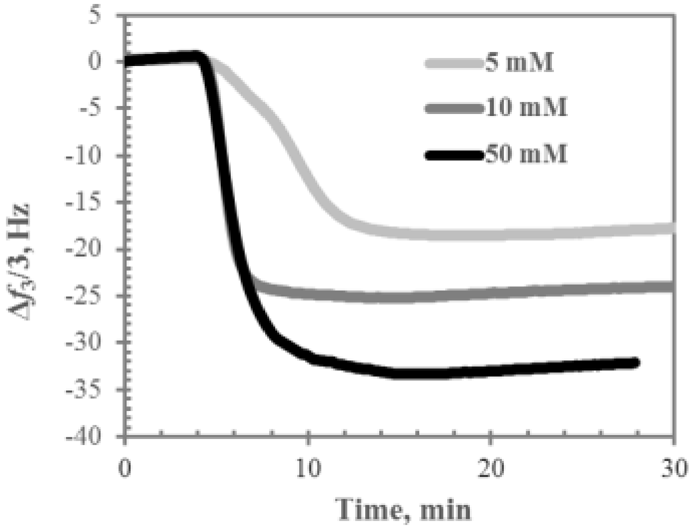

Fig. 11. Changes in the frequency ($\Delta f_3/3$) of C-PAMs at NaCl concentrations of 5 mM, 10 mM, and 50 mM

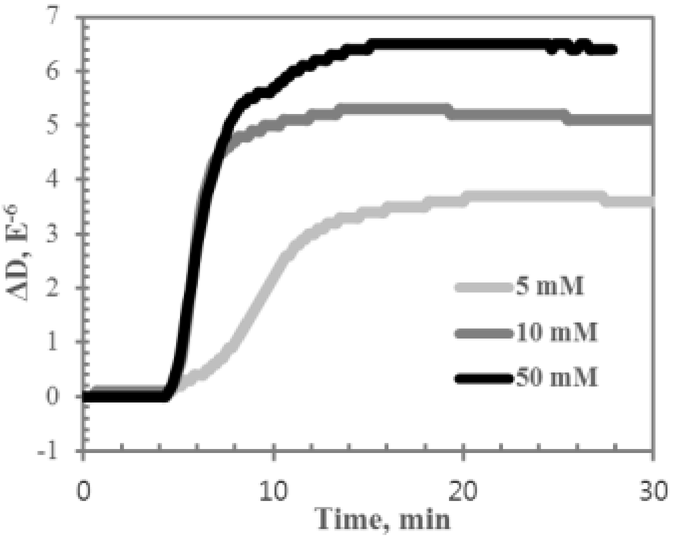

Fig. 12. Changes in the dissipation (Δ*D*3/3) of C-PAMs at NaCl concentrations of 5 mM, 10 mM, and 50 mM

CONCLUSIONS

1. Hydrolysis of C-PAM under neutral and alkaline conditions and its effect on GCC flocculation were investigated.
2. The size of the GCC flocs decreased with increasing pH and temperature. The reduction of GCC floc size was attributed to the hydrolysis of C-PAM, which released choline chloride as a hydrolysate and formed negative carboxylic groups on the main chain. Ion chromatography indicated that the degradation of the ester linkages in cationic groups dominated over the hydrolysis of amide groups.
3. Charge density measurements and ion chromatography showed that the hydrolysis of C-PAM was accelerated with an increase in pH and temperature. QCM-D experiments showed that more fully hydrolysed C-PAMs were adsorbed on the substrate with a tighter and more rigid configuration, which led to reduced bridging flocculation, thereby decreasing the size of the aggregates.

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