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The effect of cationic polyelectrolyte complexes on interactions between cellulose surfaces

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Abstract

The purpose of this work was to better understand the effect polyelectrolyte complexes have on the interactions in cellulosic systems. The surface forces between cellulose spheres immersed in solutions of positively charged polyelectrolyte complexes, formed by cationic and anionic polyacrylamides, were studied using an atomic force microscope. The effect of the molecular weight and the charge density of the polyelectrolytes, as well as the background electrolyte concentration were investigated. The adsorption of the polyelectrolyte complexes on the negatively charged cellulose surface had a strong influence on the interactions between the surfaces and the forces were clearly different as compared to the single polymer systems. The interactions between the adsorbed polyelectrolyte complex layers were mainly steric and repulsive, even at low polymer concentrations. The comparison between two polyelectrolyte complexes showed that the complex formed by high molecular weight and low charged polyelectrolytes induced a steric force ranging further than the one induced by the complex formed by low molecular weight and high charged polyelectrolytes. Also the pull-off forces measured on separation ranged longer in the former case but the pull-off force was weaker. The fact that the interaction forces are totally different using polymer complexes as compared to single polymer systems can have a drastic effect on, e.g. water removal efficiency, as well as flocculation during the formation of the paper web.
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1. Introduction

Cellulose is an essential natural polymer in pulping and papermaking. The web of cellulose fibers forms the body of the paper. Thus, the surface interactions between cellulose fibers are important in controlling their behavior in these processes. The polyelectrolytes can work as flocculants, stabilizers or adhesives, depending on the type and dosing of the polyelectrolyte [1]. The nature of the surface forces determines the role of the polyelectrolytes. When cationic polyelectrolytes are used as flocculants they improve retention, but if flocculation is too effective the paper quality may suffer. The use of polyelectrolyte complexes (PEC), instead of one component system, is a possible solution to this problem. PECs have been found to improve the flocculation and to increase the optimum con-

centration range compared to the one in single polyelectrolyte systems [2,3]. Positive effects of PECs on paper strength have been reported by Gärdlund et al. [4]. To gain better understanding of the mechanism behind these improvements, the effect of the polyelectrolyte complexes on surface properties was studied in a model system.

Measuring specific surface forces relevant to paper processes with atomic force microscope (AFM) became possible in 1991, when an application of the colloidal probe technique was introduced [5,6]. The first force measurements with cellulose using AFM were accomplished in 1997 [7]. Since then, the interactions between cellulose surfaces in systems containing single polyelectrolyte have been extensively studied using both AFM and the interferometric surface apparatus (SFA) [8–14]. In our previous study [15,16], we investigated the effect of cationic polyelectrolytes with various molecular weights (M_w) and charge density (CD) on forces between cellulose surfaces. We found that the repulsion changed from electrostatic to steric, when the charge density of the polyelectrolyte decreased and the molecular weight increased. In this aspect, an interest in

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the effect of an anionic component raised. How would polyelectrolyte complexes affect surfaces forces? What would the nature and the range of surface forces be? Despite the fact that the complexes between cationic and anionic components play an important role during papermaking, very few studies on the effect of PECs on surface forces have been conducted and, to our knowledge, there are no studies on cellulosic systems. Other cognate systems, like interactions in the presence of polymer multilayers (PEM) and surfactant–polymer complexes, have been studied to some extent [17–23]. These systems behaved in a special manner due either to the layered structure or the presence of hydrophobic components. However, PECs in paper applications are formed by random, polydisperse and charged polyelectrolytes. Their effects on the forces between cellulose surfaces have, to our knowledge, not been studied.

The purpose of this work was to study the effect of polyelectrolyte complexes formed by cationic and anionic polyacrylamide (C-PAM and A-PAM) on interactions between model cellulose surfaces by AFM. The effect of the charge density and the molecular weight of C-PAM and A-PAM at various electrolyte concentrations was studied. Polyelectrolyte complexes were compared with linear and crosslinked C-PAMs. The changes in interactions on approach as well as in pull-off forces and the compressibility of the layers were measured in order to understand the influence of the anionic component. In this way, the mechanism behind the improvements in for example dewatering and paper strength using PECs might be revealed a step further.

2. Experimental

2.1. Materials

Measurements were performed in solutions of PEC in 0.1 and 1.0 mM NaHCO$_3$. The polymer concentration was varied from 0 to 100 mg/l. Fresh polymer solutions were prepared 1 h prior to use. PECs were premixed before adding them to the liquid cell of AFM. PECs were formed by C-PAM and A-PAM (Kemira Oyj, Finland) in a mass ratio of 10:1. The properties of the polyelectrolytes used to form complexes and the size of PECs are presented in Table 1. Both M_w, determined from the intrinsic viscosity, and CD, determined by polyelectrolyte titration, of polyelectrolytes were varied in PEC A and B. The average

Table 1
The properties of PEC A, PEC B and crosslinked C-PAM (CL)

	M_w ($\times 10^6$ g/mol)	CD (meq/g)	Diameter (nm)
PEC A			
C-PAM	1.40	1.80	470
A-PAM	2.40	1.80	
PEC B			
C-PAM	0.40	3.10	280
A-PAM	0.22	6.30	
CL			
C-PAM	1.20	1.40	n.d.

n.d., not determined.

size of PEC was determined by dynamic light scattering using a N5 Submicron Particle Size Analyzer (Beckman Coulter Inc., USA). A small fraction of smaller particles (<5%), possibly free C-PAM molecules, was also observed. The charge of the PECs, determined by Coulter Delsa 440SX instrument (Coulter Electronics Ltd., UK), was positive. For comparison, the effect of crosslinked C-PAM was also studied. The precipitated spheres of cellulose II were manufactured by Kanebo Co., Japan. They were 5–35% crystalline and slightly negatively charged [24]. Their radius in electrolyte solution was 15–30 µm determined in situ by using an optical microscope and a digital camera.

2.2. Force measurements

An atomic force microscope (NanoScope IIIa multimode, Digital Instruments Inc., Santa Barbara, USA) was used to measure surface forces using the colloidal probe technique [5,6]. Briefly, a cellulose sphere was glued to the tipless end of the cantilever with a reported spring constant of 0.06 N/m (Veeco Instruments, Santa Barbara). Another cellulose sphere was glued on the mica surface to achieve a symmetric system for force measurements. The Surface force was calculated from the deflection of the cantilever using Hooke's law. The spring constants were determined by the thermal noise method [25] and the result was controlled by the reference spring method [26,27]. The surface forces were normalized by the radius of the cellulose spheres [28]. A clear constant compliance region could not be reached for the PEC systems due to compressibility of the layers. Instead, raw data (deflection versus piezo movement) was transferred to force curves by using the sensitivity value obtained for the cellulose-cellulose contact, i.e. before adding the polymer solution. For the cellulose–cellulose contact a constant compliance regime was attained due to the low spring constant of the cantilevers used in the experiments. The deviation from this reference value was used to calculate the compressibility of PEC covered surfaces. This method was chosen to achieve accurate surface forces, but on the other hand, the actual surface separation became uncertain. Hence, it is denoted relative separation. Unknown amount of PECs stayed between surfaces.

The drive speed of the cantilever was ca. 400 nm/s. No significant effect on the surface forces was observed when the drive speed varied from 200 to 1000 nm/s. All experiments were reproduced at least twice. For the sake of clarity, only one representative curve per system is shown in the figures. The cellulose spheres were let to equilibrate over night before the measurements. When changing the solution, the system was allowed to stabilize for 1 h. Furthermore, the surfaces were allowed to relax at least 10 min between the measurements.
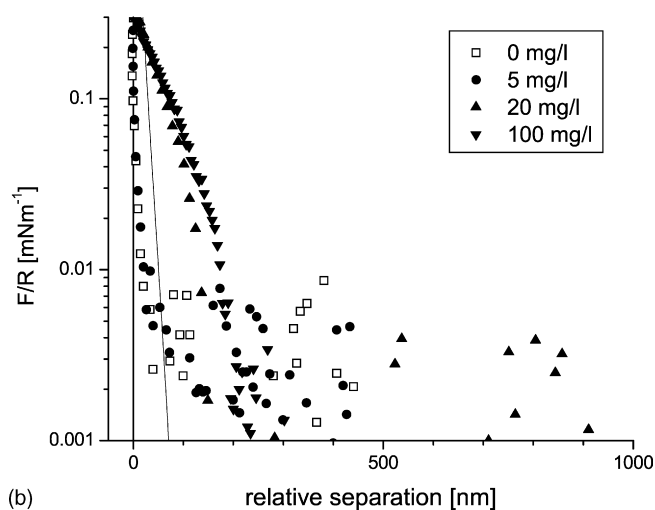
3. Results and discussion

3.1. Effect of concentration and structure of polyelectrolyte complex

The surface forces were measured in PEC solutions using AFM. The effect of PECs was studied as a function of polymer concentration in 1.0 mM NaHCO$_3$. PEC A was formed by a high
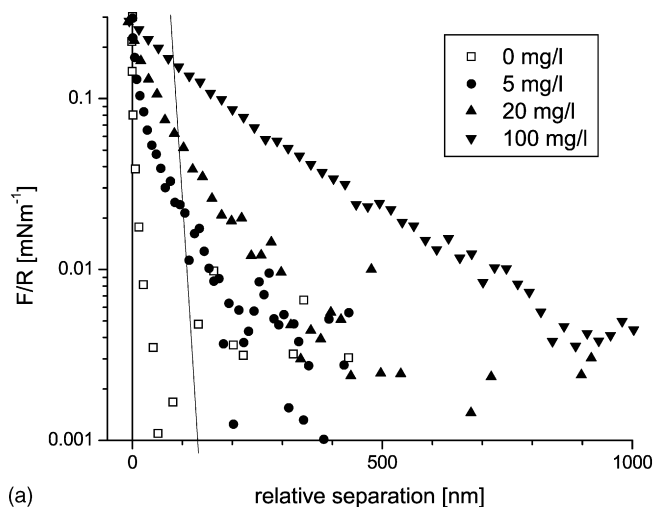
(a)

(b)

Fig. 1. Surface forces between cellulose surfaces measured in PEC A (a) and B (b) solutions of various polymer concentrations at 1.0 mM NaHCO$_3$. Only approach data is shown. The solid line represents the slope for pure DLVO forces in 1 mM electrolyte solution.

Fig. 2. Surface forces between cellulose surfaces in PEC A and PEC B solutions. In both solutions, the polymer concentration was 100 mg/l and NaHCO$_3$ concentration was 1.0 mM.

molecular weight and low charged C-PAM and A-PAM whereas PEC B was formed by low molecular weight and high charged C-PAM and A-PAM. The surface forces between cellulose surfaces in solutions of PEC A and B on approach are shown in Fig. 1a and b, respectively. The normalized surface forces are presented as a function of the relative separation. The surface forces between the pure cellulose surfaces before PEC addition (0 mg/l) were repulsive and the nature of the interactions was mainly electrostatic. The repulsion between the cellulose surfaces increased strongly with increasing PEC concentration, since more complexes were adsorbed on the slightly negatively charged cellulose surfaces. The surfaces forces did not follow the DLVO theory [29]. Thus, the repulsion was concluded to be mainly of steric origin. The overlapping of PEC layers resulted in steric repulsion between the surfaces. Evidently, the layers became thicker when the polymer concentration in the solution increased.

The influence of the complex structure on the surface interactions was investigated by comparing PEC A and PEC B. The
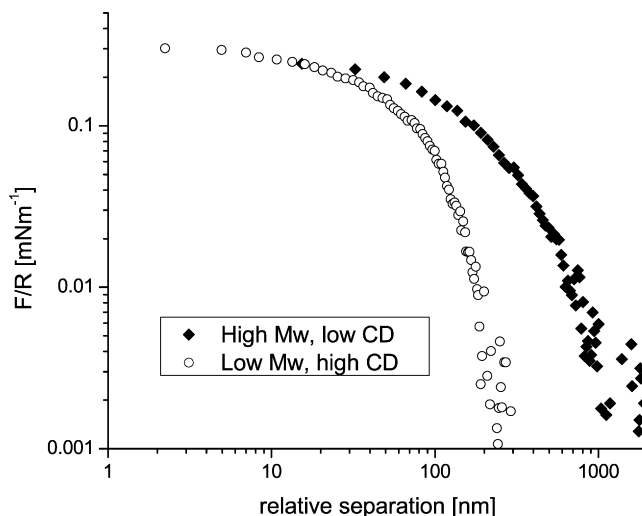
surfaces forces between the cellulose surfaces in solutions containing 100 mg/l PEC A and PEC B and 1.0 mM NaHCO$_3$ are shown in Fig. 2. Double logarithmic scale was used to emphasize the differences. The surface forces differed only in the range of the interactions. The steric force ranged over 1.0 μm in the 100 mg/l PEC A solution, whereas the range was below 300 nm in the PEC B solution. In Table 2, the ranges of repulsion and the maximum repulsion of different systems are shown. The scatter in the data is indicated. The maximum repulsion was roughly the same for both PEC A and PEC B. However, in spite of the rather large scatter in the data, there is a significant difference between the ranges of repulsion in the two systems. This was to be expected considering the size of the complexes in the solution (Table 1). PEC A was larger than PEC B. Considering the size in the solution and the charge of PEC and its components, it is logical that PEC B adsorbs as a thinner layer on cellulose than PEC A. The ranges of the steric forces in PEC A and PEC B solutions implied that the thicknesses of the complex layers were roughly 500 and 150 nm, respectively. Since it is not possible to determine the absolute thickness of the layers with

Table 2
Magnitude and range of repulsion on approach

Salt concentration (mM)	Polymer concentration (mg/l)	Maximum force (μN/m)	Range (nm)
PEC A			
0.1	20	230–310	600–1400
0.1	100	190–300	775–1850
1.0	20	250–280	265–625
1.0	100	320–350	700–1350
PEC B			
1.0	20	260–390	140–230
1.0	100	310–430	200–320
C-PAM CL			
0.1	20	200–700	220–650
0.1	100	600–700	675–1100

the AFM technique, an unknown amount of polymer was still present between the cellulose surfaces, when the relative separation was 0 nm. Hence, the real thickness of the PEC layer may have been even greater.

3.2. Effect of electrolyte concentration

In Fig. 3, the surface forces in 100 mg/l PEC A concentrations are presented as a function of relative separation across aqueous 0.1 and 1.0 mM NaHCO$_3$ solutions. The electrolyte concentration did not affect the surface forces significantly. In both cases, the forces were purely repulsive and long ranged. At the lower electrolyte concentration, the steric repulsion ranged only slightly further than in 1.0 mM NaHCO$_3$, but the repulsion at short separation was lower (see also Table 2). This supports that the repulsion was mainly of steric origin. The ionic strength was not important due to the low charge of polymers and the presence of an anionic component. The A-PAM molecules partly neutralized the electrostatic repulsion between the C-PAM molecules and, therefore, the layer structure was quite independent of the electrolyte concentration in 100 mg/l PEC A concentration. At low PEC concentration the electrolyte concentration did affect the range of the forces (Table 2). The reason for this is not quite clear. It may be that PECs form multilayers more easily at low salt concentration or that PEC adsorbs in a flatter conformation on the surface at higher salt concentration (see Table 1). To further clarify this phenomenon, the adsorption of these complexes on cellulose surface should be studied with a more convenient method.

The effect of the electrolyte concentration on the surface forces in PEC B solution was also investigated. The surface forces in 1.0 mM NaHCO$_3$ was shown in Fig. 1b. In Fig. 4, the surface forces across 0.1 mM NaHCO$_3$ in different PEC B concentrations are shown. Surprisingly, the repulsion decreased upon the addition of PEC B in contrast to the effect at a higher electrolyte concentration. This was interpreted as a result from the charge neutralization of the surface due to the adsorption
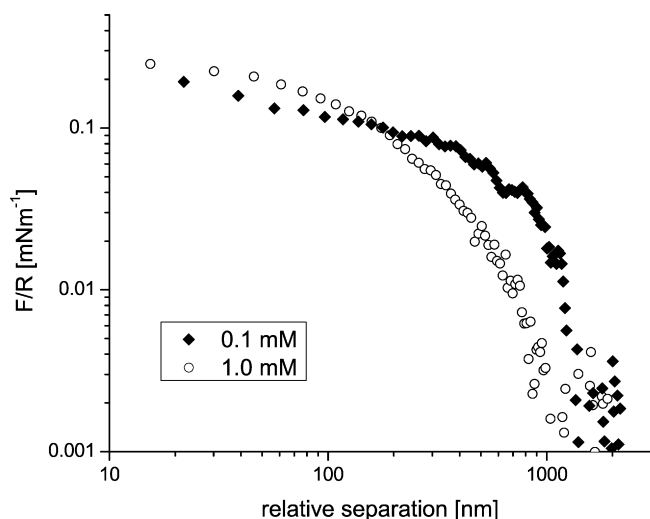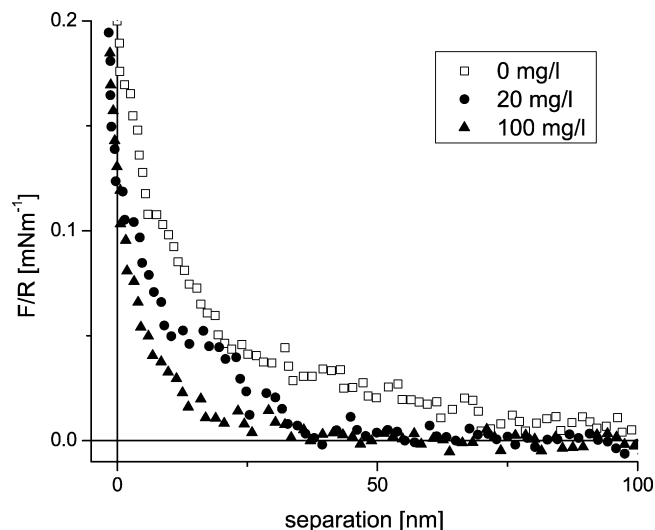

Fig. 4. Surface forces in solutions of PEC B as a function of polymer concentration at 0.1 mM NaHCO$_3$.

of C-PAM. The force curves were similar to the ones that have been observed earlier with pure C-PAM [15], but the effect was weaker, since most of the C-PAM preferred to stay in the complexes in solution. The properties of high charge C-PAM seem to dominate at low electrolyte concentration preventing the PEC B from adsorbing. Wågberg et al. [30] have studied the multilayer formation in C-PAM/A-PAM systems using QCM-D. They studied the effect of CD of C-PAM on the multilayer formation. The adsorption of C-PAM and A-PAM were not purely electrostatically driven. The A-PAM adsorption onto the C-PAM covered surface depended on the charges adsorbed on the previous layer.

3.3. Comparison to one component systems

To further clarify the effect of the anionic component on the interactions, the PECs were compared to both a linear C-PAM as well as a crosslinked C-PAM. In Fig. 5, PEC A is compared to C-PAM without the added A-PAM and to crosslinked C-PAM with a similar molecular weight and charge density. The total polymer concentration of the solutions was 100 mg/l at 0.1 mM NaHCO$_3$. The surface forces were purely repulsive on approach in all cases. The range of the repulsion, however, varied significantly (see also Table 2). The range was ca. 400 nm between cellulose surfaces coated with linear C-PAM, while the range for crosslinked C-PAM was ca. 800 nm and for PEC A, it was mainly over 1000 nm. The magnitude of repulsion was highest for the crosslinked C-PAM. The range of the repulsion was longest for PEC A but the crosslinked C-PAM showed a steeper increase in repulsion at large separation and the repulsion was also stronger at short separations (Fig. 5 and Table 2). The reason for these differences is probably the different structure of the layers. It is reasonable that a crosslinked molecule should be able to form shorter tails than a similar linear molecule, because the crosslinked molecule is "looped" by itself. A crosslinked molecule is also stiffer than a linear one. Hence, it is likely that they form more rigid layers. Our results agreed with those of
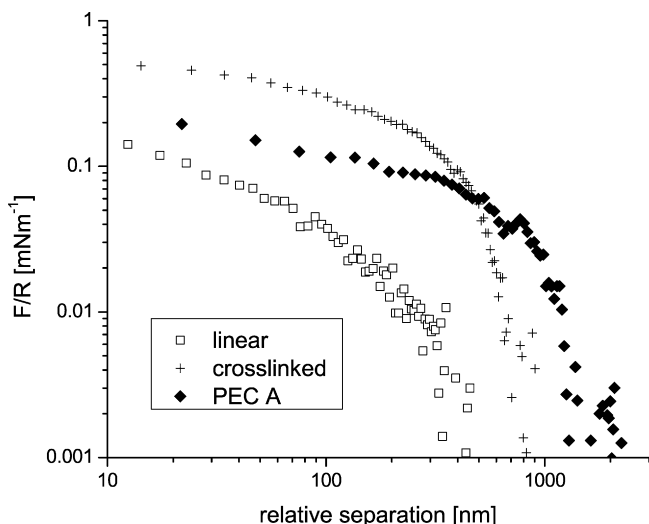

Fig. 3. The effect of electrolyte concentration on surface forces in 100 mg/l PEC A solution.

Fig. 5. The comparison of surface forces between cellulose surfaces in different high molecular weight, low charged systems at 0.1 mM NaHCO$_3$. Polymer concentration was 100 mg/l in all cases. Open squares are the forces in the presence of linear C-PAM, plus signs are the forces in the presence of crosslinked C-PAM and filled diamonds represent the forces in the presence of PEC A.

Kampf et al. [31]. They observed that crosslinking increased the strength and the range of the surface forces between chitosan layers on mica. They explained this to be due to the stiffer structure of the crosslinked layer. The crosslinked molecule was also less flexible, which could result in an ordered and even-distributed structure of the layer. The range of the repulsion is, of course, dependent on the M_w of the polymer. It should be noted that the comparison of the M_w of different type of the polymers is only indicative.

The nature of the interaction was of steric origin also in the PEC B case (Fig. 1b). In contrast, a low molecular weight, high charge density C-PAM alone is able to neutralize and overcompensate the surface charge of the cellulose, but not to induce a steric contribution to the interactions [15]. Hence, the presence of A-PAM affected the nature of the force by changing it from electrostatic to steric, increasing the range and the strength of the repulsion. A similar effect of polymer complexes on interactions has been observed in a system containing a cationic hydrophobic polymer and an anionic surfactant [19].

3.4. Pull-off forces

Surface forces on retraction, i.e. pull-off forces, were recorded together with the approaching data, but for the sake of clarity, they are presented separately. Fig. 6 shows the effect of the PEC concentration on the pull-off forces between the cellulose surfaces coated with PEC A in 0.1 mM NaHCO$_3$. In 20 mg/l polymer solution, the pull-off force was quite weak and the force minimum was observed at rather long separations. In 100 mg/l polymer concentration, the pull-off force was slightly stronger and extended gradually even further out. We suggest that the gradual pull-off force resulted from the fact that PEC layers became entangled, when the surfaces were pressed together. Tentatively, it can be suggested that C-PAM and A-PAM molecules
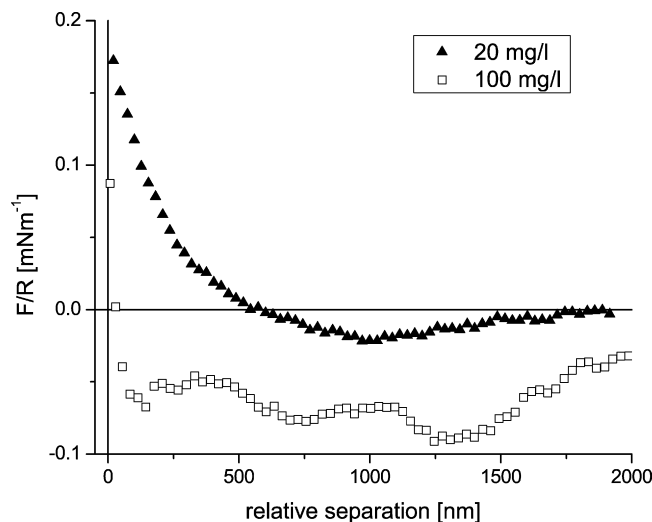
were bridging the PEC layers (and thus also cellulose surfaces) together. The minimums in the pull-off force would then be due to detaching the bridges between C-PAM and A-PAM.

The effect of the polyelectrolyte complex formed by a low molecular weight, high charged C- and A-PAM (PEC B) on pull-off force is shown in Fig. 7. The shape of the pull-off force curve was clearly different from the one with PEC A (Fig. 6). It was sharper and the force minimum was found at much smaller separations. PEC A had a larger optimum range of the maximal pull-off force than PEC B. In 1.0 mM NaHCO$_3$, the pull-off force reached a maximum at 20 mg/l and decreased at higher PEC B concentrations. The highest pull-off force was observed in 100 mg/l PEC B solution in 0.1 mM NaHCO$_3$. It was previously concluded that the effect of free C-PAM dominates in this electrolyte concentration and the shape of the curve was also similar to force curves found for low molecular weight, high charged PDADMAC [16].

Fig. 6. Pull-off forces in PEC A solutions in 0.1 mM NaHCO$_3$ at different PEC concentrations.
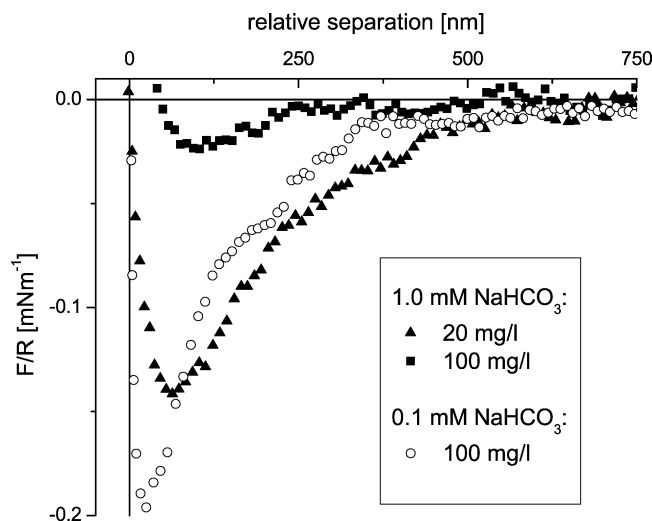

Fig. 7. Pull-off forces in PEC B solutions at different electrolyte and PEC concentrations.

Table 3a
Average pull-off forces in PEC A and PEC B solutions

Polymer concentration (mg/l)	Pull-off force (μN/m)			
	PEC A		PEC B	
	0.1[a]	1.0[a]	0.1[a]	1.0[a]
0	13 ± 2	14 ± 2	17 ± 3	15 ± 7
5	n.d.	25 ± 9	114 ± 74	37 ± 3
20	20 ± 10	13 ± 3	139 ± 78	141 ± 18
100	55 ± 25	10 ± 5	230 ± 81	36 ± 15

n.d., not determined.

[a] Salt concentration (mM).

The average pull-off forces and the range limits in PEC systems are shown in Table 3a and 3b, respectively. For PEC A, the magnitude of the pull-off force is rather low, but the range of the force is very long. Increasing the PEC concentration changes the magnitude of the force only slightly, but the range increases clearly. Upon increasing the electrolyte concentration, the pull-off force almost diminishes. Comparing to previous results on C-PAM only [16], two observations can be made. Although the magnitude of the pull-off force was approximately the same, the range of the force increased from a few hundred nanometers for the single component system to microns for the PEC system. Another difference was that maximum pull-off force was reached near charge neutralization point for C-PAM only while the pull-off force was rather insensitive to the PEC concentration.

The magnitude of the pull-off force was higher for the PEC B than for the PEC A, but the range of the force was shorter. Both the magnitude and the range of the force were higher for PEC B as compared to C-PAM alone. No pull-off force has been observed between the cellulose surfaces coated with low molecular weight, high charged C-PAM alone, while PEC B induced a pull-off force of 141 μN/m ranging to 600–800 nm. Shubin [19] has observed even stronger pull-off force (2.8 mN/m) in a polymer complex system containing cationic a hydrophobic polymer and an anionic surfactant. In this case, the pull-off force was due to hydrophobic attraction.

Gradual pull-off forces and bridging, like in the case of PEC A, has been observed earlier by Bremmell et al. [32]. They measured surface forces in cationic polyelectrolyte system. Recently, Kulcsar et al. [33] have observed similar bridging effects of PECs when studying polymer multilayers. They suggested that sequential interpenetration of polymer multilayers formed poly-

Table 3b
Range limits of pull-off force in PEC A and PEC B solutions

Polymer concentration (mg/l)	Range of pull-off force (nm)			
	PEC A		PEC B	
	0.1[a]	1.0[a]	0.1[a]	1.0[a]
20	1300–1700	ins.	300–800	600–800
100	2000–over 3200	ins.	600–800	200–300

ins., insignificant.

[a] Salt concentration (mM).

mer complexes, which bridged the surfaces together and resulted in an increasing adhesion.

A similar difference in pull-off forces, than we observed between PEC A and PEC B, was reported in systems of polyelectrolyte multilayers by Gong et al. [17]. They concluded that a sawtooth pull-off curve resulted from flexible molecules and a concave curve from stiff, binding molecules. It is fairly reasonable to see similarities between our and Gong's et al. systems. PEC A was formed by less charged polymers and, thus, it was more flexible than PEC B. Besides, an attraction between the high charged C- and A-PAM molecules in PEC B layer was electrostatically stronger than the one in PEC A layer.

No pull-off force was observed in the case of crosslinked C-PAM. We have earlier observed that high molecular weight, low charged linear C-PAM yielded 60 μN/m pull-off force in 100 mg/l polyelectrolyte solution. Hence, crosslinking decreased the pull-off force of C-PAM. A similar result has been observed with PVCB [34] and poly(L-lysine)/hyaluronan [35]. In contrast, Kampf et al. have observed that crosslinking increases adhesion, but they suggested that it resulted from bridges formed by the crosslinking substance [31].

3.5. Compressibility

The slope of the contact area in a raw force curve (deflection versus piezo movement) is a measure of surface compressibility. Ideally, a linear part in the force curve is observed when pushing the surfaces together. The slope observed, when pushing two cellulose surfaces into contact in pure electrolyte solution, remained unchanged for the cantilever used in this study. However, after adsorption of PEC the slope changed indicating that the layers deformed and no hard contact was observed. This introduced some uncertainties to the interpretation of the force curves but this phenomenon can also be used to obtain information about the polymer layer compressibility. The more the slope differed from the reference, the more compressible the layer was.

Rutland et al. [36] have shown that the conventional force curve analysis of deformable substances may generate erroneous results but also that information about surface elasticity can be obtained from the measurement. We emphasis that in the present work the sensitivity values obtained for the cellulose–cellulose contact (hard contact) was used when analyzing the force curves for the more compressible PECs. In this way, the shape of the force curve is not altered due to compressibility of the surfaces, only the actual contact point is uncertain. It must also be pointed out that, in contrast to Rutland et al., we did not find the cellulose spheres to be deformable. This is probably because cantilevers with a tenfold lower spring constant were used in this study.

The compressibility of the polymer layers in various polymer concentrations is presented in Table 4. Adsorption of the linear C-PAM does not affect the compressibility of the cellulose surfaces [15]. Crosslinked C-PAM formed an almost uncompressed layer relative to the spring constant of the AFM cantilever. However, at high polymer concentrations the layer became slightly more compressible than the reference (pure cellulose). It is not very likely that crosslinked C-PAM would form a more com-

Table 4
The compressibility of polymer layers

Polymer concentration (mg/l)	Compressibility (mN/m)				
	PEC A		PEC B		CL
	0.1[a]	1.0[a]	0.1[a]	1.0[a]	0.1[a]
0	unc.	unc.	unc.	unc.	unc.
20	125 ± 13	75 ± 4	unc.	112 ± 14	unc.
100	88 ± 8	19 ± 2	unc.	100 ± 8	194 ± 26

unc., uncompressed.

[a] Salt concenntration (mM).

pressible layer than linear C-PAM, since crosslinking has been reported to make polyelectrolyte layers stiffer [31,35,37,38]. The reason for this inconsistence is, most likely, the difference in the layer thickness, since the crosslinked C-PAM forms a considerably thicker layer on the cellulose surfaces than linear C-PAM.

When PECs were adsorbed, the surface became more compressible (Table 4). The compressibility decreased upon increasing the PEC concentration or the electrolyte concentration. The lowest compressibility was observed in a 100 mg/l PEC A solution in 1.0 mM NaHCO₃. This was reasonable, since repulsion between the molecules and between different parts within the same molecule decreased, when the electrolyte concentration increased. In this respect, the true range of the steric force in the high electrolyte concentration may be longer than in the low electrolyte concentration, if zero point is defined as a cellulose–cellulose contact. Changing the contact point would probably change the results in Fig. 3. However, this does not change the conclusion that PEC A formed a more compressible surface than PEC B. This supported, even emphasized, the results presented in Fig. 3.

3.6. Comparison of PECs, PEMs and single polyelectrolyte systems with the aspect of papermaking

Dual polyelectrolyte systems, PECs and PEMs, have been reported to increase paper strength, when compared to single polyelectrolyte systems [4,39–41]. Dual systems are able to increase polymer amount in fiber web making the fiber surface smoother, and thus increasing the bonded area between fibers [41]. This reflects, however, only partly, why the paper strength is increased.

In dual polyelectrolyte systems, the sequence of adding the polyelectrolytes is important. In this paper, we saw that surface forces on approach were repulsive, long ranged and steric in PEC solutions. The strength and range were dependent on the structure of the premixed complex. In contrast, in polyelectrolyte multilayer systems the surface forces are determined mainly by the outer layer of the system [17,18,33,42,43]. Both attraction [17,18,33] and electrostatic repulsion [17,42,43] have been observed at large separations before overlapping depending on the outermost layer. When the polyelectrolyte multilayers were overlapping, the surface force was repulsive [18,33,42,43]. When premixed cationic complexes adsorbed on the cellulose

surfaces, the pull-off forces increased. Similarly, PEMs has been reported to increase the pull-off force between mineral surfaces [17,33,42–44]. This has been concluded to be due to bridging between the layers or due to bridging induced by a complex formation during the sequential overlapping. In a recent quartz crystal microbalance study [44], it was found that the outermost layer affected the structure of adsorbed polyelectrolyte multilayers on mineral surfaces. These results were combined with studies of PEM adsorption on cellulose fibers [40]. It was concluded that the paper became stronger in the cases where the PEM was less rigid and the polymers hence more mobile. In this paper, we found that the charge density and molecular weight of the polyelectrolytes used in the PECs affected the structure of the adsorbed layer and consequently also the forces. The larger and more flexible PEC A induced a very long ranged pull-off force at a wide concentration range. For PEC B, a pull-off force was observed only at a narrow concentration range and the range of adhesive force on separation was also much shorter in this case.

In addition to improvements in paper strength, PECs have been found superior to single polyelectrolytes in enhancing process parameters, like flocculation of particles and dewatering of papermaking stock [2,3,45]. In particular, the wider optimum concentration range is beneficial. Typically optimum dewatering using single polyelectrolytes is obtained at a very narrow concentration range. Xiao et al. [45] have observed that polyelectrolyte complexes, formed by a high molecular weight, low charge density C-PAM and A-PAM, enhanced dewatering and flocculation of fines more than C-PAM alone or complexes made from high charged, low molecular weight polyelectrolytes. In recent studies using similar C-PAM and A-PAM complexes to those in this work, the PECs were found to improve retention without harming formation and dewatering [46]. The long ranged steric repulsion between PEC covered cellulose systems observed here may be a reason for the good dewatering properties of pulp in the presence of PECs. In addition, we saw that the forces were not very sensitive to the PEC concentration in the case of the high molecular weight, low charge density PEC.

In our study, the system was symmetric, i.e. the forces were measured between two PEC-coated cellulose surfaces and hence the forces were repulsive on approach. In practice, the situation may be different and, if only one of the surfaces is covered with PEC, purely attractive forces could be present. For flocculation to occur two particles have to come close enough to interact and sometimes a repulsive force barrier has to be overcome. For the flocs to be stable, the attraction has to be stronger than the shear forces present. The fact that the pull-off forces are weak but very long ranged implies that the flocs formed by these PECs would be rather flexible. This could be a reason why the flocculation may be increased without affecting the strength and the formation negatively. Using single cationic polyelectrolytes, the pull-off force may well be stronger than with PECs but the range of the attraction is very short, typically few tens of nanometers at the most. With the PECs the range is over 1 μm. This means that to completely detach the two particles they have to be drawn more than 1 μm apart.

Clearly, the use of the PECs may provide benefits in papermaking. The two-component systems are able to bind

surfaces together by bridges more effectively than single polymer systems. Benefits of using PEC compared to PEM in an industrial aspect are easiness (only one addition step), low amounts of polymer needed and a wide optimum concentration range.

4. Conclusions

A strong and long ranged steric repulsion and long ranged pull-off force were observed between the cellulose surfaces immersed in polyelectrolyte complex solutions compared to the single polyelectrolyte systems. The PEC layers were clearly more compressible than the pure cellulose. Both the steric repulsion and the pull-off force reached further, when the size of PEC increased from PEC B to PEC A. The optimum concentration range for maximum pull-off force was wider in the case of PEC A. The steric repulsion between the cellulose surfaces covered with PEC A was mainly independent of electrolyte concentration at high polymer concentration, but the pull-off force disappeared, when electrolyte concentration increased. Instead, in the PEC B case, the nature of the surface forces changed from the steric repulsion to C-PAM dominating decrease in repulsion, when the electrolyte concentration decreased. The crosslinked C-PAM was able to induce strong and long ranged steric repulsion like PEC A, but crosslinked C-PAM formed a stiffer layer and did not induce pull-off force. The increase in the range and magnitude of the steric repulsion on the one hand and of the pull-off force on the other hand gave a scientific explanation for the improvements in flocculation, dewatering and paper strength in the papermaking applications. Still, some questions concerning the adsorbed amounts and the layer structure remained unanswered. These will be studied in the future.

Acknowledgments

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