ORIGINAL RESEARCH

Adsorption of paper strength additives to hardwood fibres with different surface charges and their effect on paper strength

Mengxiao Zhao · Leif Robertsén · Lars Wågberg · Torbjörn Pettersson

Abstract Light-weight paper products that contain less fibres, but with a maintained bulk and improved strength properties, are highly desirable due to the low cost of raw materials and improved logistics of packaged goods. In this respect, the adsorption capacity of dry strength additives onto fibres, which is affected by the surface charge of said fibres, is very important for the development of these mechanically robust paper products. The influence of the surface charge on the adsorption of strength additives was investigated for, dissolving grade fibres, kraft fibres and kraft fibres modified with carboxymethyl cellulose (CMC) with different surface charge densities, but the same fibre dimensions. The strength additives investigated were cationic starch (CS), anionic polyacrylamide (APAM) and polyelectrolyte complexes (PECs), containing CS and APAM. A linear relationship was found between the surface charge of the fibres and the saturated adsorbed amount of CS. However, when either APAM or PECs adsorbed as secondary layers onto the CS, no correlation between cellulose charge and the saturation adsorption could be observed. The adsorption of APAM was dramatically affected by the pre-adsorbed amount of CS, whereas PECs were less influenced. Moreover, the additives improved the tensile strength (60%) and strain at break (> 100%) of handsheets formed with the kraft fibres and adsorbed APAM. It was also found that CS/APAM increased the sheet density while CS/PECs lowered it. In conclusion, the gained fundamental understanding of these adsorption of additives is of significant importance to facilitate the industrial development of sustainable low-cost high-end packaging products.

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Graphical abstract

Fibres with different surface charge   **Adsorption of paper dry strength agents**
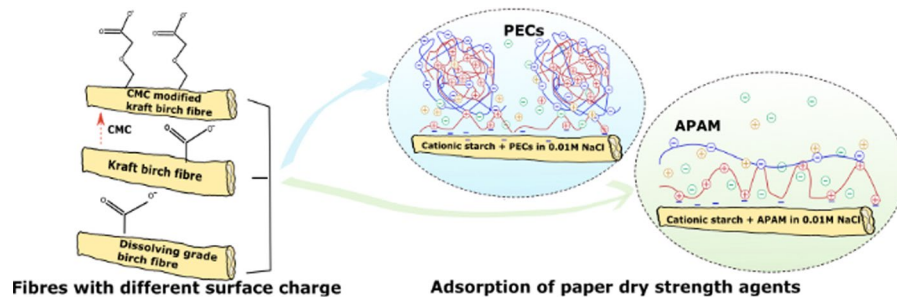
Keywords Surface charge · Birch fibres · Polyelectrolytes complexes · Paper dry strength · Anionic polyacrylamide · Cationic starch

Introduction

Due to environmental concerns, the popularity of fibre-based packaging has increased worldwide. Ideal properties of paper based packaging materials are high dry paper strength and low density; as it would be beneficial to minimise the total amount of fibres used per package. It is important that any reduction in paper density does not reduce the dry strength of the package. The dry strength of paper is affected by multiple factors; such as the joint area between the fibres and intrinsic strength of the component fibres, as well as sheet formation (Lindström et al. 2005). Dry strength additives are frequently used to optimise the mechanical properties of board made from both virgin and recycled fibres. Moreover, dry strength additives can be utilised to retain or improve the dry strength of printing papers which contain inorganic fillers that improve the optical properties and printability of the paper. Currently the most common dry strength additives used in papermaking are modified starches and polyacrylamide based polymers (Silva et al. 2015). Other chemicals including carboxymethyl cellulose, polyvinyl alcohol and polymeric latex have also been tested and used in specialised applications (Roberts 1996). An emerging additive during the last decade is polyvinylamine (PVAm), which will impart both wet and dry strength to papers (Pelton 2014).

Paper strength additives are typically cationic polymers with very high molecular weights, they adsorb to anionic fibres in a process driven by the entropic gain of counter ions being released (Wågberg 2000). Due to their high molecular weights ($> 10^5$ g/mole), the additives will predominantly interact with the fibre surface as they are too large to penetrate the fibre walls (Horvath et al. 2008). The surface charge of the fibres is therefore of utmost importance when it comes to defining the properties of the final packaging material. For cellulose based fibres, their charge is determined by their processing; for example, the pulping process and enzymatic modifications (He et al. 2005; Bhardwaj et al. 2007; Horvath et al. 2008; Ni et al. 2011; Zhang et al. 2016). The surface charge on fibres is determined by the concentration of anionic functional groups in the form of carboxyls, sulfonic acids and possibly ionisable hydroxyls. Hardwood fibres have a considerably higher charge density than softwood fibres due to the relatively higher content of charged glucuronoxylans in hardwood (Sjöström 1989; Banavath et al. 2011). The surface charge of cellulose fibres can be chemically introduced by TEMPO-mediated oxidation (Saito and Isogai 2006), bulk carboxymethylation (Horvath et al. 2006), carboxymethylated cellulose (CMC) modification (Laine et al. 2000) or by adsorbing charged hemicelluloses onto softwood kraft pulps (Köhnke et al. 2010). The total charge of cellulose fibres is comprised of both surface and bulk charges. These charges influence the development of joints between fibres, the swelling and softening of wet fibre walls and the amount of strength enhancing additives able

to adsorb to the fibres (Lindström et al. 2005). A softer fibre wall will lead to an increased molecular contact area between the fibres and hence a stronger fibre/fibre joint but at the cost of an increased fibre density of the resultant paper.

Cationic starch (CS) is typically prepared by substituting tertiary amines onto the polysaccharide backbone using glycidyltrimethylammonium chloride (Bendoraitiene et al. 2006). The positive charges enable the adsorption of CS onto negatively charged fibre surfaces. The adsorption of CS on cellulose has been thoroughly investigated and shown to enhance the strength of paper (van de Steeg 1992; Shirazi et al. 2003; Lundström-Hämälä et al. 2009). CS is a bio-based polyelectrolyte and the exact molecular structure, molecular weight distribution and charge density of the starch will affect its adsorption onto different fibre based materials (van de Steeg et al. 1992; Johansson et al. 2009; Lundström-Hämälä et al. 2010). Additionally, ionic strength, pH and temperature have been shown to influence adsorption (van de Ven 1994). By adsorbing alternating layers of CS and anionic starch (AS), multilayers can be formed (Eriksson et al. 2005). A recent study used Quartz Crystal Microbalance with Dissipation (QCM-D) and Stagnation Point Adsorption Reflectometry (SPAR) measurements to demonstrate the multilayer build-up of cationic and anionic polyelectrolytes on cellulose fibres (Benselfelt et al. 2017). Multilayers of cationic and anionic starch have also been characterised by using Atomic Force Microscopy (AFM) with a colloidal probe (Johansson et al. 2009). Using the same technique, Guan et al. investigated the relationship between adhesion force and adsorption capacity of modified starch on silica wafers (Guan et al. 2008). Excess cationic charges on the CS can further be used to anchor anionic polyelectrolytes, promoting the development of strong joints between cellulose fibres.

Polyacrylamides (PAMs) are polymers composed of acrylamide monomers (Paktinat et al. 2011). PAM itself has no net charge, but can be copolymerised with monomers containing cationic functional groups to form cationic polyacrylamide (CPAM) (Audebert et al. 1983; Rabiee et al. 2015) or anionic copolymers, such as acrylic acid, to form anionic polyacrylamide (APAM) (Sun et al. 2010; Paktinat et al. 2011). The charge density of polyacrylamide can be adjusted by altering the composition of the PAM and CPAM/APAM monomers. As well as changing the charge density, these changes in composition will also alter the molecular weight, molecular mass distribution and the properties of the final product (Audebert et al. 1983; Xiong et al. 2018). Polyacrylamide (PAM) has been widely used in different applications including but not limited to water treatment (Tekin et al. 2005; Guezennec et al. 2015), oil and gas refining (Sabhapondit et al. 2003; Guezennec et al. 2015; Swiecinski et al. 2016), and papermaking (Yuan and Hu 2012; Silva et al. 2015; Wang et al. 2018). Polyelectrolyte theory has been used to model the adsorption of CPAM onto cellulose rich fibres (Lindström 1989; Tanaka et al. 1990; Wågberg et al. 2004). APAM is commonly used for different applications because of its molecular structure and solubility in aqueous systems. It is an excellent dry strength agent, so it is widely used in the papermaking industry, particularly in recycled pulp systems. In these applications APAM needs to be combined with cationic polyelectrolytes to adsorb to cellulose surfaces (Ichiro and Yamauchi 2008). Although many aspects of PAMs have been extensively studied, a thorough characterisation of their use as dry strength additives in paper has, to the best of the authors´ knowledge, never been reported. Roberts et al. proposed that the inclusion of PAMs increases the number of inter-fibre joints in the system; the PAMs' long and flexible chains bridge the fibres without sacrificing the optical properties, density and porosity of the paper (Reynolds and Wasser 1980; Roberts 1996).

Typically, in the previous literatures only adsorption or paper strength have been the focus without linking the saturation adsorption to final paper properties. In this work, the measured saturation adsorption of the strength additives is linked to the obtained paper properties. We have investigated how the amount of anionically charged groups on the fibre surfaces influence the adsorption of dry strength agents, and the subsequent effect of this on papers made from kraft fibres was investigated. High-charged cellulose fibres were obtained by the CMC modification of fibres and were compared to moderately charged kraft birch fibres and low-charged dissolving grade birch fibres. The saturation adsorption of cationic starch, APAM and polyelectrolyte complexes (PECs) were determined by polyelectrolyte titrations for the three selected fibre types with different surface charge densities. Handsheets made from kraft fibres were formed and characterised by tensile index, strain at break and

density to evaluate the effect of the saturation adsorption for each of the strength agents investigated.

Experimental

Materials

Fibres The kraft birch fibres used in this study were industrially produced elemental chlorine free (ECF) bleached birch fibres from southern Finland, they were refined using a Voith refiner (Voith GmbH, Germany) at refiner energy of 28 kWh/t, consistency of 4 wt%, and a specific edge load (SEL) of 0.6 J/m to 25 SR before further treatment. The dissolving grade birch kraft fibres used in this study were industrially ECF bleached dissolving grade birch kraft fibres from Finland. They are used as a typical low-charged fibres in this study. Fibre dimensions analysis was performed according to ISO16065-2:14 and the results are displayed in Table S1 in the supplementary information.

Dry strength additives Cationic starch, Raisamyl 50,021 with a charge density of $+0.21$ meq/g and degree of substitution (DS) $= 0.035$; based on potato starch, $M_w = 2 \times 10^6$ g/mol were purchased from Chemigate, Finland as powder. Solutions of 1 wt% cationic starch in deionised water was prepared and heated to 97 °C for 30 min with constant stirring. Anionic polyacrylamide (APAM, charge density $= -1.1$ meq/g, $M_W = 3 \times 10^5$ g/mol) was synthesised at Kemira, Espoo, Finland. Polyelectrolyte complexes (PECs) with a charge density of -0.65 meq/g and Mw $\approx 1 \times 10^8$ g/mol were prepared by mechanical mixing of CS which contains the commonly used quaternary amine groups and APAM solutions (Chiu and Solarek 2009) at Kemira, Espoo, Finland. The size distribution of the PECs as determined by Dynamic Light Scattering (DLS) is presented in Fig. S1 and the number-based average diameter is around 30 nm. The final APAM solution and the PECs dispersions were diluted to 1% with deionised water, and the pH was adjusted to 6.5 by the addition of 0.1 M NaOH.

CMC (Carboxymethylated cellulose), DS $= 0.8$, $M_W = 4.5 \times 10^5$ g/mol, DP $= 2000$, was provided as powder by CPKelco, Finland. The CMC was dissolved to 1 wt% with deionised water before heating to 55 °C for 1 h with constant mixing.

Polydiallyldimethylammonium chloride (PolyDAD-MAC) and Polyethenesodiumsulphonate (PES-Na) that were used in the charge titration were purchased from BTG Instruments AB (Säffle, Sweden) with a pre-adjusted charge density of 0.001 meq/L. Sodium bicarbonate (NaHCO$_3$), hydrochloric acid (HCl), sodium chloride (NaCl), calcium chloride dihydrate (CaCl$_2$·2H$_2$O) and sodium hydroxide (NaOH) were purchased from VWR chemicals (Finland).

Methods

Charge determination of fibres and chemicals

The total charge was determined by conductometric titration according to the method originally developed by Katz et al. (1984). The 1 wt% fibre solution was protonated by soaking in 0.1 M HCl for 15 min, and then washed and filtered to lower the conductivity below 5 µS/cm. Approximately 1 g (dry content) of protonated cellulose fibres were dispersed in 500 ml of 1 mM NaCl solution, followed by the addition of 5 ml of 0.01 M HCl. This was then titrated against 0.05 M NaOH at 21 °C by using a Metrohm 856 conductometer (Metrohm AG, Switzerland), the solution was degassed with nitrogen and constantly stirred throughout the titration. Finally, the suspension was filtered under vacuum and dried in an oven at 105 °C overnight before recording the dry weight of the fibres. The total charge was determined using the volume of NaOH required to reach the second inflection point in the conductivity versus NaOH concentration plot and from the volume needed to neutralise the added HCl.

The surface charge of the fibres was determined using polyelectrolyte titration, as described by Wågberg et al. (1989) using a CAS touch—charge analyser (Emtec Electronic GmbH, Germany). The titration is based on the well-established assumption that there is a 1:1 stoichiometric charge interaction of two oppositely charged polyelectrolytes. The fibre suspension was diluted to 5 g/L with deionised water, followed by the addition of a pre-calculated volume of 0.001 meq/g polyDADMAC solution. The dispersion was mixed for 30 min to allow the two species to adsorb to the saturation adsorption, then filtered under vacuum through a Whatman Grade 589/1 black

ribbon filter paper. 10 mL of the filtrate was transferred to the measurement chamber of the charge titrator, and the excess polyDADMAC in the filtrate was titrated with oppositely charged polyelectrolyte (0.001 meq/L PES-Na). The charge density of the fibres is proportional to the amount of charge that adsorbs to the fibres during the titration, as determined from the saturation adsorption in the adsorption isotherms.

The charge density of the strength additives was also determined by titration with an oppositely charged polyelectrolyte. For cationic starch, 0.001 meq/L PES-Na was used; and for APAM and PECs, 0.001 meq/L polyDADMAC was used. A 1:1 stoichiometric charge ratio between the strength agents and the polyelectrolyte is assumed for these titrations. The adsorbed mass of cationic starch, APAM and PECs to the fibres was determined by measuring their adsorption isotherms in the same way as for the polyDADMAC adsorption; the only exception being that the adsorption time was 10 min for these measurements.

Surface charge modification of fibres

Highly charged cellulose fibres were prepared by the irreversible attachment of CMCs according to the adsorption method developed by Laine et al. (2000). The addition of 10 mg/g, 15 mg/g and 20 mg/g of CMC to the kraft fibres were tested, while only 20 mg/g addition was tested for the dissolving grade fibres. Each CMC solution was added to a 25 g/L fibre suspension in 0.05 M $CaCl_2$ and the pH was adjusted with 0.01 M $NaHCO_3$ to pH 8. After mixing, the samples were sealed in plastic bags and placed in water bath at 85 °C for 2 h. Kraft fibres and

dissolving grade fibres were treated in the same way except without the CMC addition, in order to evaluate if the treatment condition affected the fibre properties. After the 2 h treatment, fibres were washed with deionised water (by repeatedly dispersing and filtering) until the conductivity of the filtrate was lower than 50 μS/cm, measured using a 200 mesh wire at ambient temperature. Thereafter, the fibres were converted into the protonated form by soaking in 0.01 M HCl (pH 2) for 30 min, followed by washing until the conductivity of the filtrate was lower than 5 μS/cm. After this, the fibre counter ions were replaced with sodium by soaking in 0.001 M $NaHCO_3$ (adjusted with NaOH to pH 9) for 2 h. In the last step, the fibres were washed until the conductivity was lower than 5 μS/cm, to remove any non-adsorbed CMC.

Zeta potential

The zeta potentials of the sodium form of the fibres, with and without strength additives, were determined using Fiber potential analyser (FPA, Emtec Electronic – AFG Analytic GmbH, Germany), based on the streaming current potential method (Lindström 1989). A 0.5 wt% fibre suspension in 0.01 M NaCl (conductivity of 1 mS/cm) was prepared and the sodium form of the fibres had a pH of 6.3. Dry strength chemicals were added and mixed with the fibres for 10 min. The samples were measured in triplicate and the average values are reported.

Sheet forming and testing

Paper sheets were formed at a set grammage of 60 g/m^2 using a KCL type sheet former according to ISO 5269–1 protocols. A 2.5 g/L fibre suspension in

Table 1 Total and surface charge of the fibres and the effect of CMC modification

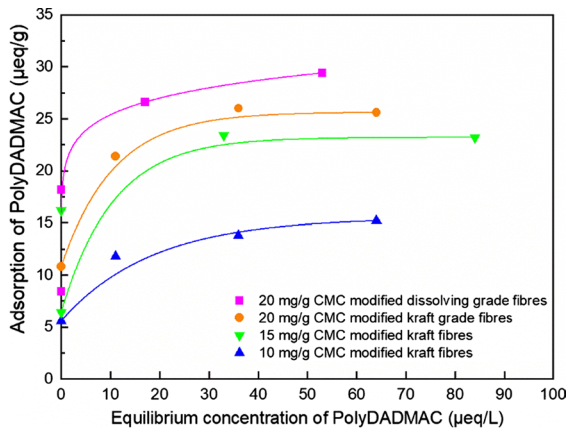| Fibre type	CMC addition (mg/g)	Total charge (μeq/g)	Surface charge (μeq/g)	Surface charge increase (μeq/g)	Calculated CMC adsorption (mg/g)
Kraft birch fibre	N/A	−60.5±1.8	−7	N/A	N/A
Kraft birch fibre	10	−66.8±0.9	−13	6	1.7
Kraft birch fibre	15	N/A	−23	16	4.6
Kraft birch fibre	20	−75.2±1.4	−24.5	17.5	5
Dissolving grade birch fibres	N/A	−30.2±2.1	−4.5	N/A	N/A
Dissolving grade birch fibres	20	−52.5±0.5	−26	21.5	6.1

Fig. 1 PolyDADMAC adsorption a surface charge determination of CMC modification of kraft birch fibres and dissolving grade fibres following different additions of CMC

0.01 M NaCl (conductivity of 1 mS/cm) was stabilised at least 4 h before further use. Cationic starch was added to, and mixed with, the fibre for 60 s; followed by the addition of APAM or PECs and a further 60 s of mixing. Once the paper sheets were formed, they were pressed with 400 kPa for 5 min to remove excess water, this was followed by a change of blotters and a repeated pressing at the same pressure for an additional 2 min. This was done to prevent the sheets from irreversibly adhering to the blotters while drying in heaters. A Rapid Köthen was then used to dry the papers at 92 °C for 8 min at a reduced pressure of 96 kPa. The final paper sheets were conditioned at 50% relative humidity (RH) and 23 °C for at least 24 h before paper characterisation. The grammage of paper sheets was measured by an L&W device according to ISO 536 protocols. The tensile strength and strain at break of the paper were determined by a L&W tensile tester according to ISO 1924–3 protocols.

Results and discussion

Charge of fibres

In order to be able to obtain fibres with a range of different charges, CMC modification was performed for both kraft birch fibres and dissolving grade fibres at different CMC addition amount. After the CMC modification the total charge and surface charge

were determined for the original and modified fibres and the results are presented in Table 1. The poly-DADMAC adsorption isotherms from the surface charge titrations of CMC modified fibres are shown in Fig. 1. All CMC modifications tested increased the surface charge of the fibres. With 10 mg/g, 15 mg/g and 20 mg/g additions of CMC, the absolute values of the surface charge of kraft birch fibres increased from 7 µeq/g to 13 µeq/g, 23 µeq/g and 24.5 µeq/g respectively. For the dissolving grade fibres, 20 mg/g of CMC increased the surface charge of the fibres from 4.5 µeq/g to 26 µeq/g. The total charge of the kraft fibres, the dissolving grade fibres and the CMC modified fibres were determined by conductometric titration to evaluate the topochemical selectivity of the CMC modification (see Table 1). The initial total charge of the kraft fibres (60.5 µeq/g) was increased to 66.8 µeq/g or 75.2 µeq/g by adding 10 mg/g or 20 mg/g of CMC, respectively. For the dissolving grade fibres, the initial total charge was 30.2 µeq/g, and the addition of 20 mg/g CMC increased the total charge to 52.5 µeq/g. The topochemical selectivity can be determined by comparing the increase in total charge and surface charge. From the results it can be concluded that most of the CMC was attached onto the surface, since the total charge increase is the same as the "surface only" charge increase within errors. Therefore, it can be concluded that there is an excellent surface selectivity for CMC modification.

Laine et al. (2000) studied different CMC modified cellulose fibres and concluded that the topochemical selectivity depends on the molecular weight and treatment conditions (e.g. pH, temperature, ionic strength) used during the adsorption of the CMC. The adsorption of CMCs can occur both on the surface and within the cellulose fibre walls, depending on the molecular mass of the CMC. According to Laine et al. (2000), when the M_w of CMC is 10^5 g/mol, 60% of the CMC was on the surface of the cellulose fibres. However, when the M_w is close to or above 10^6 g/mol, more than 90% of attached CMC adsorbed onto the surface of fibres. The CMC used in this study has a Mw of 4.5×10^5, it is therefore encouraging that the CMC was predominantly on the surface of the fibre walls as this is in agreement with the results from Laine et al. (2000).

The exact amount of CMC attached to each cellulose fibres is difficult to determine (Horvath and

Lindström 2007). However, the DS of the CMC could be used to estimate this using the following relationship:

$$\text{Charge density of CMC} = \frac{DS}{162 + 80DS} \qquad (1)$$

where "162" is the molecular weight of one cellulose monomer and "80" is the net molecular weight increase from the addition of -CH$_2$COONa. Since the DS of CMC used in this work is 0.8, the charge density of this CMC is calculated to be -3.5 meq/g. The adsorbed mass of CMC on the surface can be calculated from the increase in surface charge and the charge density of the used CMC, the calculated adsorbed masses are presented in Table 1. The mass of CMC adsorbed was 1.7 mg/g for kraft fibres with the addition of 10 mg/g CMC, 4.6 mg/g for the 15 mg/g CMC addition, 5 mg/g for the 20 mg/g CMC addition and 6.1 mg/g attached onto dissolving grade fibres when 20 mg/g of CMC was added. It is worth noting that CMC attachment efficiency is significantly lower than 100% and the adsorption efficiency is dependent on the molecular weight and the adsorption conditions. The CMC used in the present work can be compared to the CMC (Cekol MVG) used in the study by Laine et al. (2000) which had a similar DS and molecular weight. Their CMC attachment was 5.6 mg/g on softwood kraft fibres with adding

20 mg/g of CMC, which is similar to what was found in the present work.

The charge increase and total amount of CMC that adsorbed to the dissolving grade fibres was higher than the kraft fibres. There are several possible explanations for this; the charge of the untreated dissolving grade fibres is much lower than that of the kraft fibres, meaning that the repulsion between the hemicellulose and the adsorbed CMC is much lower. The dissolving grade fibres have fewer non-cellulose components than the fibres produced by the kraft process. This means that the fibre surface of the dissolving grade fibres has a higher concentration of cellulose and a much lower charge which will increase the interaction with the CMC. Similar results have also been found for polystyrene sulphonate (PSS) adsorption to carboxymethylated fibres (PSS)(Jain et al. 2021).

Based on these results, the 10 mg/g CMC modified kraft fibres were selected for further studies to compare the adsorption of strengthening agents against the unmodified dissolving grade fibres and kraft fibres. Figure 2a shows the adsorption of polyDADMAC onto the selected fibres obtained from surface charge measurements (dissolving grade fibres $= -4.5$ µeq/g, kraft fibres $= -7$ µeq/g, 10 mg/g CMC modified kraft fibres $= -13$ µeq/g). To evaluate the effect of the CMC addition treatment condition on the surface charge of the kraft fibres and dissolving grade fibres, both fibres were subject to the same CMC
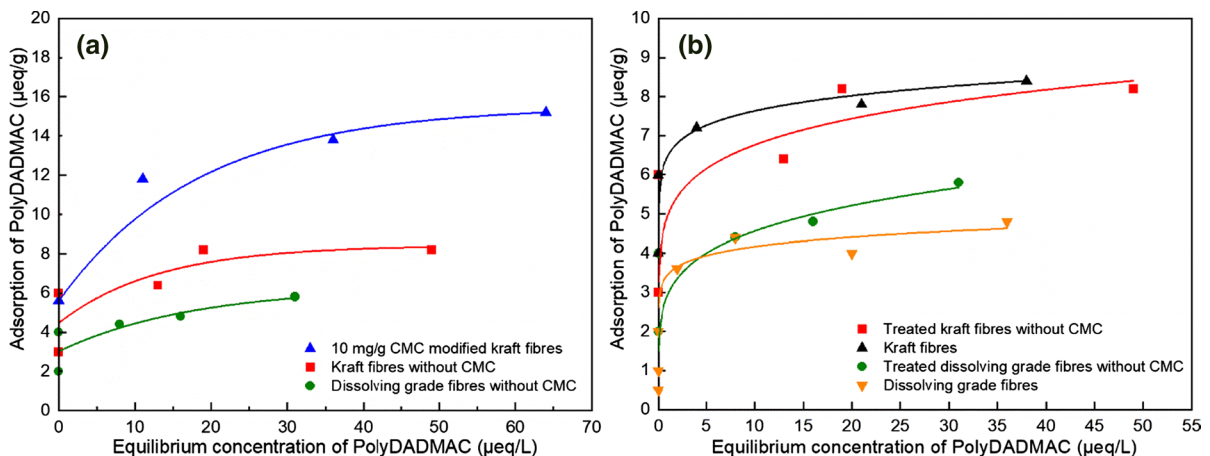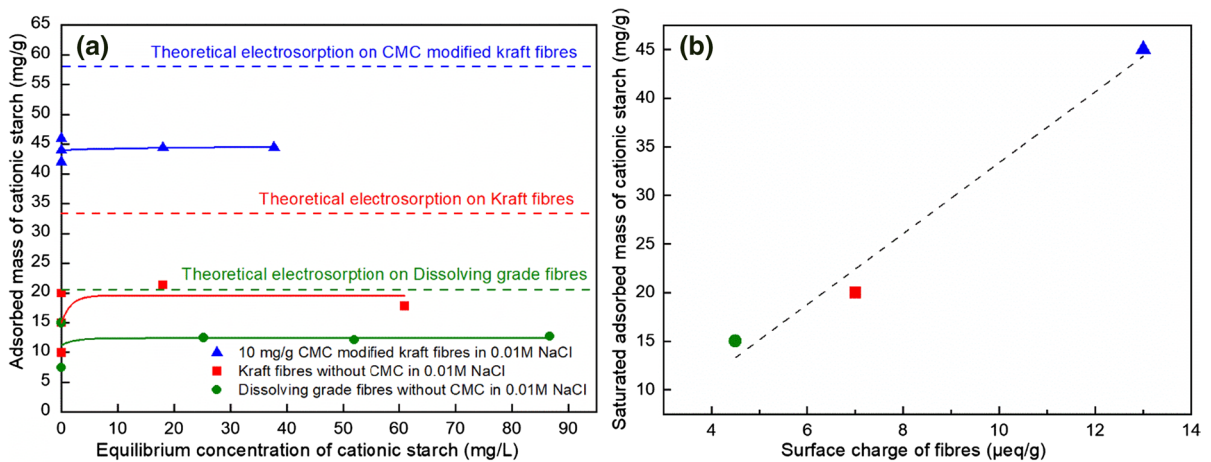

Fig. 2 Surface charge determination of different fibres as calculated from polyDADMAC adsorption isotherms. **a** Adsorption isotherms for the surface charge determination of kraft fibres, dissolving grade fibres and CMC modified kraft fibres,

b Adsorption of polyDADMAC on original fibres and fibres treated with the same protocol for the CMC attachment but without the CMC addition. Lines are included as a guide to the eye

Table 2 Summary of the charges of the strength additives used in this study determined by polyelectrolyte titrations in different ionic strength solutions a comparison is also made with theoretical values as estimated from previously established procedures

Polymer	Charge density (Deionised water) (meq/g)	Charge density (0.01 M NaCl) (meq/g)	Theoretical charge density (Functional groups) (meq/g)
CS	+0.26	+0.20	+0.21(amine content)
APAM	−1.42	−1.96	−1.1 (carboxylic groups)
PECs	−0.82	−1.02	−0.65 (carboxylic groups and amine content)

Fig. 3 Adsorption of cationic starch to different types of fibres in 0.01 M NaCl. **a** The adsorbed mass of cationic starch on fibres with different surface charges as determined by charge titration, **b** Relation between the saturation adsorption of cationic starch and the surface charge of the fibres

adsorption protocol but without any CMC being added. The surface charge measurements of these fibres are plotted in Fig. 2b and show that the surface charge did not change due to the treatment condition. Any change in surface charge can therefore be solely attributed to the adsorption of CMC and is not the result of any unwanted reactions induced by the treatment protocol; which involved increasing the pH to 8 and heating at 85 °C for 2 h, followed by multiple washing steps.

Charge density of strength additives

The charge density of polyelectrolytes is one of the major factors in determining how much strength additive that can adsorb to the fibre surfaces (van de Steeg

et al. 1992). Therefore, the charge density of the polyelectrolytes used in this study (CS, APAM and PECs) were carefully evaluated by polyelectrolyte titration. These titrations were performed using both deionised water and 0.01 M NaCl. The results are summarised in Table 2 and the titration curves are provided in Fig. S3. The charges of APAM and PECs were found to deviate from the theoretical polyelectrolyte charges (based on chemical composition), with the extent of the deviation dependent on the solution media used during the titration, i.e. deionised water or 0.01 M NaCl. The reason for this deviation is not known but was outside the scope of this investigation. The experimental charges were selected for further analysis of other data in this work.
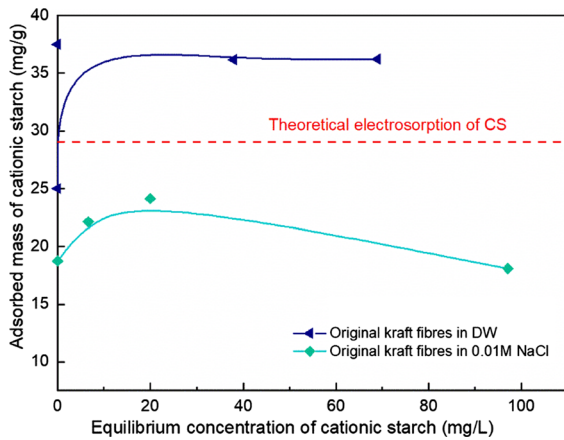
Fig. 4 Effect of electrolytes and washing on the adsorption of cationic starch

Fig. 5 Adsorption of APAM and PECs onto 10 mg/g CMC modified kraft fibres preadsorbed with 40 mg/g cationic starch. The saturation adsorption level was previously found to be 44 mg/g

Adsorption of dry-strength chemicals

Adsorption of cationic starch

The adsorption of cationic starch onto fibres with different surface charges was evaluated by polyelectrolyte titration, the corresponding adsorption isotherms in 0.01 M NaCl are shown in Fig. 3a. The saturation adsorptions were estimated to be 44 mg/g, 20 mg/g and 12.5 mg/g for the 10 mg/g CMC modified fibres, kraft fibres and dissolving grade fibres respectively. The saturation adsorbed mass of cationic starch onto the fibres is proportional to the surface charge of the fibres, as shown in Fig. 3b. This is consistent with a pure electrosorption, as defined by the self-consistent mean field (SCF) theory for polyelectrolyte adsorption (Fleer et al. 1993). The amount of cationic starch that absorbs is the amount required to neutralise the surface charge of the fibres. This means that there is an ion exchange between the charges on the cellulose fibres and the starch, driven by the entropic gain obtained when the counter ions are released. The amount of cationic starch that adsorbs to the cellulose fibres is slightly lower than what would be expected when the titrations are performed in 0.01 M NaCl, Fig. 3a. There are several possible explanations for this. Firstly, the polyDADMAC and cationic starch are different sizes and the polyDADMAC could encounter less steric hindrance to adsorption than the starch. Secondly, since the adsorption is driven by the release of counterions, performing the measurements
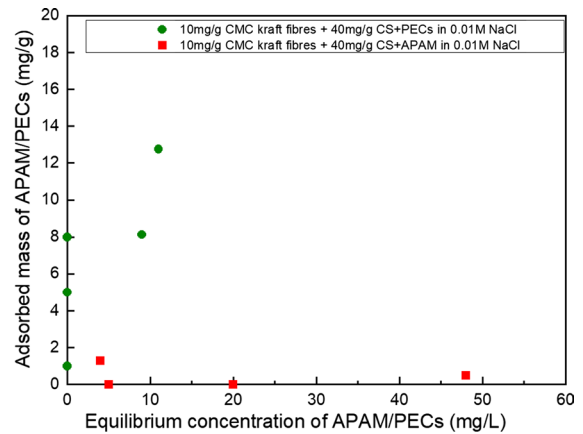
in 0.01 M NaCl as opposed to deionised water will theoretically decrease the saturation adsorption (Wågberg and Kolar 1996). To further investigate the second explanation, the adsorption of starch to untreated kraft fibres in deionised water was measured, the results are provided in Fig. 4. The saturation adsorption of cationic starch in 0.01 M NaCl is 23 mg/g while it is 37 mg/g in deionised water. Assuming a 1:1 stoichiometric ratio between the charges and that all the adsorption sites are available, the second of these values is actually higher than that would be theoretically expected. The explanation of why the saturation adsorption is higher in deionised water than would be theoretically expected lies in the conformation of the starch molecules at the cellulose surface. The initial stochastic adsorption conformation, when the starch molecules adsorbed onto the fibres, it is not the most thermodynamically stable state for the CS. As a result there is a rearrangement of the starch at the cellulose surface in which some of the starch will desorb. This process is known to be slow (Cohen Stuart and Fleer 1996). Knowledge of this process is important for the subsequent adsorption of anionic layers onto the cationic starch to form multilayers. The theory of how ionic strength influences polyelectrolyte adsorption to oppositely charged surfaces has also been well explained by Horvath et al. (2006). The difference in the results when the experiment is performed in the presence or absence of salt further indicates that this is a pure electrosorption, entropically driven by the
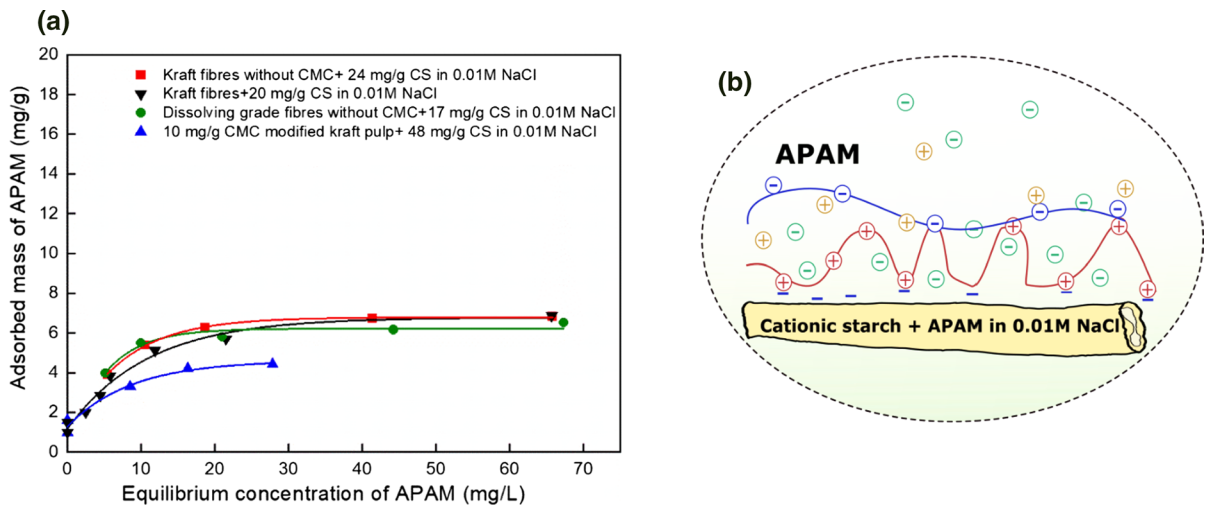
Fig. 6 a Adsorption isotherms of APAM on different surface charged fibres. **b** Schematic representation of APAM adsorbed on fibres
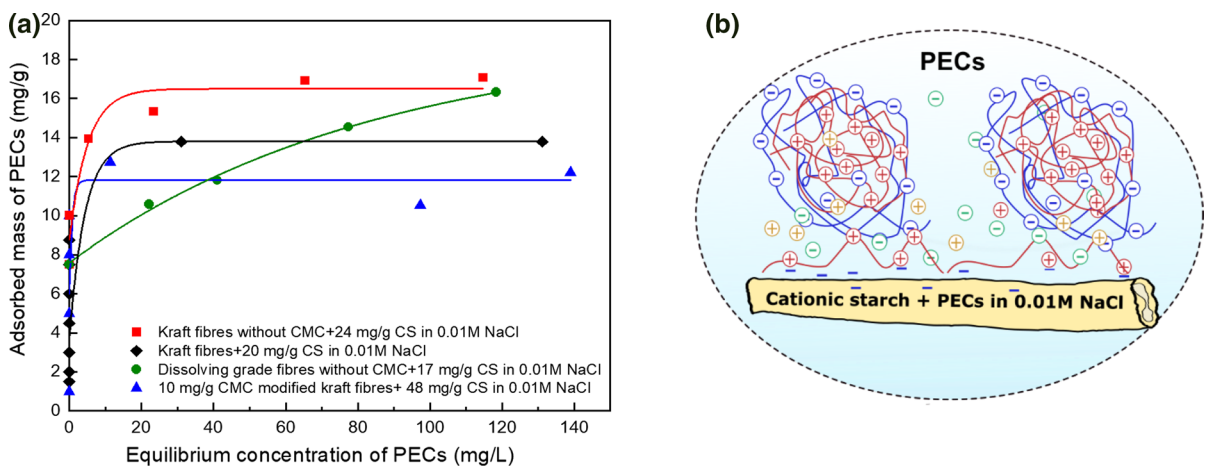

Fig. 7 a The adsorption isotherms of PECs on fibres with different surface charges. **b** Schematic representation of PECs adsorbed on fibres

release of counterions. The results also show that any shrinking of the starch when in the 0.01 M NaCl solution as opposed to in deionised water has no significant impact on the saturation adsorption.

The concentration of fibres used in the preparation of the handsheets (2.5 g/L) is lower than the concentration used in the surface charge determination measurements (5 g/L). Typically, this lower concentration of fibres should not be any concern for the saturation adsorption. To test this, the saturation adsorption of CS on 2.5 g/L of kraft and dissolving grade

fibres were measured, see Fig. S3. It was concluded that changing the concentration of the fibres had no significant effect on the saturation adsorption and the results of the adsorption measurements could be used for evaluating the effect of the chemical additives on the properties of the handsheets.

Adsorption of APAM and PECs

Measurements of the adsorption of APAM and PECs were performed for fibres pre-saturated with cationic

starch. Initially it was found that the detected saturation of starch, 44 mg/g (Fig. 3), however, as shown in Fig. 5, the addition of 40 mg/g was not sufficient to allow for adsorption of APAM to the treated fibres. The PECs, on the other hand were able to adsorb to these fibres. There might naturally be several explanations to this but as shown earlier the initially adsorbed cationic polymers will reconform to a flat conformation with time and this will hence lead to a decreased interaction with an added APAM. This means that if the CS barely is able to recharge the surface it will be difficult to adsorb the APAM to these surfaces. The PECs with a different structure, i.e. 3D structure, and also containing both anionic and cationic polymers will be able to interact with the pre-adsorbed starch and maybe also some uncovered CMC spaces on the fibres. This is a very interesting result that merits further investigation but it is beyond the scope of the present work. To overcome the problem with the lack of APAM adsorption it was therefore decided to increase the addition of CS with 20% to 48 mg/g and as shown in Figs. 6 and 7 this allows for a clear adsorption of the APAM and PECs to the treated fibres.

The concentration of cationic starch added to each of the different fibres were as follows: 48 mg/g to 10 mg/g CMC modified kraft fibres, 24 mg/g to kraft fibres, 17 mg/g to dissolving grade fibres. A schematic figure depicting the APAM/cationic starch/cellulose fibre interface is provided in Fig. 6b. PECs with both cationic and anionic monomers will naturally adopt a different conformation compared with the APAM, as schematically shown in Fig. 7b. The mass of APAM adsorbed to the fibres was calculated based on the measured APAM charge density rather than the theoretical charge density since they were so different. From Fig. 7a, it can be seen that the mass of APAM adsorbed to the fibre surfaces increases as more APAM is added to the system until a saturation level is reached. The saturation level for the kraft and dissolving grade fibres were both 6 mg/g; but for the CMC modified kraft fibres it was 4 mg/g. This lower saturation level for the CMC modified fibres is attributed to the steric repulsion between the CMC and APAM.

When comparing the adsorbed mass of APAM and PECs, it can be seen that the absorbed mass of PECs is higher. The saturation adsorption for treated kraft fibres without CMC is 16.5 mg/g, for original kraft fibres, it was 14 mg/g, and 12 mg/g for CMC modified kraft fibres. The dissolving grade fibres value is harder to obtain since the curve never truly plateaus. The lower saturation adsorption mass attributed to the lower charge density of the PECs which will lead to a higher adsorbed mount of PECs, assuming a 1:1 stoichiometric ratio of charges. This inversely proportional relationship between the charge density and the amount of polyelectrolyte adsorbed is expected and holds true for almost all cases. However, the relationship between saturation adsorption and polyelectrolyte charge density has been shown to break down when the DS of charged monomer decreases below a value around of 0.01; both through experimental modelling (van de Steeg et al. 1992) and experiments (Wang and Audebert 1988). All these results also show that the adsorption of APAM and PECs are dominated by the entropic release of counterions, i.e. a pure electrosorption. The adsorption of PECs shows a more complicated pattern that deserves further investigations.

In an eralier study of polyelectrolyte Layer-by-Layer formation including cationic and anionic starch (Lundström-Hämälä et al. 2010), it was found that a minimum charge of +0.34 µeq/g of CS was required for multilayer formation in 0.01 M NaCl. It should therefore be possible to form layers of APAM and PECs in the present system. The data in Figs. 6a and 7a show that it was indeed possible to adsorb APAM and PECs onto fibres pre-adsorbed with CS.
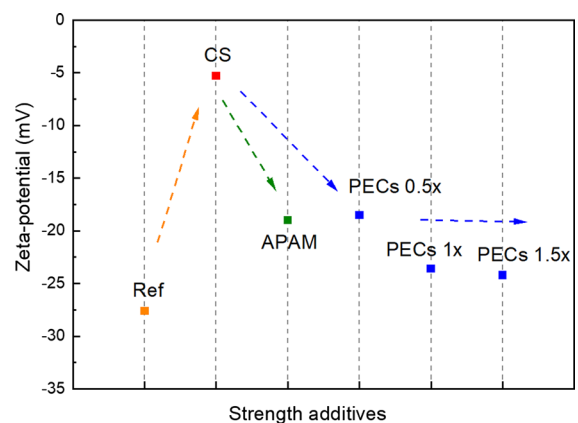

Fig. 8 Zeta-potential of processed kraft fibres without CMC with different strength additives. The dashed arrow lines have been added to guide the eye

This means that the charges of the surface have been reversed by this level of CS adsorption.

Apart from pure electrosorption it is also necessary to consider the excluded volume created by the adsorbed polyelectrolyte, i.e. will the adsorbed polyelectrolyte or polyelectrolyte complexes block the surface for further adsorption before a 1:1 stoichiometry between the charges has been achieved. This has been discussed earlier (Wågberg 2000), but since it is possible to detect a relationship between the adsorbed amount and the charges of the pre-adsorbed layers this does not seem to be the limiting case in the present work.

Paper forming and paper characterisations

The data from the adsorption experiments are naturally used as a base for the fibre treatments before

Table 3 Components of the handmade kraft fibres paper sheets, there reference sample was processed kraft fibres without any CMC

Abbreviations	Recipes
Ref	Reference
CS	24 mg/g cationic starch
APAM	24 mg/g cationic starch + 7.5 mg/g APAM
PECs 0.5x	24 mg/g cationic starch + 7.5 mg/g PECs
PECs 1x	24 mg/g cationic starch + 15 mg/g PECs
PECs 1.5x	24 mg/g cationic starch + 22.5 mg/g PECs

sheet preparation. However, to make sure that the surface properties are changed after polyelectrolyte addition zeta-potential measurements were used to characterize the effect of the additives. The results from these measurements are shown in Fig. 8 and as can be seen the CS addition can basically reduce the surface charge of the fibres and upon addition of the APAM or the PECs the fibres are again tuned back to more negative zeta-potentials. This indeed shows that the starch is adsorbing to the fibres and that the APAM and the PECs respectively can adsorb onto the pre-adsorbed starch layer. The still negative zeta-potential for the starch treated fibres indicate that the fibres are not totally recharged. This means that there would be space for more starch molecules on the fibre surface. However, as the APAM and the PECs are interacting with the adsorbed CS-layer indicates that the fibres are at least partially cationic and that the starch layer is able to interact with the anionic additives. The net negative charge of the treated fibres also indicates that the fibres will not be flocculated which is important for the formation of papers with a good formation.

Paper sheets were formed from the reference fibres and the fibres with strength additives to establish how the strength additives affected the paper density, tensile strength and strain at break of papers formed from these materials. For these tests, the fibres with the intermediate charge (kraft fibres that were processed but no CMC added) were used. Since 20 mg/g of cationic starch would have saturated these fibres, 24 mg/g of starch was used to ensure complete
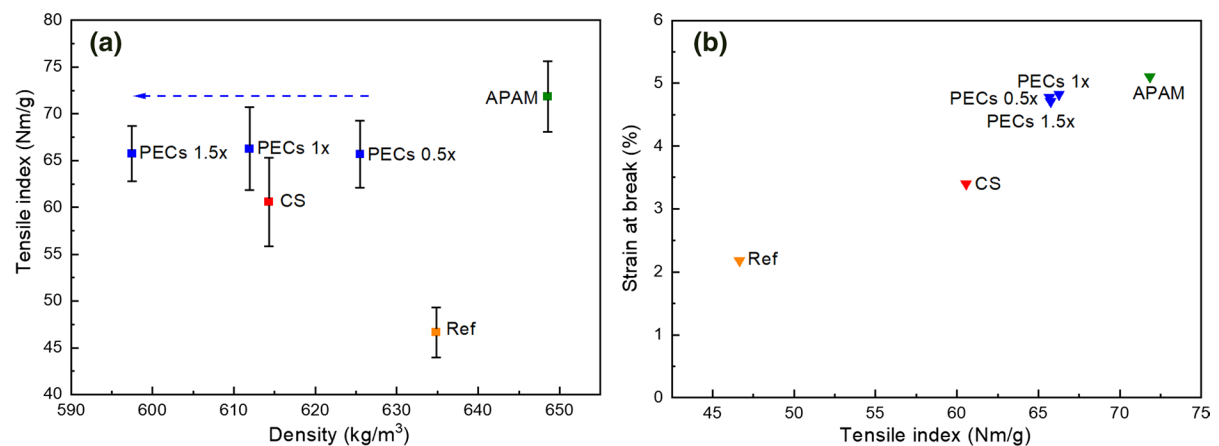

Fig. 9 Paper properties, a The tensile index and density of papers made from kraft fibres, the dashed arrow indicates the increased addition of PECs b Strain at break and tensile index and of papers made of kraft fibres

saturation of these fibres. After the CS was adsorbed onto the fibres, 7.5 mg/g of APAM was added; which should be sufficient to saturate the surface. As discussed above APAM adsorption is not 100% efficient so not all of the APAM would have been adsorbed to the surface. Alternatively, instead of APAM, PECs were added at either 7.5 mg/g, 15 mg/g or 22.5 mg/g in order to assess how the dosage of PECs affect the adsorption mass and the corresponding zeta-pontential. For a full list of the components in the different papers tested, see Table 3.

The tensile index (45 Nm/g) and paper densities (635 kg/m^3) of the reference paper made from kraft fibres are provided in Fig. 9a. The addition of 7.5 mg/g of APAM increased the tensile index significantly to 72 Nm/g while only resulting in a minor increase in density to 648 kg/m^3, indicating a significant increase in joint strength between the fibres(Lindström et al. 2005). The addition of 7.5 mg/g PECs also resulted in a large increase in the tensile index to 66 Nm/g. In Fig. 6a it is shown that this addition of PECs is only 50% of what is needed to saturate the fibres and when another 7.5 mg/g was added there was only a minor increase in tensile index to 67 Nm/g. The increased addition of PECs also decreased the density of the paper significantly (PECs 0.5x = 625 kg/m^3, PECs 1x = 612 kg/m^3, PECs 1.5x = 597 kg/m^3). This decrease in density indicates that as the surfaces are completely covered with PECs there is a decrease in joint strength between the fibres(Lindström et al. 2005). To the knowledge of the authors this has not been shown earlier and it indicates that in order to fully utilize the properties of the PECs they should be able to interact with available CS on opposing fibre surfaces in the fibre/fibre contact.

The strain at break for the different papers are shown in Fig. 9b. The reference paper had a strain at break of 2.1% and when saturated with cationic starch the strain of break increases to 3.2%. The further addition of APAM increases the strain significantly break to 5%, which is the highest of any of the papers tested and is more than double the value measured for the reference paper. The inclusion of PECs instead of APAM resulted in a strain at break of 4.6%, for all the concentrations of PECs tested. The high values in combination with an increased tensile index of the papers naturally means that the tensile energy

absorption of the papers will be significantly increase by the additives.

The charge densities of APAM and PECs are 1.1 µeq/g and 0.65 µeq/g respectively. APAM has a higher charge density and formed a paper with a higher tensile index. Whilst the charge densities of paper strength additives affect the saturation adsorption, they do not necessarily correlate with the tensile index of the paper (Zhang et al. 2000). Likewise it has previously been shown that the molecular weight of the strength additive is not crucial in determining the tensile strength of the papers they are used to form (Pelton 2004). This is supported by our findings in which the PECs have a Mw of 10^8 g/mole and the APAM has a Mw of 10^5 g/mole, but they both have similar tensile strengths. For light weight board, a good strength additive should reduce the number of joints per volume while keeping or increasing the net joint strength. Charge density and molecular weight directly influence the saturation adsorption, but they may not tell the full information of the final joint strength. The synergy between the cationic strength additives and the anionic strength additives are equally important to the final strength and the bulk of papers.

Conclusions

In this work, the importance of commonly used paper dry-additives have been investigated, due to their practical significance and large potential for developing high-end packaging products, to decrease the over-all cost and to optimize the full potential of the fibre raw materials. In the present work, cationic starch (CS), anionic polyacrylamide (APAM) and net anionically charged polyelectrolyte complexes (PECs) were adsorbed onto different types of fibres (dissolving grade, kraft and CMC modified kraft fibres) in order to compare fibres with different surface charges but with the similar morphology. It was found that a lower amount of CMC was required to induce the same relative increase in surface charge density for dissolving grade fibres as compared to kraft fibres. A linear relationship between the surface charge density of the fibres and the adsorbed amount of CS was also observed. However, the amount of APAM and PECs that could be adsorbed onto the CS pre-saturated fibres were independent of the initial fibre surface

charge. Moreover, a higher amount of PECs were adsorbed onto CS pre-treated fibres, due to its lower charge density compared to APAM. Furthermore, the results also show that APAM could only adsorb onto fibres that were saturated with CS, whereas the PECs could adsorb also onto partially CS covered fibres. In fact, the CS coverage of the fibres had a small effect on the adsorption of the PECs.

The relationship between the saturation adsorption of the additives and the mechanical properties and bulk of the papers formed from these fibres was also carefully evaluated. First of all, the adsorption of the dry strength additives on the fibres increased the tensile index of the paper; and the highest response was found from the CS/APAM combination which increased the tensile index by 60%. Regardless of the amount used, a CS/PECs combination induced a 49% increased tensile index increase, while both PECs and APAM increased the strain at break of the paper significantly (>100%). A saturation adsorption of CS, only, imparted a 33% increase in the tensile index. More importantly, it was also found that the CS/PECs combination induced a decrease in density, while CS/APAM increased the density of the paper sheets formed from kraft fibres; which is proposed to be due to their respective molecular weights. We are convinced that these findings can be utilised practically by industry to develop even more sustainable and robust paper dry-strength additives to be used for strong, lower grammage papers that can further be used to develop low-cost, light-weight packaging products.

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