INTERACTIONS BETWEEN CATIONIC POLYELECTROLYTE AND PULP FINES

Elina Orblin* and Pedro Fardim

Papermaking pulps are a mixture of fibres, fibre fragments, and small cells (parenchyma or ray cells), usually called pulp fines. The interactions between pulp fines and a cationic copolymer of acrylamide and acryloxyethyltrimethyl ammonium chloride were investigated based on solid-liquid isotherms prepared under different turbulence, and subsequent advanced surface characterization using X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The surface charge and surface area of pulp fine substrates were measured by methylene blue sorption-XPS analysis and nitrogen adsorption combined with mercury porosimetry, respectively. The driving force behind polyelectrolyte adsorption was the amount of the surface anionic charge, whereas surface area appeared to be of less importance. Based on a comparison of solid-liquid and XPS sorption isotherms, different polyelectrolyte conformations were suggested, depending on the types of fines: A flatter conformation and partial cell-wall penetration of polyelectrolytes on kraft fines from freshly prepared pulp, and a more free conformation with extended loops and tails on lignocellulosic fines from recycled pulp. Additionally, ToF-SIMS imaging proved that recycled pulp fines contained residual de-inking chemicals (primarily palmitic acid salts) that possibly hinder the electrostatic interactions with polyelectrolytes.

Keywords: Fines; Polyelectrolytes; XPS; ESCA; ToF-SIMS

*Contact information: Åbo Akademi University, Laboratory of Fibre and Cellulose Technology, Porthaninkatu 3, FI-20500, Turku/Åbo, Finland; *Corresponding author: elina.orblin@abo.fi*

INTRODUCTION

Charged high molecular weight polymers are traditionally used as papermaking additives to improve the retention and drainage in paper machine wet-end. These polymers, called polyelectrolytes (PE), are water-soluble and in solution carry either cationic or anionic charge via which they interact with papermaking fibres. PE adsorption is controlled by several parameters, which have as well been studied rather extensively. It is known that the interaction between cellulosic pulp and cationic PE is of electrostatic nature (Winter et al 1986; Horvath et al. 2006), and it is in addition subject to the accessibility of anionic groups (AG) in pulp, which is related to the morphology of the pulp and the reaction conditions. Important factors in the reaction conditions are for example pH, which is affecting the ionisation of the pulp anionic sites and in some cases also of the PE, and conductivity, if being too high, shrinks the effective size of the polymer and reduces its potency, and further, polymer concentration and stirring, which are affecting the conformation of polymer in the solution (van de Ven et al. 2004; Wu et al. 2007; Fatehi and Xiao 2008). In addition, the adsorbed PE go through rearrangements and replacements if a thermodynamically favoured cation or conformation is available (Mocchiutti and Zanuttini 2005; Fardim et al. 2005). Multivalent cations such as Al^{3+} can adsorb strongly (irreversibly) to anionic sites in a complex type of bond, and block the site for further reaction with other cationic chemicals. Also, the effect of shear has been studied previously, for example by Taipale et al. (2010), stating that the charge density of the PE (high compared to low) determines whether the adsorption is improved by added turbulence or not. Yet again, addition of electrolytes in the solution may help the smaller PE's to better pass into the pores in the fibres by causing PE's to shrink (Horvath et al. 2006; Hubbe et al. 2007a), and further, the behaviour is dependent on the charge density of the PE (van de Steeg et al. 1992). Higher charge density in the PE leads to a more stretched conformation in the solution and thus to a flatter deposition of the PE on the adsorbent surface. On the other hand, a higher polymer concentration leads to a more coiled conformation and a lower adsorption stoichiometry (Wågberg et al. 1988). It is not clear, if or to which extent PE's can adsorb into the porous structure of cellulosic fibre cell wall (the structure itself being debated, e.g. by Hubbe, 2006) but there is supporting data for the PE charge density being the decisive factor for the penetration (Shirazi et al. 2003; Horvath et al. 2008a; Horvath et al. 2008b; van de Ven 2000). The conformation of adsorbed polyelectrolyte is difficult to measure directly. The affect on salt addition on the adsorbed PE layer has been studied by ellipsometry (Ödberg et al. 1995), showing that added salt makes the layer to expand. However, the subject is far from fully understood.

The term papermaking pulp fines generally refers to short fibre fragments and small wood cells like parenchyma and ray cells, and in some cases also filler. By fines we mean material that passes through a 75 μm hole, which is a commonly agreed definition for fines. The fines in mechanical and in chemical pulp are somewhat different materials. Chemical pulp fines are often divided into primary and secondary fines, which are found in the pulp before and after beating, respectively. The cationic demand for charge neutrality is reported to be higher for the fine fraction than for fibres, and the adsorption of cationic PE flocculants is also faster to the fines (Lindström and Söremark 1976). In addition, kraft fines have been reported to adsorb cationic starch more than the fibres, and the amount was dependent on the type of the fines (Wågberg and Björklund 1993). Mechanical fines can be divided into fibrillar and flake-like fines. Fibrillar fines contain a large surface area compared to the fibre fraction (Herrington and Petzold 1995) and thus set a higher demand for retention aids. Also, the charge of the fines can differ significantly from the pulp fibres (Mosbye et al. 2001).

AGs are different ionisable sites in pulp. The majority of them are carboxyl groups; phenolic groups are not dissociated under normal papermaking conditions. In chemi-mechanical pulps there are also sulfonic acid groups. The solid–liquid interface of pulp in water carries a negative charge, as the AG are dissociated. AG interact with papermaking chemicals and contribute for example to fibre swelling and paper sheet strength (Laine and Stenius 1997). Further, the AG that are located on the outer surface of fibres (surface anionic groups, SAG) are largely interesting from the pulp and fines flocculation point of view. The adsorption of high molecular weight PE's onto fibres is thought to be restricted to the outer surfaces of fibres (Wågberg et al. 1988) and can thus be used as an estimation of SAG. The assumption of one-to-one stoichiometric adsorption of high molecular weight pDADMAC (poly-diallyldimethyl ammonium chloride) (Laine and Stenius 1997) is one example of such methods. Methylene blue (MB) adsorption assessed with X-ray photoelectron spectroscopy (XPS) (Fardim and Holmbom 2003) is a method which is not affected by the polymer molecular weight and charge density. Also pDADMAC adsorption on fibres has been assessed by XPS, through monitoring the N content on the pDADMAC treated sample surfaces (Fardim et al. 2005; Horvath et al. 2006). Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a more surface-sensitive technique, the analysis depth being less than 2 nm and thus in the order of one monolayer. ToF-SIMS has been used within pulp and paper research for mapping different fibre components, moieties or additives, and for distinguishing the detailed surface chemistry of paper (Mancosky and Lucia 2001; Kleen 2005; Fardim and Holmbom 2005). The advantage of the technique is that both mass spectral analysis and surface distribution maps are obtained simultaneously.

The starting point to this work was an observation in mill experiments that the fines of recycled pulp (mixture of deinked newsprint and magazine) had lower response towards retention chemicals than fresh kraft pulp fines, and the reason for this was to be discovered. Kraft fines retains very well in the fibre network in during paper formation, whereas recycled pulp, especially those containing mechanical fibres, are problematic in retention. Recycled pulp is always a heterogeneous material, the nature of which depends on the fibre species and the chemical and mechanical history of the fibres (Hubbe et al. 2007b), and there are in fact no previous reports on the interactions of recycled pulp. However, it was here used as an example of low-reactivity pulp material, as the focus was in making basic research on the interactions of cationic PE in controlled laboratory conditions, yet using mill-made pulps. The effect of turbulence on the adsorption of PE was of interest, and the conformation of the adsorbed PE on the pulp surfaces was clarified. A previously unreported approach is taken here as surface-sensitive instruments are utilised for assessing the PE adsorption quantity and lateral distribution on the exterior of the pulp fines.

EXPERIMENTAL

Materials

Two different types of pulp fines were used in this study, representing chemically and morphologically different adsorption substrates. The fresh cellulosic fines were produced by refining (ProLab Refiner, SM fillings, 350 kWh/t) and screening (Valmet TAP, 0.06 mm slits) from fully bleached and mill dried eucalyptus kraft pulp. The kraft fines composition was investigated visually by light microscopy, and parenchyma cells, ray parenchymas, broken fibres and fibrils, as well as some broken vessel elements and long fibres were observed. The second substrate was recycled lignocellulosic pulp (denoted LC-DIP) fines, screened by an unpressurised laboratory screen (Metso Inc., Finland) from de-inked pulp made from 60% newspaper clippings and 40% old magazine, with the filler content approximately 5%. According to visual examination with light microscopy, LC-DIP fines consisted of parenchyma cells, ray parenchyma, broken fibres, fibrils, and mineral particles. The ash content was measured at (575±25)°C over night, and it was determined to be 18.5%.

The polymer used for investigating the turbulence effect on the adsorption was a commercial cationic PE, Fennopol K3400R (manufacturer Kemira). It is a water-soluble copolymer of acrylamide and acryloxyethyltrimethyl ammonium chloride (Fig. 1) with a charge of approximately 1 meq/g and a molecular weight approximately 7 Mg/mol. Hereafter in this paper, the name PE-1 is used for the product. A 0.5% stock solution of the PE was prepared using de-ionized water (+23˚C) and a magnetic stirrer, mixing time 60 min, and it was stored in a refrigerator and used within two weeks. The exact concentration (as equivalents per litre) of it was determined by titration with an anionic titrant, potassium polyvinyl sulphate (PVSK), the exact concentration of which was previously determined by titration with a standard 4 mM methyl glycol chitosan (hyamine) solution. The rate of titration was controlled at 0.02 mL/min. The end points of all titrations were detected with Mütek Particle Charge Detector 03. Dilution of the PE solution to 0.05% was made immediately before use by using a 10^{-5} M NaCl solution. The filter papers used for filtering were glass fibre filters (Schleicher and Schuell).

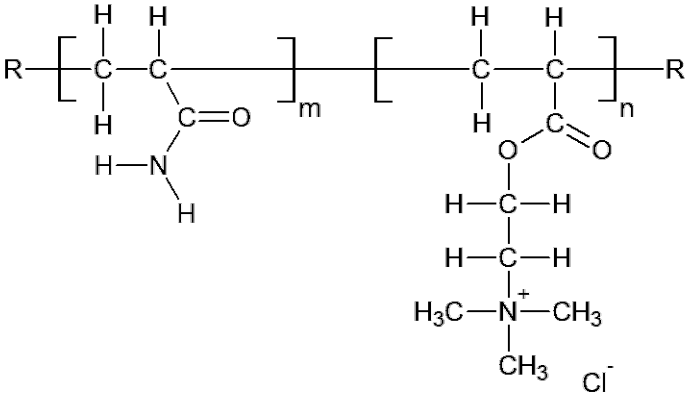


Fig. 1. The chemical structure of PE-1. R stands for repeating polymer chain.

Methods

The pulp fines substrates were characterised regarding their surface chemical composition, total and surface anionic charge, and surface area and porosity. Total adsorption isotherms of PE were made, and the surface concentration as well as the surface distribution of the adsorbed PE was measured.

Surface analyses

The XPS used was a Physical Electronics PHI Quantum 2000 ESCA/XPS, equipped with a monochromatic Al Kα X-ray source. The surface coverage by carbohydrates, lignin, and extractives were calculated using the XPS data, applying the O/C method (Ström and Carlsson 1992) on the kraft fines and the C1 method (Kleen et al. 2002) on the LC-DIP fines. For that, extraction of the kraft fines was carried out in Soxhlet device for 5 h, using acetone-water mixture (9:1 acetone-water), and for the LC-DIP fines in a reflux device for 5 h, using acetone-water-acetic acid mixture (Fardim et al. 2004). In XPS low resolution survey mode, the pass energy was 187 eV, the step size

1.6 eV, and the exposure time 3 min. In high resolution mode C 1s, the pass energy was 23.5 eV, the step size 0.2 eV, and the acquisition time 10 min. Together with the extracted samples an acetone-extracted filter paper (Schleicher & Schuell Blue ribbon) was analysed as a reference, monitoring the carbon contamination in the analysing chamber. Three different spots were analysed on each sample.

The total AG content was measured by the methylene blue (MB) method as described in (Fardim and Holmbom 2003). The AG determination is based on the assumption that MB has access to all AG in the pulp. Surface anionic charge (SAG) was determined by XPS from the MB treated samples, using the pass energy 93.6 eV and the scanning time 20 min for O, C, S, and N. At least four spots of each sample were approved. The N/S ratio was controlled, and only the spots with N/S = 3 ± 1 were approved. The SAG was calculated as,

$$SAG = \left[\frac{S(32.06)}{C(12.00)+O(15.99)+N(14.00)+S(32.06)}\right] x \left[\left(\frac{1}{32.06}\right)10^{6}\right] \qquad (1)$$

where the factors 32.06^{-1} and 10^{6} were used to convert the SAG results to (µmol g^{-1}). The PE treated samples were analysed by XPS in similar manner, scanning the elements O, C, and N. The amount of PE adsorbed on the sample surfaces (SPE) was calculated as,

$$SPE = \left[\frac{N(14.00)}{C(12.00)+O(15.99)+N(14.00)}\right] x \left[\left(\frac{1}{14.00}\right)10^{6}\right] \qquad (2)$$

where the factors 14.00^{-1} and 10^{6} were used to convert the results to (µmol g^{-1}).

The ToF-SIMS device used was a Physical Electronics PHI TRIFT II. All measurements were done using a Ga+ ion gun with 25 keV primary ions over the mass range of 1 to 1000 Da in positive mode, with charge compensation. The lateral distribution of SAG's, labelled with MB, was detected by ToF-SIMS imaging on one measured point at the saturation level (SL) of the MB adsorption isotherm.

Polyelectrolyte sorption

PE adsorption isotherms were done as described in Fardim et al. (2005) but using 10^{-5} M NaCl solution for background conductivity. Seven portions of 100 mg (dry weight) pulp fines were weighed in flasks, mixed with the NaCl solution, and let soak for an hour. Different dosages of PE were added in a rising series by changing the added volume of the 0.05% solution. The total volume of the suspension was kept constant (30 mL) by adjusting the volume of the NaCl solution, see above. The pH of the reaction medium was 7.3±0.2, and the temperature was ambient, approximately +23°C. In the case of PE-1, the turbulence level was adjusted by using stirring rates 750 rpm and 1250 rpm. The reaction time was 30 min, after which the suspension was filtered, and the filtrate was analysed for the amount of un-adsorbed PE by back-titration with PVSK. Blank titrations were also made in order to determine the amount of polymer adsorbed on the glassware and filter paper by using respective stirring rates. The filter cakes were air-dried and analysed by XPS, and one sample from the SL of every PE was analysed by ToF-SIMS. SL is the first isotherm plateau, where a monolayer of adsorbent was assumed to be formed, as a Langmuir type of interaction was considered (Fardim et al.

2005). Because it is theoretically possible that adsorbed multilayers are created (by physisorption) when the PE concentration is very high, test runs were first performed with lower PE dosages, and no isotherm plateaus were detected with smaller dosages than the ones presented here.

Surface area

The samples were freeze dried before the specific surface area determination by N_2 gas adsorption. The instrument used for the sorption experiments was Micrometrics ASAP 2010. Degassing before analysis was performed over night in +100°C. The sample was immersed in liquid nitrogen at 77 K before the sorption measurements were taken. The Brunauer-Emmett-Teller (BET) equation was applied to determine the specific surface area (Adamson 1990a).

The macroporous (pore diameter >50 nm) volume of the freeze dried samples was determined by Hg porosimetry (Adamson 1990b). The measurements were performed with Micrometrics Autopore 3. The evacuation pressure was 50.00 μmHg and time 5 min. The mercury filling pressure was 2.14 psi and the equilibrium time was 10 s. The calculations were performed with software provided by the instrument manufacturer.

RESULTS AND DISCUSSION

Surface Chemistry of Pulp Fines

The untreated and extracted samples were analysed by XPS (Table 1). The main elements present were C and O in all samples, which is normal for cellulosic fibres. In kraft fines, they were the only elements detected. In LC-DIP fines, trace elements (0.5 to 3%) Si, Al, and Ca were detected by the XPS survey mode, originating probably from fillers. The O/C ratio was high, especially in the extracted LC-DIP fines because of oxides present. After extraction, reduction in the alkyl carbon content (C1) was detected in both samples. The difference in the C1 content before and after extraction gives an estimation of the amount of extractable material on the surface of pulp, and the calculated values of surface coverage by extractives as well as carbohydrates and lignin are given in Table 2.

For kraft fines the coverage percentages were calculated using the O/C method. The values for surface compositions were as expected. The surface coverage by lignin on LC-DIP is lower than that on pure mechanical pulp (Kangas and Kleen 2004); however, the DIP in question is a mixture of old newsprint and magazine. In several studies, both primary and secondary fines have been found to contain more extractives and more lignin than the coarse fibres in kraft pulps (Thalib and Hejnesson Hulten 2006; Liitiä et al. 2000, 2001) as well as in mechanical pulps (Kangas and Kleen 2004). Further, in Table 2, the fines were analysed by N_2 and Hg porosimetry. LC-DIP fines showed approximately double the surface area of kraft fines.

The BET surface area for kraft fines here was somewhat smaller than previously reported values (6–9 m^2/g) for freeze-dried eucalyptus fines (neutral sulphite semichemical pulp) by N_2 adsorption (Donnan 1981). The beating and the screening in the fines production have an effect on the surface area. Also, the pulping technique or wood raw material can affect the value. The LC-DIP fines had more small pores, as the total pore area was larger but the average pore diameter smaller than for kraft fines. As commonly known, chemical pulp contains macropores in the cell walls where lignin and hemicelluloses have been removed and cavities with the diameter 50-100 nm are formed instead (Alince 2002; Maloney and Paulapuro 1999). Such large macropores are not thought to be present in mechanical pulps. Also in delignified pulps, these cavities are at least partially shut when the pulp is dried, many of them permanently. Here, the pore size distribution was taken in dry state, which has to be taken into account.

Table 1. XPS Results for Untreated and Extracted LC-DIP Fines and Kraft Pulp Fines, the Reference (Ref.) being Extracted Filter Paper Representing Pure Cellulose

Sample	Survey		High resolution C 1s			
	O/C	Traces	C1	C2	C3	C4
LC-DIP	0.70 (0.03)	Si, Al, Ca	26.9 (4.5)	44.9 (1.8)	24.0 (4.5)	4.3 (1.3)
LC-DIP extr.	0.89 (0.07)	Si, Al, Ca	16.8 (2.6)	53.4 (4.4)	27.2 (6.5)	2.7 (0.5)
Ref. for LC-DIP	0.82 (0.01)		11.8 (0.4)	65.2 (1.9)	19.8 (2.6)	3.2 (0.5)
Kraft	0.66 (0.04)	Si	28.9 (1.2)	54.1 (0.8)	14.6 (0.4)	2.4 (0.3)
Kraft extr.	0.75 (0.02)		19.9 (1.4)	57.4 (1.9)	19.4 (2.1)	3.3 (1.1)
Ref. for kraft	0.76 (0.02)		17.1 (2.2)	54.9 (8.1)	21.9 (6.7)	6.0 (3.2)

The total anionic charge of the fines was studied by MB adsorption, and the SAG was estimated by MB-XPS (Table 2). The total anionic charge was clearly higher for the LC-DIP fines, compared to the kraft fines. Mechanical pulp in general has a higher charge than chemical pulp; so these results were well in line with the origin of the respective fines. However, kraft fines showed a higher amount of SAG than the LC-DIP fines. Further, AG ratio (SAG in relation to total AG) was clearly higher for the kraft (6.5 versus 1.8), which may be part of the explanation to the better reactivity of the kraft fines to the papermaking chemicals compared to the LC-DIP fines.

Table 2. Surface Coverage by Carbohydrates, Lignin and Extractives on Kraft Fines and LC-DIP Fines, SAG and the Hg Porosimetry and N_2 Sorption Results

Sample	Surface coverage %			AG	SAG	Average pore diameter	Total pore area	BET area
	Φ(carb)	Φ(lignin)	Φ(extr)	µmol/g	µmol/g	nm	m^2/g	m^2/g
Kraft	97.9	2.1	15.0	84	556	143	186	3.5
LC-DIP	89.9	10.1	10.1	164	297	125	210	5.5

The surface chemical compositions of the untreated fines were assessed by positive ion ToF-SIMS spectrometry. The most salient components detected on the fines' surfaces are presented in Table 3.

In the ToF-SIMS spectrum (Fig. 2) of LC-DIP fines, long chain hydrocarbons were dominating. The range 200–400 m/z of the mass spectrum were dominated by wood extractives, as well as fatty acids and their salts, which were presumed to be residuals from de-inking collectors, mainly palmitic acid and Ca-palmitate. In addition, different metals (Al, Ca, K, Na, Si, Fe and Mg) were detected, probably originating from fillers and printing inks remains.

Table 3. Surface Components on Kraft and LC-DIP Fines Detected by Positive Ion ToF-SIMS

Component	Peaks (m/z)[a]	Kraft fines	LC-DIP fines
		Normalised[b] peak intensity (*10^{-3})	
Long chain hydrocarbons	15, 27, 41, 55, 69	114.9	145.5
Carbohydrates	127, 145, 115, 133	13.9	9.4
Hardwood lignin	137, 151, 167, 181	3.9	–
Softwood lignin	137, 151	–	3.1
Free fatty acids (palmitic, oleic, stearic)	257, 239, 283, 265, 285, 267	1.4	2.1
Ca-palmitate	296, 551	0.1	0.5
Resin acids	301, 302	0.2	0.3
Optical brightener (paperchemical)	356, 357, 358, 372, 373	–	0.4

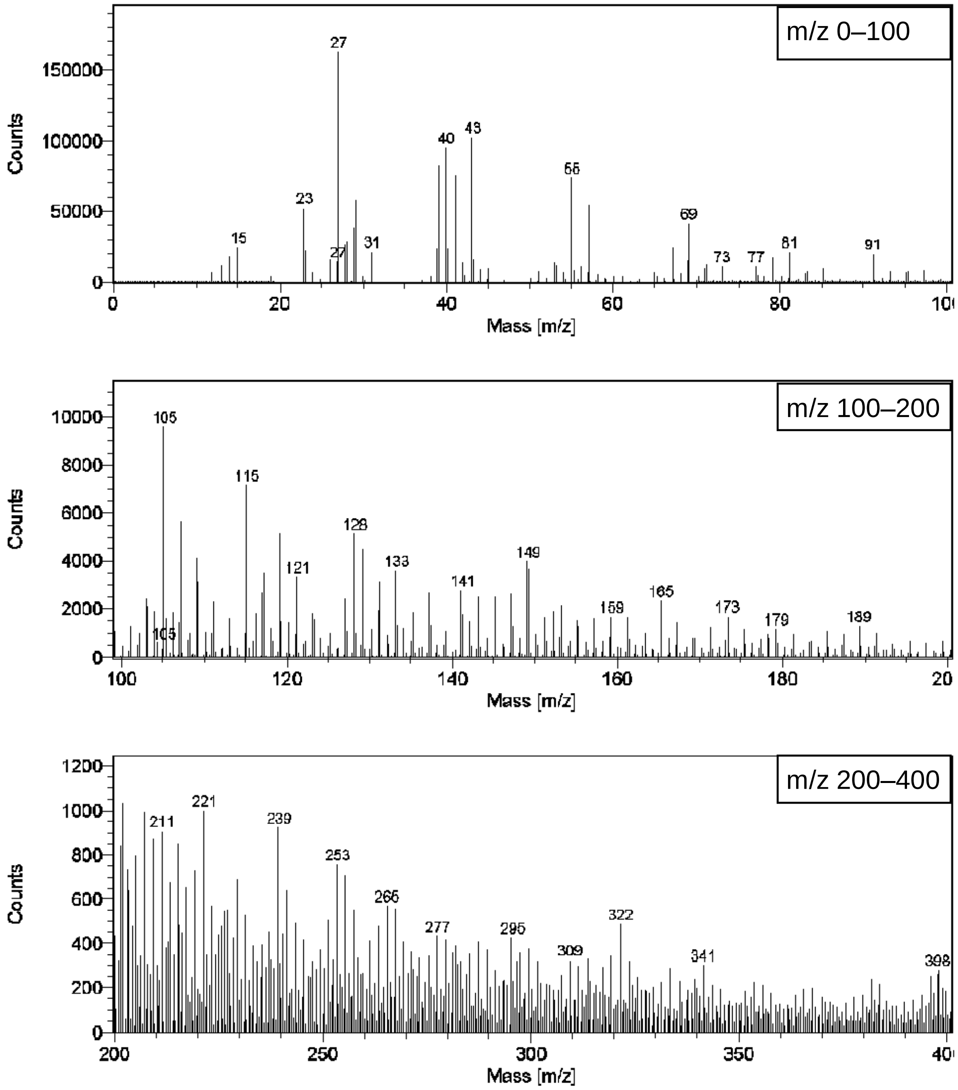
[a] Taken from Fardim and Duran (2005); Kangas and Kleen (2004); and Fardim and Holmbom (2005).
[b] The peak counts for each component were added and the sums normalised by the spectra total ion counts.

The most probable reason for the lower AG ratio in LC-DIP is the residual chemicals, especially fatty acids and their salts, which decrease the surface activity of DIP by blocking the active sites. It is plausible that they influence the interaction between pulp and new papermaking chemicals in the manufacture of recycled paper.

Lateral Distribution of Surface Anionic Groups

The lateral distribution of SAG, labelled by MB, was detected by ToF-SIMS imaging, Fig. 3. Lighter pixels indicate higher detected signal from the molecule of interest. The total ion image is also included, representing the total ion count from the sample.

The characteristic peaks used in the imaging of SAG were 284 Da ($C_{16}H_{18}N_3S$) and 268 Da ($C_{11}H_{16}N_3S$) (Fardim and Holmbom 2004). The SAG's were found to be evenly distributed on the pulp surfaces, yet slightly less even on the LC-DIP than on the kraft fines


m/z 0–100

m/z 100–200

m/z 200–400

Fig. 2. ToF-SIMS spectrum m/z 0–400 of the LC-DIP fines

Polyelectrolyte Adsorption on Fines

When isotherms of PE adsorption on pulp are built, theoretically all the anionic sites available in the sample are occupied by cationic sites of the polymers. It is not realistic to think that the charge stoichiometry of the reaction is exactly one-to-one even on the surface, since the large polymers most likely form tangles and loops, especially as they are available in excess. However, a monolayer can be assumed, since the cationic polymers do not have noteworthy interaction with each other. A minor contribution of physical adsorption is also possible. In general, the affinity between the studied PE and the pulp fines was strong, as the isotherm plateau was reached with relatively low amounts of free PE in the solution. By studying the effect of turbulence on the PE adsorption, different behaviour was detected for the two types of fines.

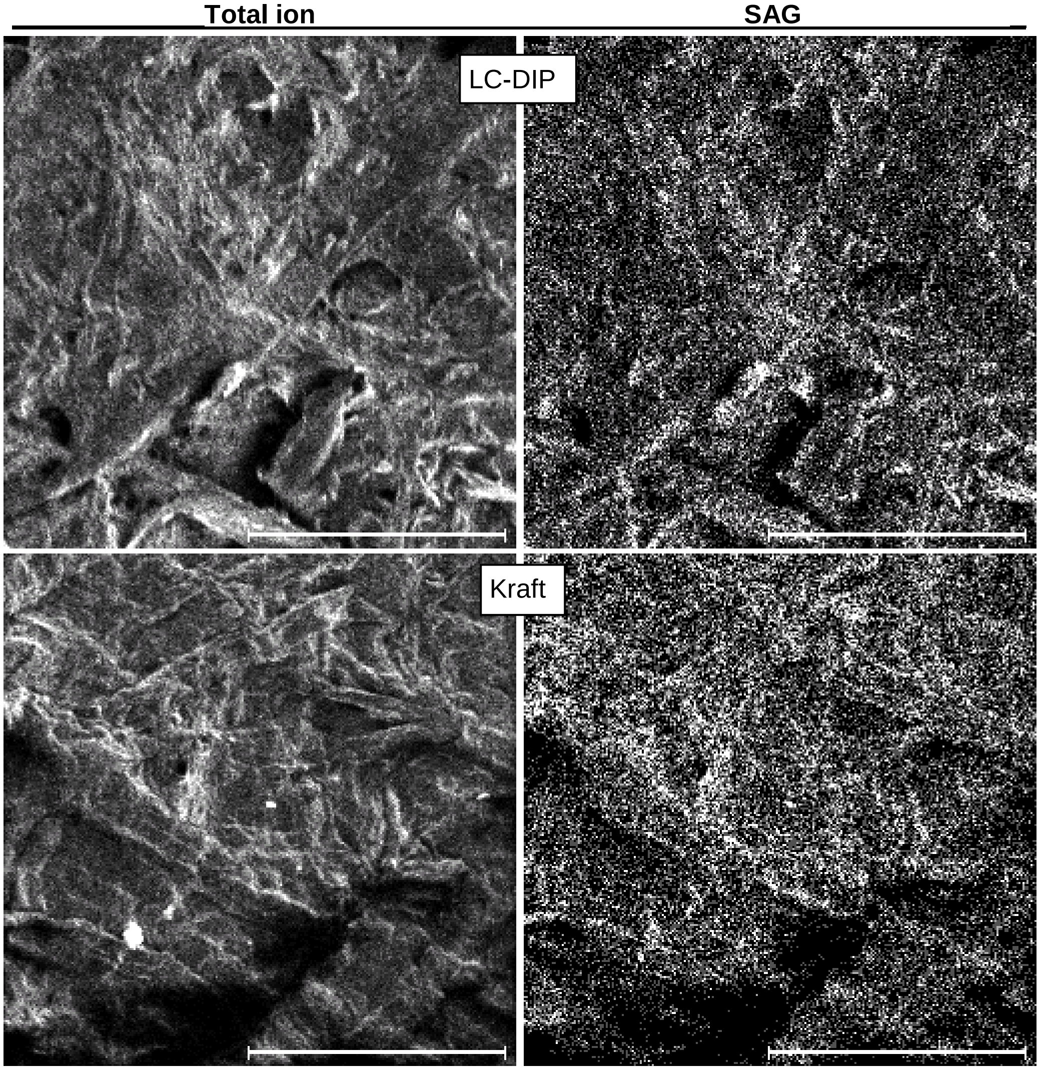


Fig. 3. The distribution of SAG on LC-DIP and kraft fines. The scale bar is 100 μm.

The adsorption isotherms of PE-1 were made using two different turbulence conditions, with stirring rates 750 rpm and 1250 rpm. Kraft fines adsorbed as a whole more PE than the LC-DIP fines. Using the lower stirring rate the difference was, however, small. An interesting result was that the increase of agitation affected the kraft and the LC-DIP fines in an opposite way (Fig. 4). When the PE adsorption was approximately on the same level for both of the fines at the lower mixing rate, addition of turbulence caused the LC-DIP fines to adsorb less and the kraft fines to adsorb more PE. That indicates a relatively weak bond between the polymer and LC-DIP fines, so that the polymer was desorbing easily when in turbulence, or was not able to attach at all. Kraft fines, on the contrary, adsorbed more with a higher mixing rate compared to the lower rate, which indicated that polymers may be forced in with turbulence and absorbed into the larger pores in the cellulosic pulp. The difference was not explained by electrostatic interactions, as the background conductivity was the same in both cases. The lignin present in LC-DIP may also give rise to some contribution of non-ionic interaction with the PE (Enarsson et al. 2009).

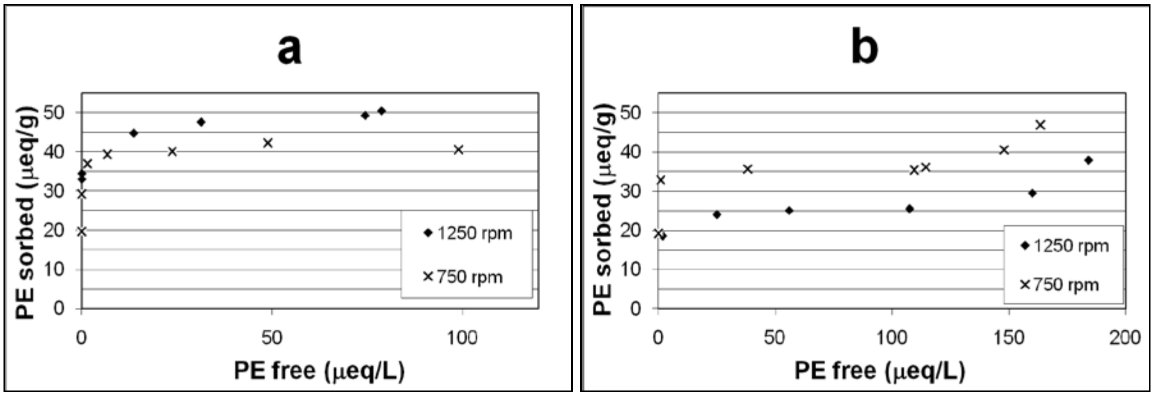


Fig. 4. PE-1 sorption isotherm for a) kraft and b) LC-DIP fines in different turbulence conditions: 750 rpm and 1250 rpm mixing.

The surface adsorption of polymers (SPE) was assessed by XPS on the polymer treated samples, and the results for PE-1 are presented in Fig. 5. XPS performed well in detecting the perpendicular distribution of PE in the pulp surface. A much higher proportion of PE was found in the surface layer of the fines, both in LC-DIP and in kraft, compared to the total amount of PE sorbed. Kraft fines showed no significant difference in the amount of adsorbed PE when using the higher or the lower mixing rate. Indeed, the surface charge stoichiometry (SPE/SAG) was <2, and thus almost all of the cationic sites of the adsorbed SPE were attached to pulp anionic sites. In LC-DIP fines again, the SPE saturation level was in the range of 2500 µeq g^{-1}, slightly depending on the mixing rate. The SPE/SAG for ONPf was 9 by milder mixing and 8 by stronger mixing. Perhaps the gentler mixing allowed the polymer to better penetrate into the pulp, but this reaction was not physically preferred and thus not favoured by the heavier stirring. The polymers adsorbed on the outer surfaces could then be more easily removed with turbulence.

Surface Distribution of Polyelectrolyte

The distribution of PE-1 on the samples was assessed by ToF-SIMS imaging, by monitoring the characteristic peaks at 44 (CH_2NO) and 58 Da (C_3H_8N) (Fardim and Holmbom 2005, see Fig. 6). Although there was a slight unevenness in the SAG distribution on LC-DIP (Fig. 3), the distribution of the PE-1 did not differ between the two types of fines. It was uniformly spread in both cases. This can be explained by the size of the molecules, as large polymers cover the surface much more expansively than just the attachment point or points because of the formation of tangles and loops.

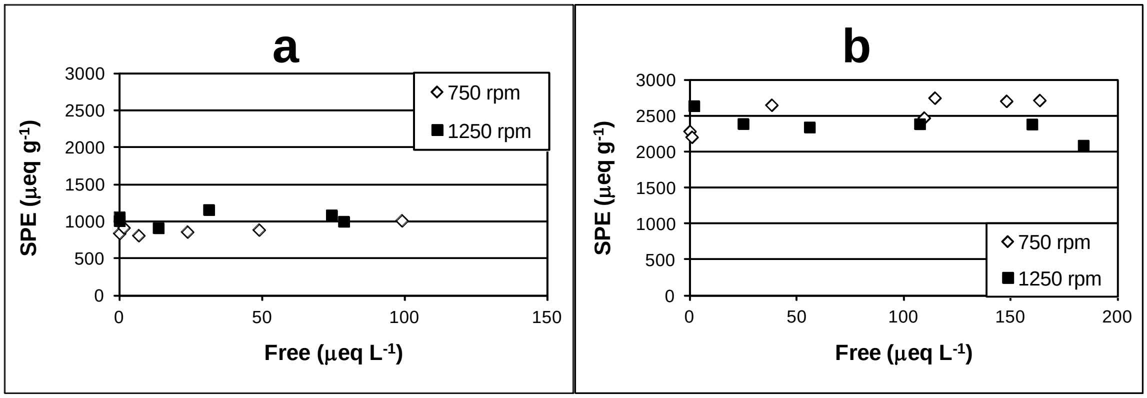


Fig. 5 Surface adsorption of PE-1 as detected by XPS, on a) kraft and b) LC-DIP fines using two different turbulence conditions, 750 rpm and 1250 rpm mixing.

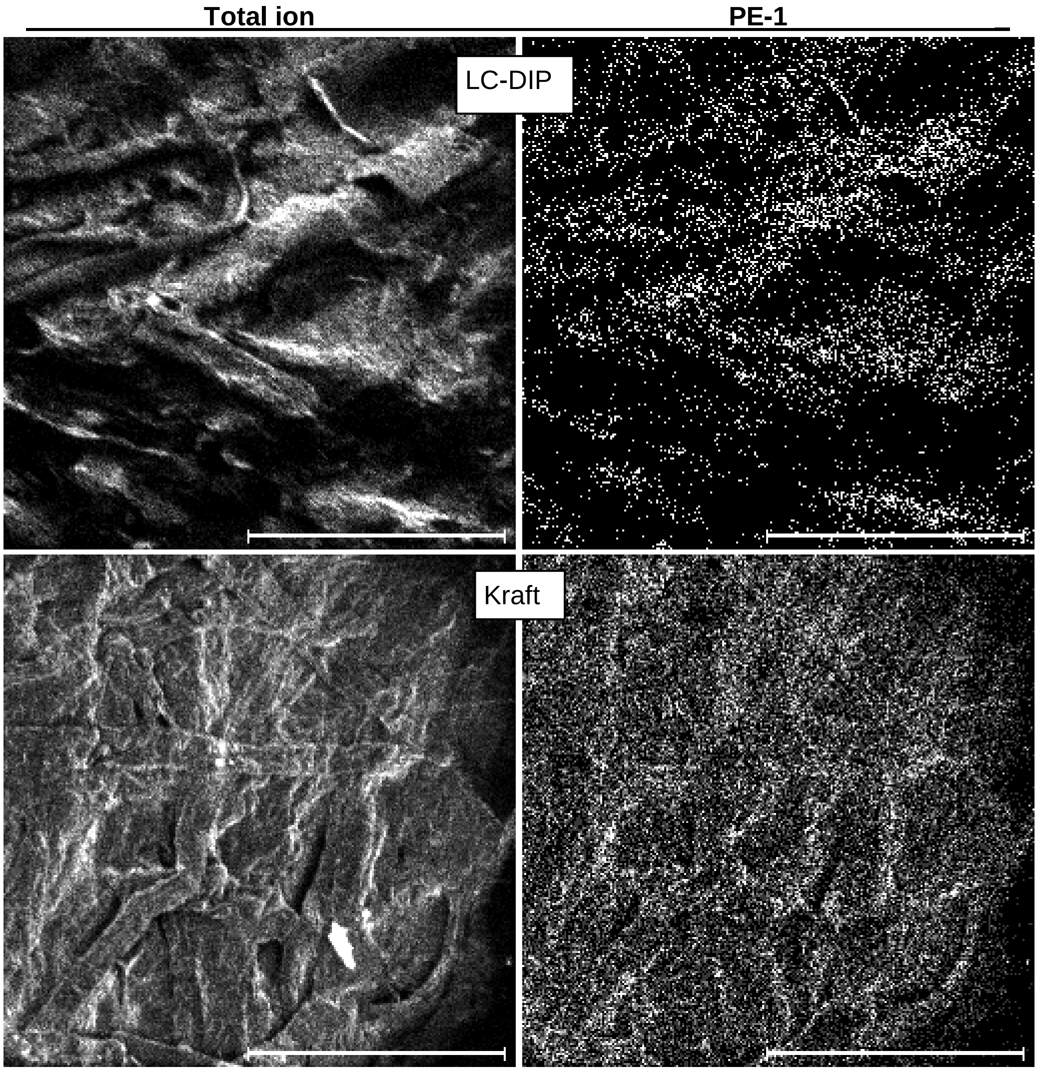


Fig. 6. The surface distribution of PE-1 on LC-DIP and kraft fines. The scale bar is 100 µm.

Interactions Between Pulp Fines and Polyelectrolyte

Based on the results presented here we may discuss the interactions between PE and pulp fines. On LC-DIP fines, the total charge was high but the surface proportion of the charge was minor. Cationic PE adsorption was restricted on the outermost surfaces, despite the high total charge and the pulp porosity. Kraft fines, on the contrary, had high amount of accessible SAG and adsorbed more PE, especially in the presence of turbulence. Further, a small proportion of the adsorbed PE penetrated deeper into the kraft fibre structure, below the detection depth of XPS. This can be explained in the following way: As the amount of SAG was lower on the LC-DIP fines, PE could attach only on few points and most of the polymer length is reaching out from the surface either as large loops or as long tails. Thus, a steric and electrostatic hinder was formed on the particles, preventing more PE's from approaching particle surface. Even if there were pores and more AG's available deeper in the fibre wall, the adsorption was restricted to the outmost fibre wall. The low number of attachment points made the PE weakly bonded and also makes the adsorption under turbulence more difficult. On kraft fines again, the higher number of SAG promoted dense bonds between PE and pulp surface, which lead to a flat alignment of PE. Consequently, there was less hinderance for more PE to approach the surface and reach the AG's available in fibre wall pores. As a result, the total adsorption quantity became higher despite of the lower total charge and smaller surface area.

It must be noted that the contact times used in this study and in papermachine are disparate. Further, the levels of application of synthetic PE flocculants in papermaking processes are relatively low, often less than 1%. The low dosage contributes not only to the maximum fines retention and sheet strength but also the highest uptake of colloidal and dissolved carbohydrates, whereas high dosages of low-charge density PE are known to give rise to steric stabilisation and dispersion of colloidal material (Rojas and Neuman 1999). The PE adsorption process consists of primary attachment via one or few points, and after that, flattening of the conformation and reaching an equilibrium configuration with time (Wågberg et al. 1988). The first PE adsorption quantity, obtained within less than 1 s contact time, is dependent mainly on the outer surface area of pulp and the volume of gyration of the PE, in other words, the probability of collisions (Falk et al. 1989). The adsorption process does not come close to reaching equilibrium during the brief contact time between PE and pulp (a few seconds) on the paper machine. Here again, the interaction was studied in form of equilibrium adsorption isotherms, which reveals the maximal adsorption capacity in certain conditions. It seemed to be dependent on the amount of SAG and, to some extent, the pores in the pulp material but not the surface area. Clear differences between kraft and LC-DIP were found in the PE adsorption behaviour, as described above. In terms of papermaking, what is causing the weak response of recycled fines towards retention agents? In bridging-type of flocculation, as with the types of high mass cationic PE used in this study, the range of the PE protruding out from the particle surface contributes strongly to flocculation. However, the binding between the PE and fibre has to be strong enough to be able to resist the forces of turbulence, and it has to be formed quickly. The amount of SAG is a plausible factor. In addition, it is possible that the partial penetration of the retention chemical plays a role in flocculation.

CONCLUSIONS

1. XPS provided a powerful tool for detecting the surface concentration of the adsorbed polyelectrolyte.
2. The adsorption quantity as well as the surface conformation of cationic polyelectrolyte was governed by the amount of surface anionic groups in the pulp substrate, and to minor extent by the pulp porosity.
3. For kraft fines, the charge stoichiometry on the surface (adsorbed PE/surface anionic group) was < 2, and the surface content of the adsorbed PE was about 20 times that of the total amount adsorbed PE. For recycled lignocellulosic fines, the surface stoichiometry was approximately 8, and the surface content of PE was almost 100 times higher that the total amount. This refers to a flat conformation and some PE penetration on the first-mentioned and a more free conformation with protruding tails and no PE penetration on the latter.
4. Added turbulence promoted the total PE adsorption quantity on kraft fines and impaired that on recycled lignocellulosic fines.

ACKNOWLEDGMENTS

Metso Paper Inc. is acknowledged for the materials and financial support. A PaPSaT graduation school grant has enabled the writing of the paper. We also thank Top Analytica Ltd. for providing us with the surface analytical instruments.

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Article submitted: December 23, 2010; Peer review completed: April 2, 2011; Revised version accepted: April 29, 2011; Published: May 6, 2011.

ERRATUM

This is a corrected version of the article published in BioResources May 6, 2011, and as printed copy August 2011, Vol. 6, issue 3. The correction was submitted January 21, 2012.

Corrections were made in the Methods/Surface Analyses, where the calculations of SAG and SPE are presented in the correct form. In the original publication, a reference was used for the calculation. Recently, a numerical mistake was found in the referred publication by the author of that. This influences the reported values for SAG and SPE in the Results and Discussion; the corrected values are 100 times higher than previously reported. The surface proportion of adsorbed polyelectrolyte is remarkably higher than first reported. This is corrected in Results and Discussion and in Conclusions/point 3.