The Effects of Polyelectrolyte Complexes on Dewatering of Cellulose Suspension

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SUMMARY: The objective of this study was to investigate the effects of complexes formed by oppositely charged polyelectrolytes on dewatering of cellulose suspension. The size and charge of the polyelectrolyte complexes were characterized by different methods (mobility, turbidity, particle size and viscosity). The properties of the complexes depended on the charge ratio, the charge density and the molecular weight of the polymers. The effects of the polyelectrolyte complexes on drainage and retention of papermaking stock were studied with a Dynamic Drainage Analyzer. The best dewatering performance was shown by the complexes of low charge density and high molecular weight anionically and cationically modified poly(acrylamide) (A-PAM and C-PAM), while complexes formed by high charge density and low molecular weight polyelectrolytes had no clear effects on dewatering. It was shown that the use of the complexes of A-PAM and C-PAM as drainage and retention aids enhanced the drainability of cellulose suspension, compared to C-PAM alone. The optimum concentration range of the dewatering effect induced by A-PAM/C-PAM complexes was broader than that of a single C-PAM. The drainage efficiency of A-PAM/C-PAM complexes can be controlled by changing the amount of polyelectrolyte complex and the A-PAM/C-PAM ratio as well as the properties of the complex.

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Introduction

Drainage and retention aid technology develops continuously, concomitantly with the changes towards higher usage of high yield pulps, fillers, and recycled fibres (Roberts 1996). This introduces high amounts of fines, fillers and various contaminants with detrimental effects on the retention and drainage properties of papermaking stock. Hence, various chemical systems have been developed to improve wet-end drainage and retention. Most of them include polymers or a combination of polymers (Norell et al. 1999; Scott 1996). Derivatives of polyacrylamide (PAM) are widely used as aids for strengthening, retention, dewatering and dispersion (Roberts 1996). Microparticle systems are also widely used in paper manufacture providing superior retention, drainage, and formation characteristics (Main and Simonson 1999). However, the demand for cost-effectiveness of the drainage and retention aids makes it necessary to improve their efficiency and to develop new less expensive aids.

The complexes formed by oppositely charged polyelectrolytes in solution have gained great interest and importance in recent years. The structure of the polyelectrolyte complex (PEC) can be tuned by changing the properties of polyelectrolytes (Thünemann et al. 2004). Several earlier studies have shown that polyelectrolyte complexes can be used as additives and synergistic properties can be achieved by combining the properties of the polymers composing the complex. The complexes have been utilized for surface modification (Buchhammer and Lunkwitz 1996; Kramer et al. 1997a, 1997b; Nyström et al. 2003a) and it has been found that they have unique flocculating properties (Buchhammer et al. 1999; Lu et al. 2002; Nyström et al. 2003b; Petzold et al. 1996, 1998; Xu and Somasundaran 1993). Furthermore, it has been reported that PECs can be used as dry/wet strength additives (Ankerfors 2008; Gärdlund et al. 2003; Torgnysdotter and Wågberg 2006) and retention aids (Nyström and Rosenholm 2005; Petzold et al. 1996). PECs have been reported to contain a wider optimum range of concentration and to form more stable flocs than single polymer systems (Nyström et al. 2003b; Petzold et al. 1998). However, little attention has been paid so far to the dewatering effect of polyelectrolyte complexes.

The purpose of the present study was to evaluate the effects of pre-formed complexes of different anionic and cationic polyacrylamides (A-PAMs, C-PAMs) and poly(diallyldimethylammonium chloride)s (PDADMAC) on the dewatering of the papermaking stock. The correlation between the properties of the complexes and their dewatering performances, as well as the possibility of controlling dewatering by choosing a suitable complex type was investigated.

Materials and Methods

Pulp

The composition of stock was 50 % bleached thermomechanical pulp (TMP) and 50 % chemical pulp. The TMP was unwashed pulp from UPM-Kymmene Oy (Kaipola, Finland). ECF bleached kraft pulp made mainly from spruce was from Metsä-Sellu (Äänekoski, Finland). The bleached mechanical pulp was hot-disintegrated to a freeness of 40 CSF according to SCAN-M 10:77. The chemical pulp was beaten to SR 22 in a Valley Beater according to SCAN-C 25:76, and washed into sodium form according to the procedure described by Swerin et al. (1990).

Polymers

Anionic polyacrylamides, A-PAM, were synthesized by copolymerization of acrylamide and acrylic acid. Cationic polyacrylamides, C-PAM, were copolymers of acrylamide and dimethylaminoethyl acrylate quaternized with methyl chloride $(CH_2=CHCO(CH_2)_2N^+(CH_3)_3Cl^-)$. The C-PAMs and A-PAMs were obtained from Kemira Oy, Vaasa, Finland. Poly(diallyldimethylammonium chloride), PDADMAC, was from Ciba Specialty Chemicals Ltd, England. *Table 1* provides the properties of the polymers. The rationale for choosing these polymers was to vary the molecular weight (M_w) and the charge density (CD) of polyelectrolytes independently, in order to evaluate their effect on the properties of the polyelectrolyte complexes (PEC). C-PAM I, C-PAM II and C-PAM III were polymers with low charge densities and different molecular weights. C-PAM IV and PDADMAC were highly cationic, but the molecular weight of C-PAM IV was higher than that of PDADMAC. The charge densities of A-PAM I and II were low while the molecular weight of A-PAM I

was lower than that of APAM II. A-PAM III was highly anionic. The polymers were used as delivered from the manufacturer. To adjust the ionic strength, electrolytes of analytical grade (NaCl and $NaHCO_3$) were used. The water was deionised and distilled.

Table 1. Properties of polymers.

Sample	Degree of subst., DS mol-%	Molecular weight, M_w 10^6 g/mol	Charge density, CD meq/g
C-PAM I	10	0.52	1.7
C-PAM II	10	1.6	1.6
C-PAM III	10	6.0	1.0
C-PAM IV	40	0.60	4.1
PDADMAC	100	0.30	6.0
A-PAM I	10	0.46	2.0
A-PAM II	10	1.7	1.8
A-PAM III	50	0.77	6.3

Dewatering measurement

The stock consistency of pulp was 0.30 % and the volume was 800 ml. The pH was about 8.3 and the ionic strength was kept constant by adding 1 mM $NaHCO_3$ and 9 mM NaCl. The approach of using the complexes with different charge ratios (Fig. 9) was similar than presented in next chapter, but also the effect of the total polymer concentration was studied (Fig. 10).

A dynamic drainage analyzer (DDA) was used for recording the dewatering time. The initialization time before drainage was 30 s. The vacuum was kept at 0.25 kPa. The stirrer speed was 500 rpm. The turbidity of the filtrate after dewatering, measured with an Analite Nephelometer, was taken as an indicator of fines retention.

The drained water was centrifuged for 30 min at 30 000 rpm, and then the amount of polyelectrolyte-bound anionic groups remained in the supernatant was determined by the polyelectrolyte titration (Koljonen et al. 2004; Terayama 1952; Wågberg et al. 1989). The water was carefully separated from the precipitate using a pipette. 0.5 ml cationic polymer (1,5-dimethyl-1,5-diazaundecamethylene polymethobromide, Polybrene) was added to 9.5 ml water after the centrifugation. The excess of the Polybrene and a blank of Polybrene (0.5 ml + 9.5 ml deionised water) were then titrated with an anionic polymer (polyethylene sulphonate, Pes-Na) (concentration 0.260 g/l, charge density 2 meq/l). The point of equivalence was determined using a particle charge detector (Mütek PCD 03, Germany) as described by Koljonen (2004).

Properties of polymer complexes

Complex formation was studied for mass ratios (A-PAM : C-PAM) in the range 0.04-2, using the same ratio as in the dewatering experiments (0.04, 0.08, 0.16, 0.24, 0.4, 1 and 2). The ratio of the number of anionic groups in the anionic polymer to the number of cationic groups in the cationic polymer will be referred to as the charge ratio. According to Ström and Stenius (1981), a complex formation does not depend significantly on total concentration as long as the mass ratio of the complex forming polymers is unchanged. Our results are consistent with this observation. The combinations of the different cationic polymers and anionic polymers formed five types of PECs, as *Table 2* shows. The charge ratios corresponding to the mass ratios are presented in *Table 3*. The properties of the complexes in solution were determined under the following conditions: the quantity of cationic polymers was kept constant (1 g/l), and then anionic polymers were added to form the polyelectrolyte complexes with the desired charge ratio. Next the solution was diluted in a total volume of 50 ml and the ionic strength of solutions was kept constant at 1 mM $NaHCO_3$ and 9 mM NaCl.

Table 2. The composition of PEC systems. CD = charge density. M_w = molecular weight.

PEC systems	Polymer components
A-PAM I / C-PAM I	A-PAM I: low CD, low M_w C-PAM I: low CD, low M_w
A-PAM I / C-PAM II	A-PAM I: low CD, low M_w C-PAM II: low CD, intermediate M_w
A-PAM II / C-PAM III	A-PAM II: low CD, intermediate M_w C-PAM III: low CD, high M_w
A-PAM III / C-PAM IV	A-PAM III: high CD, intermediate M_w C-PAM IV: high CD, intermediate M_w
A-PAM II I / PDADMAC	A-PAM III: high CD, intermediate M_w PDADMAC: high CD, low M_w

Table 3. The mass ratios and the corresponding charge ratios of polymer components in different PECs.

Mass ratio	Charge ratio				
anionic/cationic	A-PAM I/ C-PAM I	A-PAM I/ C-PAM II	A-PAM II/ C-PAM III	A-PAM III/ C-PAM IV	A-PAM III/ PDADMAC
0.04:1	0.05:1	0.04:1	0.07:1	0.06:1	0.04:1
0.08:1	0.09:1	0.09:1	0.14:1	0.12:1	0.08:1
0.16:1	0.19:1	0.17:1	0.28:1	0.25:1	0.17:1
0.24:1	0.28:1	0.26:1	0.42:1	0.37:1	0.25:1
0.4:1	0.47:1	0.43:1	0.7:1	0.61:1	0.42:1
1:1	1.18:1	1.08:1	1.75:1	1.53:1	1.06:1
2:1	2.36:1	2.16:1	3.5:1	3.06:1	2.08:1

The mixtures were equilibrated in tightly closed test tubes by continuous turning over for 1 h in a thermostat at 25 °C and allowed to stand for at least 20 h. After this, the particle size was measured by the means of dynamic light scattering at 90° scattering angle using a N4 Submicron Particle Size Analyzer (Beckman Coulter Inc., USA). The turbidity of the solution was measured with an Analite Nephelometer. The electrophoretic mobility was measured by the Laser-Doppler electrophoresis (Coulter Delsa 440SX, Coulter Electronics Ltd., UK).

Viscosity

Viscosity was determined with a computer-controlled Ubbelohde capillary viscometer system (Schott-Geräte, AVS 350). The samples were allowed to equilibrate for 10 min in the thermostatic bath at 25 °C before measurements. Three parallel points per sample were investigated. Results are reported as specific viscosities η_{sp}, given by

$$\eta_{sp} = \frac{\eta}{\eta_o} - 1 = \frac{\eta - \eta_o}{\eta_o} \tag{1}$$

where η is the viscosity of the solution and η_o is the viscosity of the solvent.

Results and discussion

Complex formation and properties of complexes

Depending on the mixing ratios, mixing the polymer solutions resulted in clear or turbid solutions or precipitation of polymer complexes. Clear solutions were formed when the addition of A-PAM into C-PAM or PDADMAC was low. As more A-PAM was added to a C-PAM or PDADMAC solution, the clear solution became turbid. When further A-PAM was added, flocs were formed around the charge neutralization point and the system separated into two phases. When an excess of A-PAM was used, the precipitate partly dissolved and a colloidally stable dispersion was formed again. These phenomena are due to an associative phase separation of two oppositely charged polyelectrolytes (Biesheuvel and Cohen Stuart 2004; Thünemann et al. 2004) and have been observed in many similar mixtures of polyions (Dautzenberg and Rother 2004; Fredheim and Christensen 2003; Frugier and Audebert 1994; Li et al. 1994; Ström et al. 1985). The association of oppositely charged polyions is mainly entropically driven due to the release of counterions from the polyions. To analyze the formation and properties of different PECs further, the electrophoretic mobility, turbidity, size and viscosity of the colloidal particles formed upon the phase separation were measured as a function of charge ratio of the components and the role of polyelectrolyte properties to PEC properties were considered.

Electrophoretic mobility

Fig 1 shows that the sign of the polyelectrolyte complexes formed upon mixing oppositely charged polymers depended primarily on the mixing charge ratio. When the solution contained clearly more cationic than anionic polyelectrolyte, the complex had a net cationic charge, whereas when an anionic component was dominant in the solution, the complex was negative. *Fig 1a* indicates that the sign of the complex formed by polymers with low charge density and different molecular weight changed from negative to positive at polymer charge ratio higher than 1, i.e., an excess of A-PAM was required to induce the formation of neutral complexes, indicating that the reaction between C-PAM and A-PAM was not fully stoichiometric. Colloidal particles were formed at A-PAM concentrations both below and above the charge neutralization ration. Moreover, the charge ratio at which a non-charged complex was formed, was shifted to higher values for complexation of higher molecular weight polymer components with a low charge density. This indicates that complex formation was not only driven by electrostatic attraction, i.e. the release of the counterions. Other driving forces can be, e.g. enthalpic favouring of mixing similar polymer structures. PECs can also be non-stoiciometric, because some charges may be inaccessible due to their structure, inability to reconform or the low charge density of polyelectrolytes (Ankerfors 2008; Koetz et al. 1996; Thünemann et al. 2004; Vanerek and van de Ven 2006). In addition, differences in mixing procedure or the history of complexation can lead to the different structures of PEC and they can even freeze the structure far off the thermodynamically most stable one (Dragan and Schwarz 2004; Thünemann et al. 2004).

In the high charge density systems (*Fig 1b*), the complex behaved slightly differently. For A-PAM III/C-PAM IV and A-PAM III/PDADMAC systems, the complex changed sign below charge ratio 1, i.e when cationic polyelectrolyte was dominant in solution. In this case less A-PAM was required to neutralize the complex. It seems that molecular weights (chain lengths), the positions of the functional groups and charge densities of the complex-forming components played important roles in the reactions between the polyions. These phenomena have also been observed in many similar mixtures of polyions (Mende et al. 2002; Ström et al. 1985; Thünemann et al. 2004).

a.

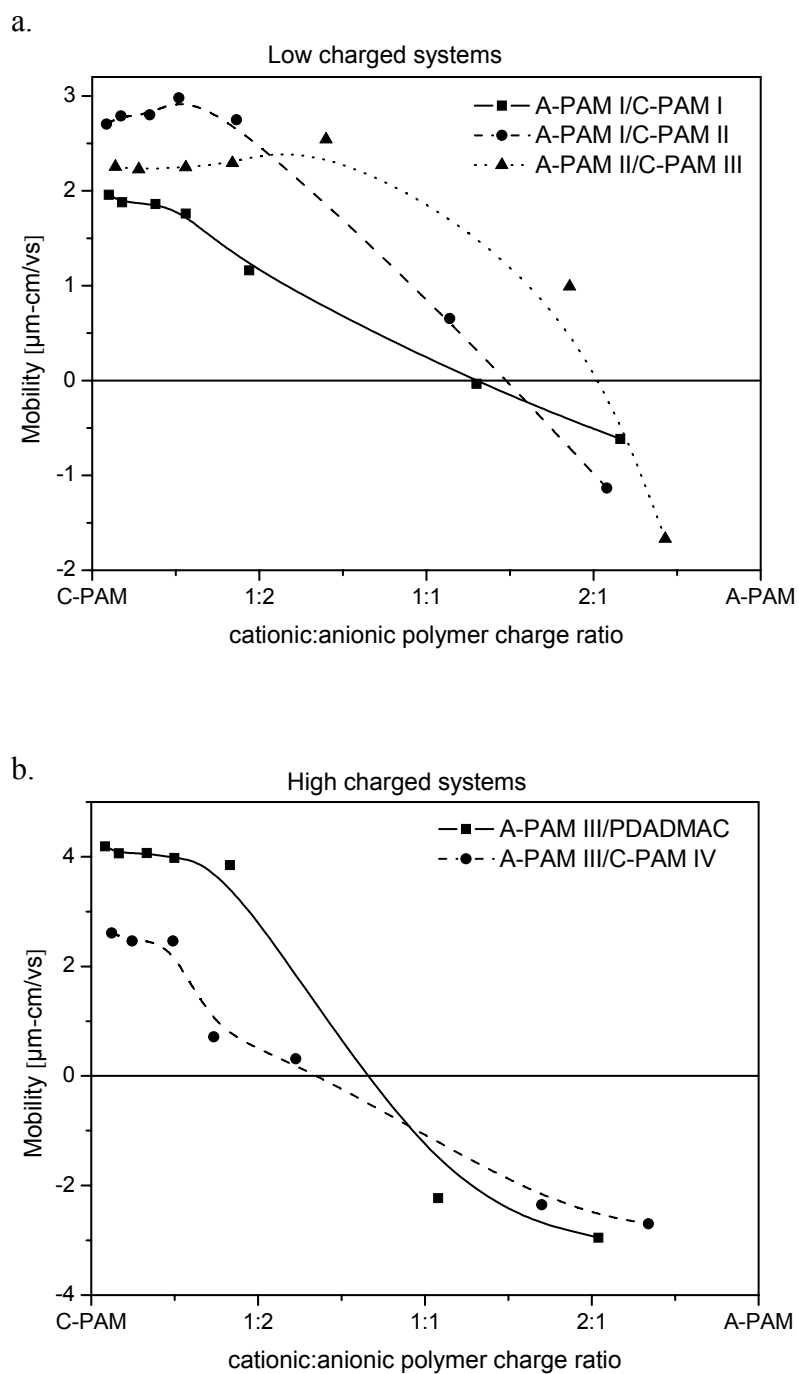Low charged systems

b.

High charged systems

Fig 1. Electrophoretic mobility of complexes formed by A-PAM and C-PAM or PDADMAC with a. low charge density and different molecular weight and b. high charge density and different molecular weight. Lines are drawn to aid the eye only.

Turbidity

Fig 2 shows turbidity as a function of the polyelectrolyte charge ratio. The turbidity initially increased with increasing anionic/cationic charge ratio and reached a maximum at certain composition. Above this ratio, the turbidity decreased because of the precipitation of the complex particles. For all systems presented in *Fig 2* excluding APAM I/CPAM I, a minimum turbidity corresponded to a maximum precipitation. As shown by the electrophoretic mobility of the particles (*Fig 1*), it is evident that the maximum turbidity was obtained close to the charge neutralization point for the A-PAM I/C-PAM I complex, which precipitated as colloidally stable particles. In the other systems, the turbidity minimum occurred near the charge neutralization of PEC. This was due to the formation of a clear supernatant solution and a gel-like precipitate (e.g. A-PAM I/C-PAM II) or macroscopic flocs (e.g. A-PAM II/C-PAM III) that deposited on the walls or at the bottom of tube. Colloidally stable PECs are often thought to be coiled structures with a charge-neutralized core and an outer zone consisting of a charged polyelectrolyte layer (Ladam et al. 2000). On close to neutral PECs, the stabilizing polyelectrolyte is missing, leading the colloidally instable PEC and the aggregation of PEC (Dautzenberg and Rother 2004; Koetz et al. 1996; Mende et al. 2002; Thünemann et al. 2004).
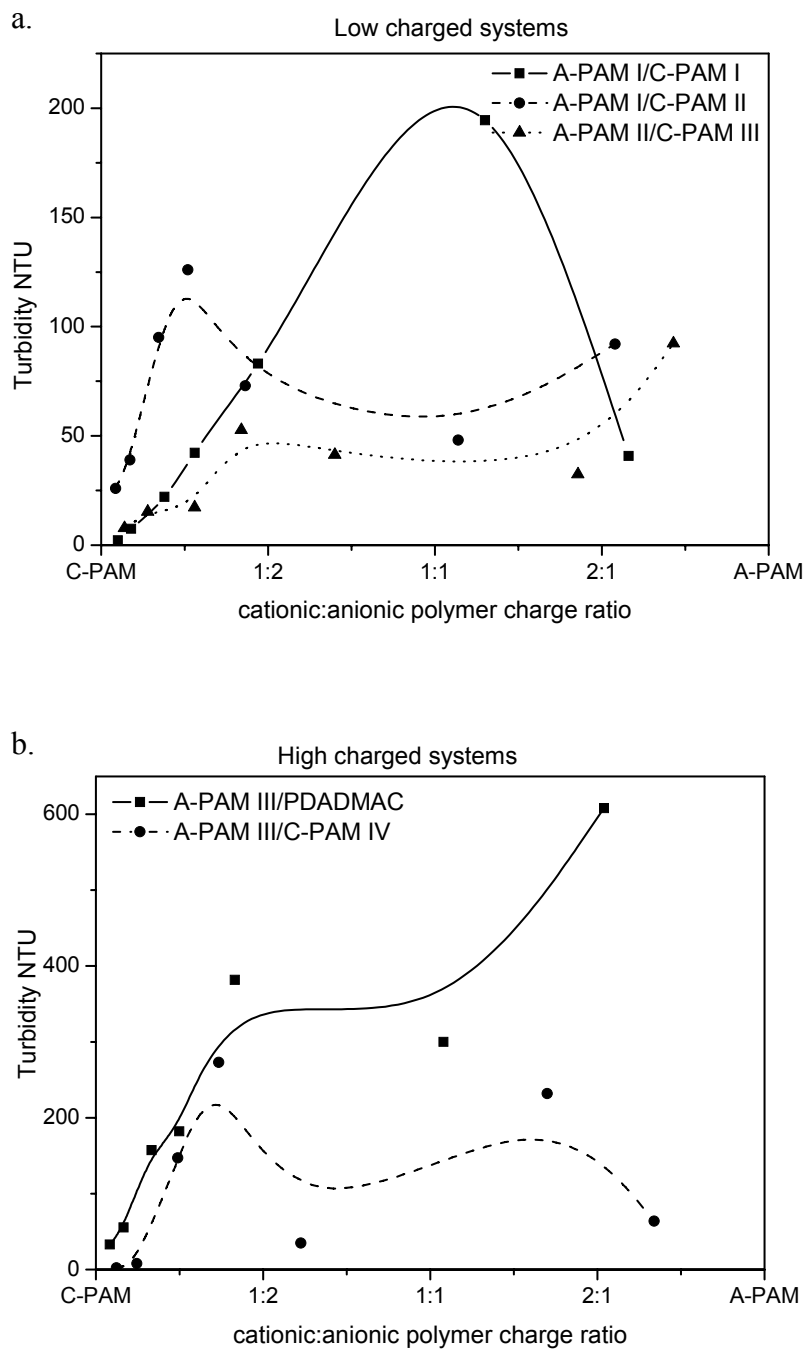
Fig 2. Turbidity of complex solutions formed by A-PAM and C-PAM or PDADMAC a. with low charge density and different molecular weights and b. with high charge density and different molecular weights as a function of the anionic/cationic charge ratio. Lines are drawn to aid the eye only.

When an anionic polymer was added in excess of charge neutralization, the precipitates dissolved, *i.e.* soluble (or colloidal) complexes were formed. This has been reported earlier for some systems (Mende et al. 2002; Ström and Stenius 1981; Ström et al. 1985). The decrease in the turbidity beyond the second maximum (*Fig 2b,* A-PAM III, C-PM IV) was due to formation of more soluble complexes and not to aggregation and sedimentation of colloidal particles.

Particle size

Fig 3 shows how the particle size of the complexes changed when the anionic/cationic polymers were mixed in different charge ratios. Note that for charge ratios giving rise to the precipitation of polymer complexes, it is the size of residual colloidal particles in the solution that is shown in this figure.

The size of the complex correlated with the molecular weight of the components, including the low charge density polymers (*Fig 3a*). The particle size of A-PAM II/C-PAM III grew more rapidly and was larger over the entire charge ratio range than in the case for PECs formed by lower molecular weight polymers. This was very likely due to the ability of the large A-PAM II molecules to bind a higher number of polycations and to the large molecular weight of CPAM III. On the other hand, the probability of C-PAM molecules with a lower molecular weight to interact with many A-PAMs at the same time would be lower, which resulted in the formation of smaller particles. This indicates that when lower charge density polymers were used as components in the complex formation, the molecular weight was the main factor influencing particle size. The sizes of A-PAM/C-PAM complexes are congruent with the results reported by Saarinen et al. (2008). In addition, the comparison between *Figs 1* and *3* show that for A-PAM I/C-PAM I, which did not form macroscopic precipitates, the highest particle size was achieved when charge equivalent amounts of the two polyelectrolytes were mixed.
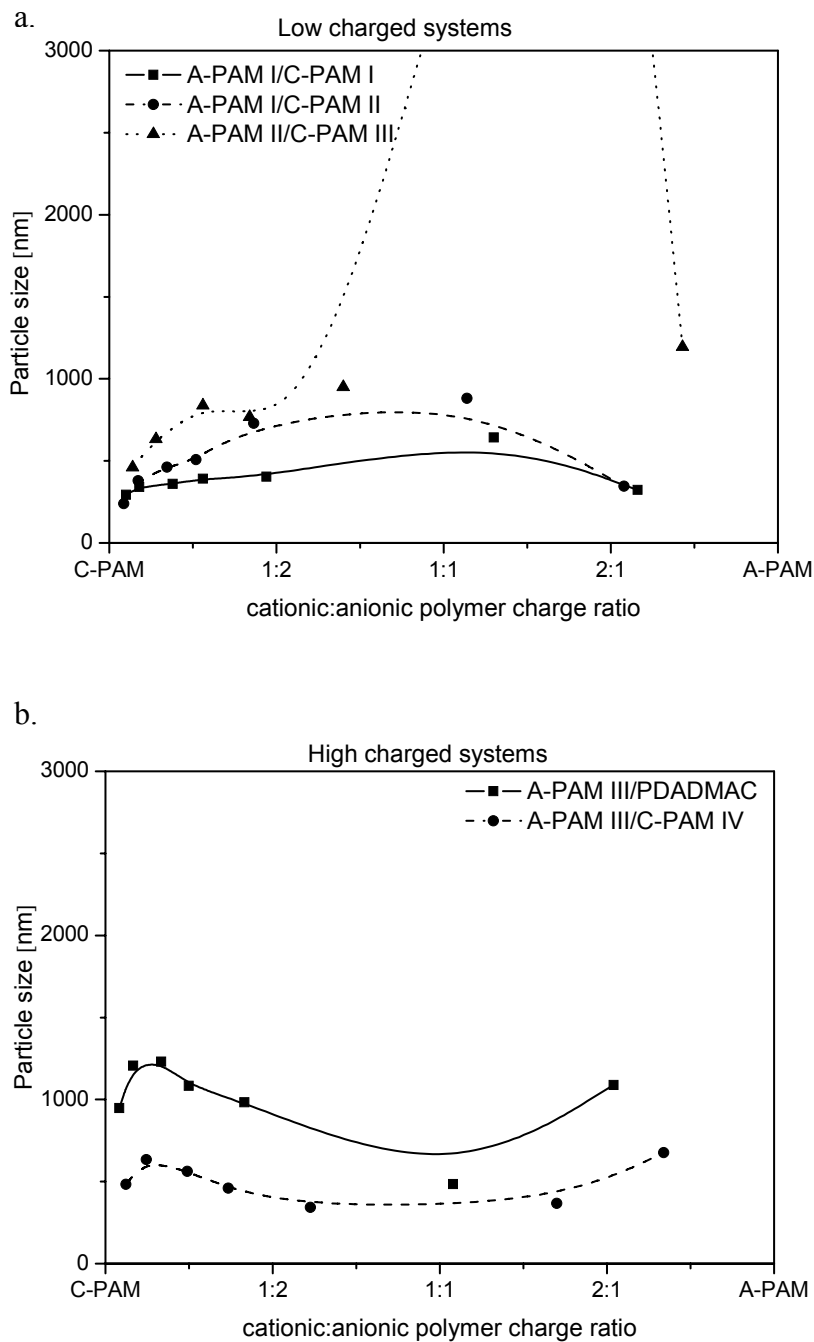
Fig 3. Size of complex particles formed by A-PAM and C-PAM or PDADMAC: a. with low charge density and different molecular weights and b. with high charge density and different molecular weights as a function of the anionic/cationic charge ratio. At A-PAM II:C-PAM III ratios around 1:1 very large particles formed.

Fig 3b shows the particle size of complexes formed by two oppositely charged polymers with a high charge density and different molecular weights. It is evident that

the minimum particle size occurred in the neutral range. Thünemann et al. (2004) has reported similar observations. This deviates from the observations in low charged systems. PECs formed by low charge density (and high molecular weight) polyelectrolytes often form coacervates; liquid-like and mobile structures (Biesheuvel and Cohen Stuart 2004; Vanerek and van de Ven 2006). The size of A-PAM III/PDADMAC complex was larger over the entire charge ratios compared to that of A-PAM III/C-PAM IV. The reason may be that a better match in chemical structure, charge density or configuration between A-PAM III and C-PAM IV relative to that between A-PAM III and PDADMAC produced a more compact complex structure (Dautzenberg and Jaeger 2002; Mende et al. 2002; Nyström et al. 2004; Thünemann et al. 2004). The effect of charge density of polyelectrolytes can be seen by comparing A-PAM I/C-PAM I to A-PAM III/C-PAM IV complexes. They were at the same scale. This leads to the conclusion that the molecular weight of the complex components was a more relevant factor influencing the size of PEC than charge density of polyelectrolytes, but the mechanism of complex formation is different for low charge and high charge polymers.

Viscosity

Fig 4 compares the specific viscosities of A-PAM I/C-PAM II solution with those of the pure C-PAM I solution. The viscosity of the C-PAM I solution increased steadily, when C-PAM concentration increased. By contrast, when A-PAM I was added to the solution, the viscosity decreased and was lower throughout than the viscosity of the pure C-PAM at the same polymer concentration. This indicates that the complex formation, i.e. the binding of the A-PAM and the C-PAM molecules together, released counterions and water molecules bound to polymers, thus compacting the polymer coils and lowering the viscosity. The decrease in viscosity should make dewatering easier with PEC systems than with single polymer systems.
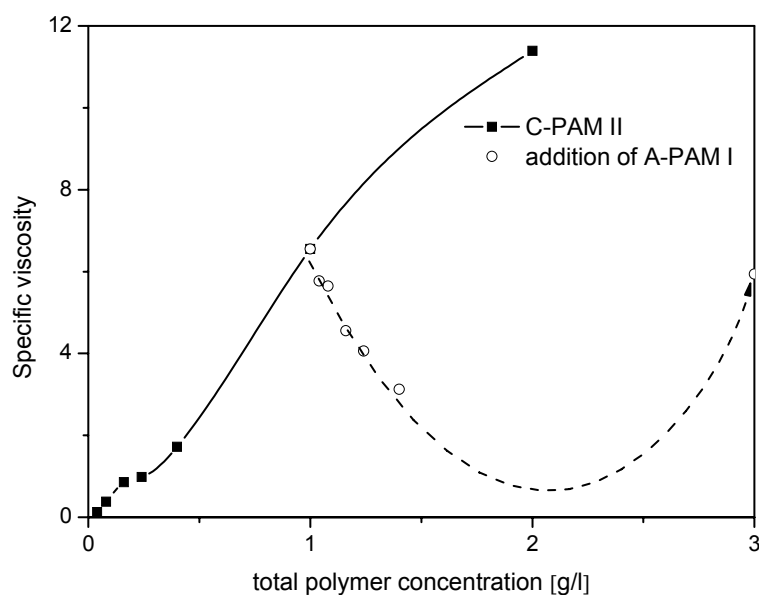
Fig 4. Dependence of the specific viscosity of C-PAM and polyelectrolyte complexes (A-PAM I/C-PAM II) on different polymer concentrations (C-PAM concentration is 1 g/l in complex formation).

Fig 5 shows the specific viscosity of systems containing PECs as a function of a total polymer concentration at constant mass ratio of PEC. When the molecular weight of PEC components increased, the viscosity increased in solutions containing PECs formed by low charged polyelectrolytes. Low charge density, high molecular weight polymers (A-PAM II/C-PAM III) will be loosely associated, forming complexes with long and flexible polymer strands, which result in a higher viscosity and larger particle size. Their water content could also be quite substantial (Ankerfors 2008; Gärdlund et al. 2007). The reorganization of lower molecular weight polymers is easier. Therefore, the particles formed by mixing a low charge density, low and intermediate molecular weight polymers (A-PAM I/ C-PAM I and A-PAM I/C-PAM II) will be more compact. These kinds of PEC structures had been found in many similar mixtures of polyions (Koetz et al. 1996).
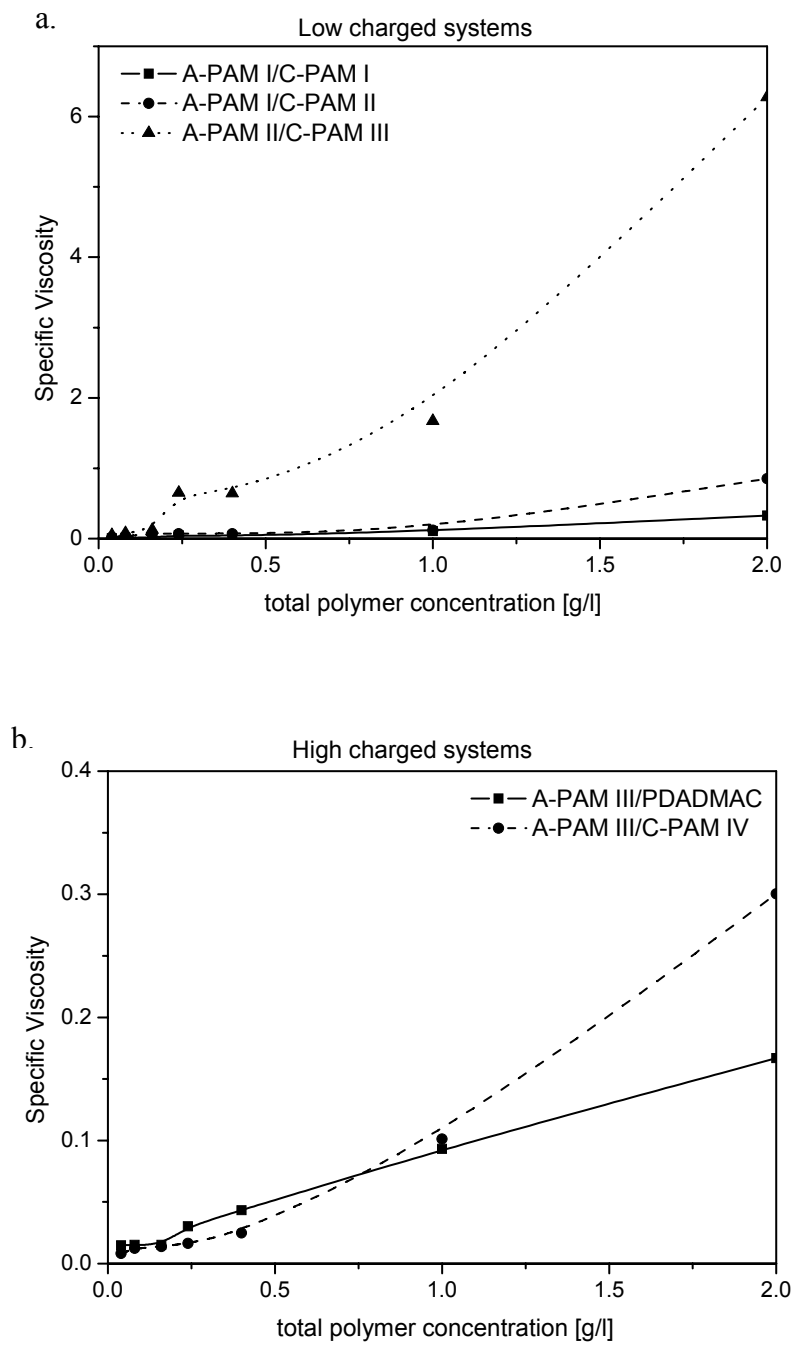
Fig 5. Specific viscosity of complex solution formed by A-PAM and C-PAM or PDADMAC a. with low charge density and different molecular and b. with high charge density and different molecular weights as a function of total polymer concentrations at anionic/cationic mass ratio 0.16:1. All of dispersions here are colloidal stable.

Fig 5 depicts that the specific viscosities of the complexes formed by high charge density polyelectrolytes with low and intermediate molecular weight (A-PAM III/PDADMAC and A-PAM III/C-PAM IV) were similar to that of the low charged polyelectrolytes with the same molecular weight (A-PAM I/C-PAM I). Actually, the specific viscosity of A-PAM III/C-PAM IV and A-PAM I/C-PAM I complexes were almost the same through the polymer concentration range. The sizes of the complexes formed by these polyelectrolyte pairs did not differ very much, but there was a clear difference in the size only at the mass ratio of 0.16:1 (*Fig 3*). This further supports the conclusion about the dominant effect of molecular weight on the viscosity, while the charge density of polyeletrolyte had a minor influence on the structure and viscosity. Only the complex containing the PDADMAC was an exception of this conclusion, but it is probably because of its different structure and chemical nature. Overall, *Fig 5b* confirms the formation of the compact structural complex particles by oppositely charged polymers with high charge.

Effects of polyelectrolyte complexes on dewatering

One component system vs. PEC

The C-PAM systems were studied to evaluate the benefit of using polyelectrolyte complexes on the drainage of the stock. *Fig 6* shows the dewatering time as a function of C-PAM dosage. For all C-PAMs, dewatering time initially decreased rapidly and then started to slowly increase with an increasing addition of C-PAM. In all cases the dewatering efficiency substantially deteriorated at doses higher than 0.4 % o.d. pulp. For the polymer with a high charge density (C-PAM IV) the dewatering time was about 14 s at the optimal dosage 0.12 %, while it was about 18 s at the optimal dosage 0.24 % for the polymer with a low charge density and a similar molecular weight (C-PAM I). Thus, the drainability increased with an increasing charge density, and the dosage of C-PAM required to attain a given drainability decreased simultaneously. *Fig 6* also shows that the drainability of stock improved when the molecular weight of C-PAM with a low charge density increased (compare C-PAM I and C-PAM II). The lowest dewatering time of all (about 8 s) was achieved when 0.24 % of C-PAM II with a low charge density and an intermediate molecular weight was added. C-PAM III with the lowest charge density and the highest molecular weight improved dewatering even further (not shown in the figure). It can be concluded that C-PAM

with a low charge density and high molecular weight has the best effect on drainability.
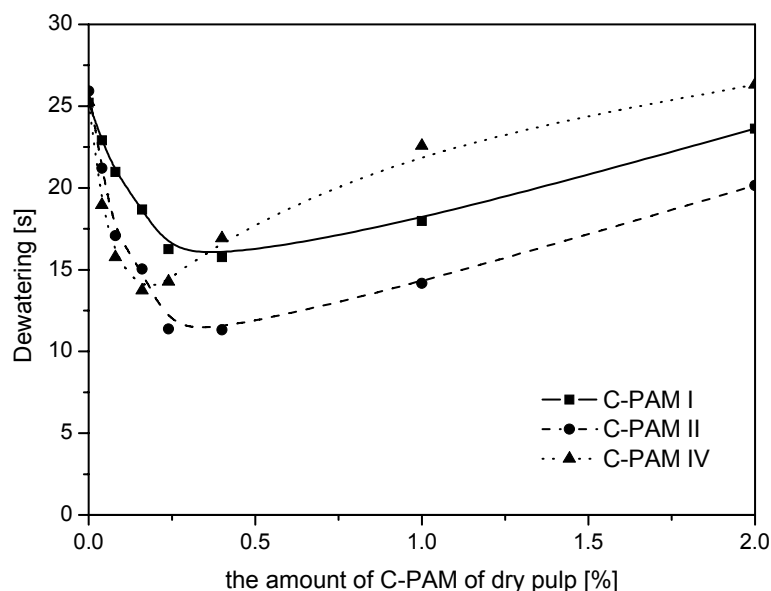

Fig 6. The effect of C-PAM on dewatering time of pulp.

With an increasing addition of a cationic polymer the charge in the solution, detected by the polyelectrolyte titration, changes from negative to positive. Concomitantly, as shown by *Fig 7*, the drainage time passes through a minimum when the anionic polyelectrolytes or particles in the aqueous phase are more or less neutralized by the added CPAM. This explains the result of *Fig 6*, i.e. that more of the lower charged polymer (C-PAM II) is needed to achieve the optimum drainage than what is achieved with a high charge density polymer (C-PAM IV).

The main rationale for using cationic polymeric retention and drainage aids is that they are thought to bind fine material flocculated through a charge neutralization and bridging onto the long fibres already in the stock suspension before the fibre mat is formed (see e.g., Forsberg and Ström et al. 1994; Norell et al. 1999; Scott 1996). In the presence of C-PAM, the negative fines are partly neutralized, the double-layer forces are reduced and the fines start to flocculate. *Fig 7* shows that the dosage of C-PAM that results in the fastest drainage coincides with the dosage that renders the residual particles in the filtrate neutral. Thus, at least under the conditions used in this

investigation, the charge neutralisation which renders the electrostatically stabilized fine material colloidally instable seems to be an important factor in the formation of an easily drainable sheet. At C-PAM dosages higher than the optimum dosage, the surface charge of fibres and fines is partly reversed due to the adsorption of excess polymer, which restabilizes the fine material, slows down dewatering and reduces fines retention.
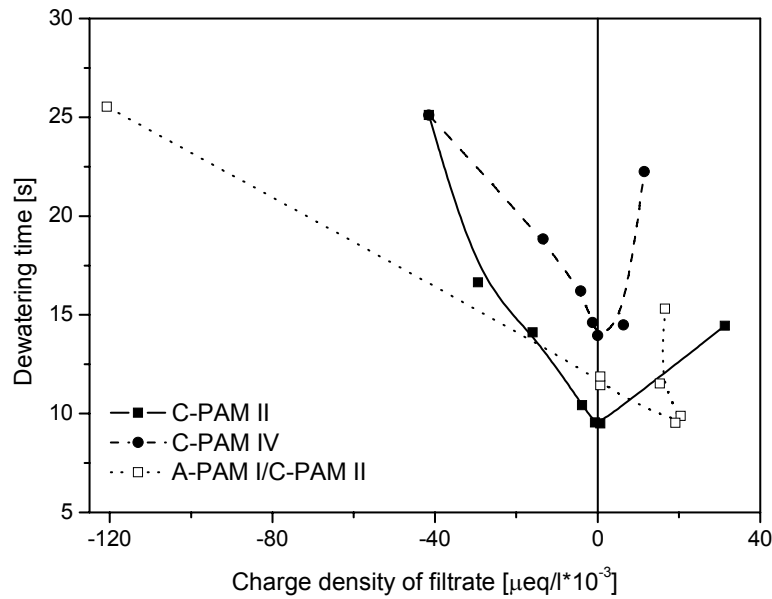
Fig 7. Dewatering time as a function of charge in water phase of filtrate when adding C-PAM II or C-PAM IV, and PEC formed by A-PAM I and C-PAM II. The dosages for polymers used here are same as those in Fig 6 and the charge ratios for the complexes are presented in Table 3.

For retention and drainage aids with a low charge density and a high molecular weight, the molecular weight of the polymer is a key factor, because that kind of polymer mainly forms bridges between the particles to form flocculation. In this case the flocculation will increase as the length of the molecular chain of C-PAM increases. Indeed, *Fig 6* shows that C-PAM II with an intermediate molecular weight and a low charge density yielded a more rapid dewatering than the C-PAM I with a low molecular weight irrespective of their charge density. This result differs from the observation by Liu (1986) that C-PAM's role as a drainage aid on reed pulp is independent of its molecular weight at high charge density. Evidently, the charge density of the polymer is also an important factor for flocculation ability due to its

influence on the adsorption and conformation of the polymer on the surface of particles. If the charge density of the polyelectrolyte is high, the polymer adsorbs in a flatter configuration on the surface of particles, which may have a negative effect on bridging flocculation (Abson and Brooks 1985). This is in accordance with conclusions from force measurements (Salmi et al. 2007a). They observed that bridging was the main mechanism in surface interactions and that the molecular weight influenced the range of attraction if the charge density of polyelectrolyte was low; otherwise the effect of molecular weight was insignificant. A flat configuration is logically less sensitive to the molecular weight.

The results shown in *Fig 7* enable us to compare pure C-PAM II and A-PAM I/C-PAM II complexes. The PEC did not show any clear improvement in dewatering compared to C-PAM. The optimum drainage occurred on the positively charged side of the filtrate when the excess C-PAM dominated, i.e. the PEC was also positively charged. The effect of adding A-PAM to C-PAM is to create a weakly charged complex that flocculates the fine material by bridging and not just by charge neutralization. However, in this experiment the optimum range of PEC concentration or the optimum mixing ratio of the complex was still unknown, and thus, further analysis was needed.

To analyse the effect of PEC further, the PEC containing high molecular weight and low charge density polyelectrolytes was chosen, because the high molecular weight seemed to be beneficial for dewatering. *Fig 8* compares the dewatering times of single C-PAM III, which contained the most advantageous dewatering properties of the single polyelectrolytes in this study, and premixed complexes of A-PAM II and C-PAM III, which was the optimum choice of the complex to improve dewatering (shown later) and which had the largest size of the complexes investigated in this study *(Fig 3)*. When the positively charged PEC was added in the solution, a shorter optimum dewatering time and a slower increase in the dewatering time after optimum was obtained than when adding C-PAM only. The decrease in dewatering time at low additions of C-PAM only or PEC was probably caused mainly by the formation of interparticle bridges, which presumably was strongly promoted by A-PAM molecules acting as a link between C-PAM molecules in the complex. The deviations at higher amounts of polyelectrolytes may be a sign of changing from pure complex-induced

bridging to an A-PAM promoted mixing of complex layers, but the actual mechanism can not be stated with certainty from the result presented here. However, supporting the mechanism, Saarinen et al. (2008) have observed that the large C-PAM/A-PAM complexes form a thick and loose layer on cellulose. Furthermore, Salmi et al. have reported that C-PAM/A-PAM complexes introduced long-range (over 1 μm) attractive forces, when PEC covered cellulose surfaces were separated (Salmi et al. 2007b). Thus, while adding large amounts of pure C-PAM III resulted in charge reversal and restabilization of the fine material (Salmi et al. 2007a), the complexes were able to act as relatively efficient flocculants also when added in excess of the optimum dosage.
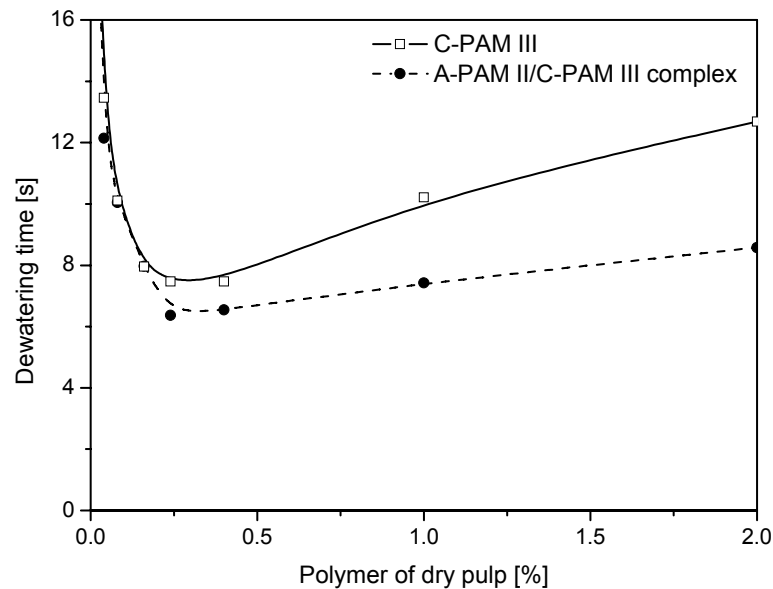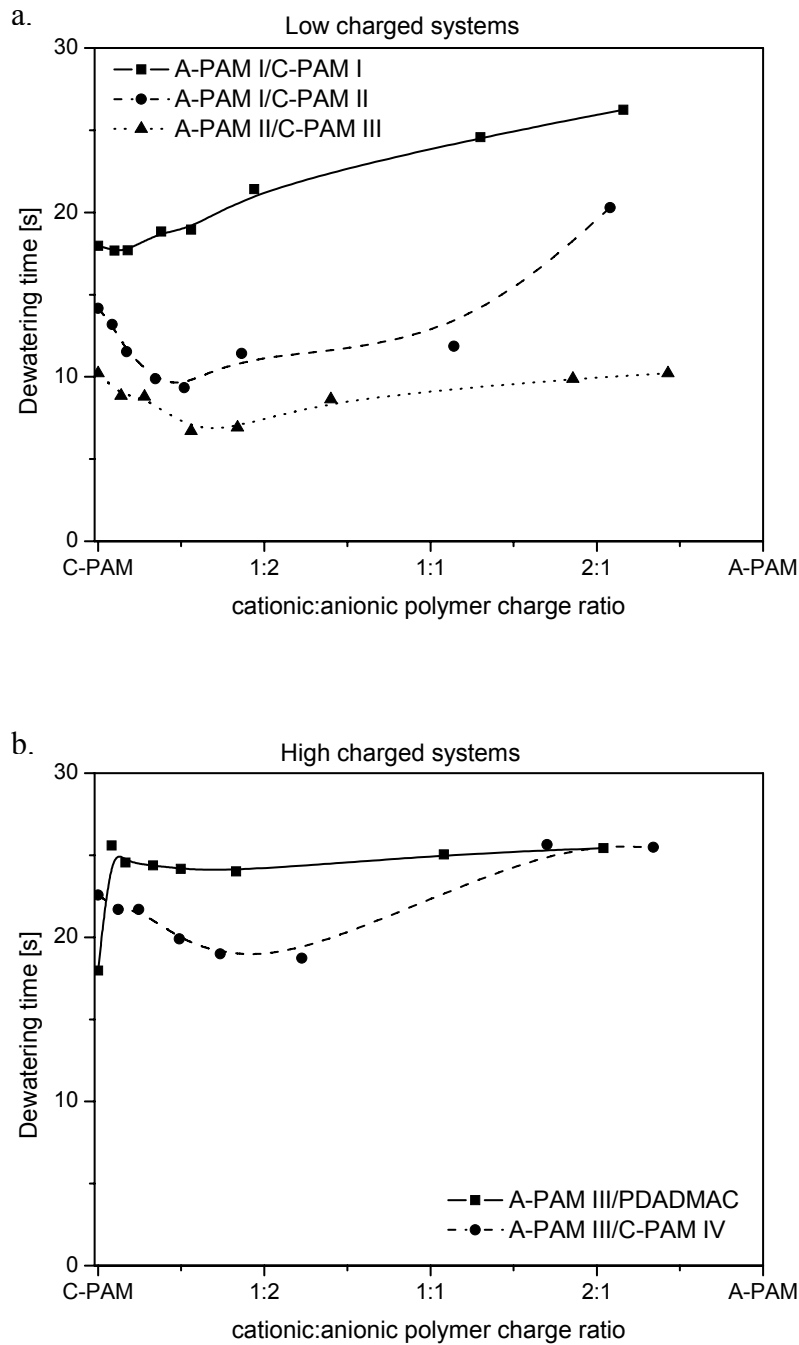

Fig 8. The dewatering effect of complex formed by A-PAM II/C-PAM III and of C-PAM III alone as a function of the total amount of polymer added. A-PAM II: C-PAM III charge ratio was 0.28:1.

Effects of PEC properties on dewatering

To gain a better understanding of the mechanism by which polyelectrolyte complexes affect dewatering, dewatering by different PECs was studied and the results were compared to the PEC properties. *Fig 9* shows the differences in drainage efficiency

between the complexes formed by polymers with different charge densities and different molecular weights. The complex formed by low charge density and high molecular weight polymers (A-PAM II/C-PAM III) was the most effective as a drainage aid over the entire A-PAM concentration range, although the solution of A-PAMII/C-PAM III complexes had the largest viscosity (*Fig 5*). This suggested that its effect on retention was advantageous. Moreover, the A-PAM II/C-PAM III complex showed a good dewatering ability even when the complex was neutral or negatively charged. These results indicate that the size of the PEC is crucial. The larger the PEC, the better it is able to form bridges and, hence, to improve dewatering.

When the complexes formed by oppositely charged polymers with a high charge density and a low molecular weight were compared to low charge density polymers, no clear improvement was observed. On the contrary, the PEC containing PDADMAC increased the dewatering time. However, the effect of charge density remains somewhat unclear, because the molecular weights of the components in these PECs were low. However, the structure of the complexes formed between high charge density and low molecular weight polymers was compact. This further supports that efficient flocculation required a large and flexible PEC. Even when the complexes were close to neutral or even anionic, dewatering was effective due to the linking ability of the A-PAM and the increased total polymer dosage.

a.

b.

Fig 9. The effects of complex formed by A-PAM, C-PAM and PDADMAC a. with low charge density and different molecular weights and b. with high charge density and different molecular weights on dewatering time.

The effect of the concentration of polyelectrolyte complexes solution was also studied. *Fig 10* shows that the dewatering behaviour of the polymer complex formed by low charged, high molecular weight polyelectrolytes (A-PAM II/C-PAM III)

depended on the total concentration of polymers at different A-PAM/C-PAM charge ratios. The drainage time went through minimum when the total polymer concentration increased, as it was observed also in pure C-PAM systems. The minimum in dewatering time, however, shifted slightly towards the higher polymer concentration when the A-PAM/C-PAM charge ratio was increased, i.e. the optimum concentrations for dewatering could be adjusted by changing A-PAM/C-PAM ratios. The lowest dewatering was recorded using the polyelectrolyte containing a small amount of A-PAM (in the charge ratio of 0.28:1). The dewatering property of this positively charged complex was further enhanced by the largest optimum concentration range. This all supports the A-PAM's important linking role in the complex. In addition, the A-PAM is capable to link C-PAMs together even when the surfaces are occupied by adsorbed complexes. A-PAM linking is based on that A-PAM feels affinity to the C-PAM molecules of the opposite PEC layer, when PEC layers are overlapping. Complexation reaction between A-PAM and C-PAM is possible. This favours that the opposite layers hold together even when the surfaces are occupied by the complexes. The flexible structure of the complex is essential for this mechanism. A-PAM linking renders the dual polymer system an effective additive in dewatering. The practical use of PECs is easy because of the low sensitivity to concentration and to the addition in a single step. Interestingly, good wet and dry strength of paper have been reported for large PECs with a charge ratio of 0.9 (slightly cationic) (Gärdlund et al. 2003). One mechanism for this has been proposed to be an increased bonding area due to a higher amount of polymer than in a single polymer system (Gärdlund et al. 2003; Torgnysdotter and Wågberg 2006). Therefore the positive effect of a larger polymer dosage cannot be neglected, even if it is not essential for good dewatering. Importantly, PEC systems tolerate a large amount of polymer without loosing good dewatering abilities.
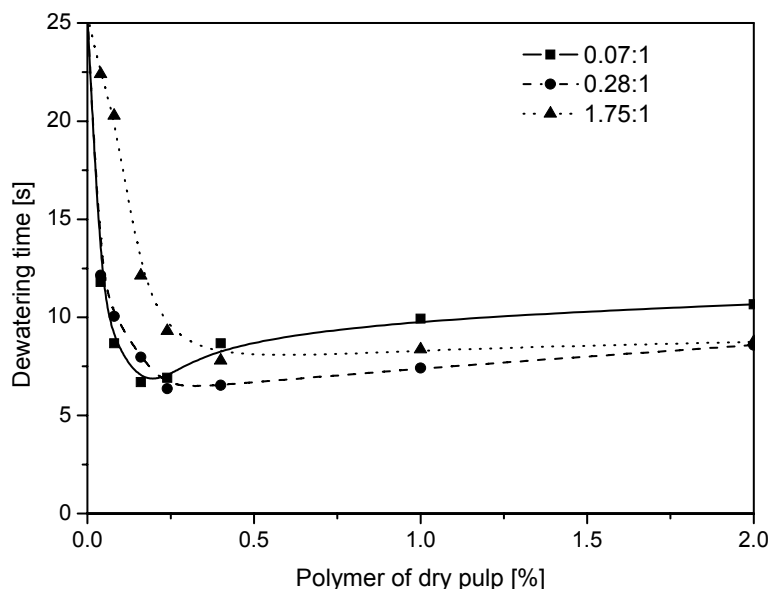
Fig 10. The effects of complex on dewatering as a function of the total amount of polymer added at different charge ratios of premixed A-PAM II and C-PAM III.

Conclusions

The properties of PEC complexes depend on the polymers charge ratio, the charge density and molecular weight of complex polymer components. The use of premixed A-PAM/C-PAM complexes enhances the drainability (drainage times are reduced) of papermaking stock compared to using C-PAM alone. The most characteristic feature of the dewatering effects induced by the A-PAM/C-PAM complex was broader optimum concentration range than for single C-PAM. An optimum drainage occurs when a small amount of A-PAM is present in the complex. Complexes formed by low charge density and high molecular weight A-PAM and C-PAM show the most advantageous dewatering performance. It is suggested that the bridging and the linking abilities of the A-PAM together with the large size, i.e. the large outreach of the complex, are the main reasons for the improved dewatering results. The drainage efficiency of A-PAM/C-PAM complexes can be well controlled by changing the

amount, ratio and molecular weight of the A-PAM and C-PAM. The ability of pre-formed PEC complexes to reduce the dewatering time is less sensitive to the amount of polymer added than to the addition of single cationic polymers.

Acknowledgements

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