Aldehyde Starch Complexes: Adsorption on Cellulose Model Film and Performance as a Strength Additive for Papermaking

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The complexes produced by mixing oppositely charged starches containing aldehyde groups (cationic aldehyde starch, CAS, and anionic aldehyde starch, AAS) were compared with complexes consisting of polyamidoamine epichlorohydrine (PAE) and AAS regarding adsorption properties and efficiency in providing paper strength. Quartz crystal microbalance with dissipation (QCM-D) studies showed that the complex of CAS and AAS adsorbed less on the model film of nanofibrillated cellulose (NFC) than CAS by itself due to the acetal and hydrogen bonds formation in the complex structure blocking available groups to be adsorbed. The wet tensile index of the paper produced with CAS-AAS complex also decreased, and this was attributed to less adsorption on the cellulose surface, as indicated by the QCM-D results. At a higher concentration, the aldehyde starch complexes provided better tensile strength than the CAS addition. The adsorbed amount of PAE-AAS complex onto cellulose model film was more than PAE. This complexation decreased PAE efficiency in giving the wet tensile strength while dry strength of the paper increased at further complex addition. Atomic force microscopy (AFM) results showed that CAS-AAS complexes filled gaps between fibrils making a more flattened layer due to the higher adsorption and bigger particle size compared to the PAE-AAS complex.

Keywords: Aldehyde starch; Polyamidoamine epichlorohydrine; Wet strength; Nanofibrillated cellulose

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INTRODUCTION

Biopolymers have gained the attention of researchers and replaced synthetic polymers in many industrial applications. Among these polymers, starch has been used increasingly in different areas, especially in the food and papermaking industries, because of its low cost, availability, and ability to change functionality for a wide range of products, as well as less environmental problems (Clerck 2009; Maurer 2009). In the paper industry, different kinds of starches are used for different purposes, such as strength enhancement of paper, retention and flocculation of fine materials, and surface sizing of papers (Maurer 2009). Starch is mainly composed of two homopolymers of glucopyranose with different structures. Amylose consists of units of D-glucose linked through α–D–(1–4) linkages; amylopectin, the branched polymer of starch, is composed of α–D–(1–4)-linked glucose segments in α–D (1–6) branches (Bertolini 2010). The modification of starches is needed for their specific applications. The cationization of starch occurs with cationic monomeric units, such as N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride, at hydroxyl groups resulting in different degree of substitutions. Cationic starches are generally used for binding fibrous materials and filler together to give sufficient retention and dry strength properties to paper (Pal *et al.* 2005).

Ionic interaction between cationic sites of starch and negative charges on the fibres and fillers is the driving mechanism during the papermaking process. Additionally, hydrogen bonding also plays a role in starch adsorption to the fibre surface (Roberts 1996). Oxidation reactions on starches are used to adjust viscosity and to give anionic and/or aldehyde functionality (Bertolini 2010). Catalysed oxidations have been used to provide better control, faster reaction, and higher selectivity. The selective oxidation of starch with periodic acid/periodate ions takes place at adjacent hydroxyl groups on the C_2-C_3 bond to form two aldehyde groups and produce a product called as dialdehyde starch (DAS) (Holik 2006). Other oxidative processes with potassium permanganate/hydrogen peroxide, dinitrogen tetraoxide, sodium chlorite/hydrogen peroxide, and sodium hypochlorite/sodium bromide have been applied to carbohydrates to create aldehyde groups (Chiu and Solarek 2009). Sodium hypochlorite (NaOCl), hydrogen peroxide (H_2O_2), and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) have been also used for DAS production with high carbonyl content. During TEMPO oxidation, nitroxyl radicals specifically convert primary hydroxyl group at the C_6 position of glucose segments to carboxyl and carbonyl groups. DAS has been used for enhancing temporary wet strength properties of tissue papers whose water resistance is needed for a short period. It has been considered for other industrial applications, such as packaging, superabsorbent, cleaning trap, drug carrier *etc.*, due to the cross-linking ability. However, the large part of DAS is consumed as a wet strength additive in the paper industry (Fiedorowicz and Para 2006; Chang *et al.* 2008; Yi *et al.* 2013). Aldehyde groups of DAS can react with hydroxyl groups of cellulose by forming hemiacetal and acetal bonds. Since cellulosic fibre has negative charges inherently, cationic aldehyde starch (CAS) is more effective due to its higher affinity to fibre. CAS is produced by the reaction of DAS with betaine hydrazide hydrochloride, resulting in anchoring quaternary ammonium groups to starch. Cimecioglu and Thomaides (2003) prepared CAS with higher carbonyl content by using TEMPO/NaBr/NaOCl meditated oxidation at a pH of 9.5. The oxidized cationic waxy maize starch was used as a temporary wet strength additive, with successful results depending amounts of aldehyde and carboxyl groups.

In papermaking, polyelectrolytes used for different purposes can be added to the fibre suspension individually, sequentially, and/or mixing with other suitable additives. Mixing oppositely charged polyelectrolytes results in polyelectrolyte complexes (PEC) and the complexation mechanism is mainly driven by an entropy increase due to the release of small ions surrounding each polyelectrolyte. Specific interactions such as hydrogen bonding, van der Waals forces, charge transfer, and hydrophobic interaction, can also occur between polyelectrolytes (Kulkarni *et al.* 2016; Thünemann *et al.* 2004). Nonstoichiometric mixing of polyelectrolytes results in cationic and/or anionic charged PECs depending on the charge ratio. The electrolyte concentration and solution pH, charge density, molecular weight, and molecular structure of the polyelectrolytes, charge ratio and concentration, and mixing method are important parameters affecting PEC properties (Dautzenberg and Rother 2003; Biesheuvel and Cohen 2004; Kovacevic *et al.* 2007; Ondaral *et al.* 2010). They have been of interest in large industrial applications such as for membranes, binders, flocculants, and coatings, as well as for different biotechnical, biomedical, and pharmaceutical applications (Fredheim and Christensen 2003; Hubbe *et al.* 2005; Malay *et al.* 2008; Mazumder *et al.* 2008; Silva *et al.* 2008).

Ankerfors *et al.* (2009) studied both PEC and polyelectrolyte multilayer (PEM) by using cationic polyallylamine hydrochloride and anionic polyacrylic acid. They reported that the tensile strength of paper reached higher levels when PEM was applied. However, PEC showed better performance than PEM at the same dosage. Johansson *et al.* (2009) studied the PEM technique based on cationic and anionic starches, and it was recorded that adhesion force between the probe and surface, which were covered by starches, was higher for PEM compared with that of the single cationic starch addition. These PEMs were also very effective in providing higher strength to paper (Lundström *et al.* 2009). Gardlund *et al.* (2003) showed that PECs prepared by mixing polyamidoamine epichlorohydrin (PAE) with carboxyl methyl cellulose (CMC) and polyallylamine chloride and polyacrylic acid (2005) provided higher wet strength to paper than the single addition of polymers.

Although there are several studies about PEC with different polyelectrolytes especially in Scandinavian countries, there has been no research on aldehyde starches. In the present study, the complexes formed by mixing CAS, prepared by oxidizing commercial cationic starch, and AAS were compared with the complexes consist of PAE and AAS. Their adsorption behaviours were studied by means of QCM-D technique having ability to detect the adsorbed mass and viscoelastic properties of polymeric layer built on the model film composed of nanofibrillated cellulose (NFC). Additionally, efficiencies of complexes in providing paper with wet and dry strength properties were also investigated.

EXPERIMENTAL

Materials

Polyamidoamine epichlorohydrine (PAE) with a brand name of PWS125, which is used for giving permanent wet strength to paper, was kindly supplied by Setaş Chemical Co., Tekirdağ, Turkey. PAE had the following properties: 0.80 meq/g charge density, 13.92 mg KOH/g acid value, 1.085 mg HCl/g amine value, and 22 cP viscosity at a 12.5% solids content. The cationic starch (Pencat 700) and anionic aldehyde starch (AAS) were provided by Penford Products Co., Colorado, USA and Solam Gmbh, Nordhorn, Germany, respectively. The bleached Mg bisulphite pulp from Biocel Paskov a.s. was used for NFC production. The bleached softwood kraft pulp, which is used for tissue papers mixing with bleached hardwood kraft pulp, was used to manufacture test papers. Polyethylene imine having 750.000 g/mol of average molecular weight was purchased from Sigma Aldrich. Other chemicals were purchased from Merck (Darmstadt, Germany).

Methods

Preparation of cationic aldehyde starch (CAS)

CAS was produced by the modification of cationic starch with TEMPO/NaBr/NaClO oxidation (Cimecioğlu and Thomaides 2003). Before oxidation, 35 g of cationic starch was gelatinized by exposing it to steam under vigorous mixing for 30 min and cooled to room temperature. TEMPO (0.1% based on moles of anydroglucose) and NaBr (10% mole) were added to the starch solution and mixed while being cooled to 5 ± 1 °C in an ice bath. The pH was adjusted to 9.5 by adding 0.1 M NaOH and sodium hypochlorite (30% mole based on moles of starch ASU) to the solution dropwise keeping the temperature below 15 °C. When the pH was stable after addition of hypochlorite solution, oxidation was completed by adding 25 mL of ethyl alcohol to consume all hypochlorite. The pH of the solution was reduced to 4.8 by adding 0.1 M HCl. The modified starch was precipitated with ethyl alcohol and filtered with a coarse filter paper through a Buchner funnel. The starch was then dried at room temperature and stored inside a plastic bag. The aldehyde and carboxyl contents were determined to be 0.5 mmol/g and 0.1 mmol/g, respectively (Saito *et al.* 2007; Sirvio *et al.* 2011).

Complex preparation

Complexes were produced by adding the AAS to the cationic CAS or to the PAE using a peristaltic pump at 50 mL/min dosage rate while the solution was being mixed with a mechanical stirrer at 750 rpm. The complexes were produced at different charge ratios, which was calculated as dividing the anionic charge concentration by the cationic charge concentration (q-/q+).

Adsorption on model cellulose film

Adsorption properties of complexes, CAS, and PAE were investigated using cellulose model film. NFC was used to prepare model cellulose film on the silicon oxide crystal used in Quartz Crystal Microbalance with Dissipation (QCM-D) experiments. The NFC was prepared from Mg-bisulphite pulp (dissolving pulp) with using TEMPO/NaBr/NaClO oxidation according to a procedure reported in a study of Saito and Isogai (2006). This dissolving pulp with minimal hemicellulose content is the most suitable resource to produce nano-scaled cellulose materials, however, there is no limitation to use any kind of pulp. The mole of COOH of NFC was determined as 1.5 mmol/g (Saito *et al.* 2007). The cellulose film was built on the crystal surface with a spin coater. Before using the SiO_2 crystal, it was treated with piranha cleaning solution (H_2SO_4:H_2O_2 = 3:1) for 1 min. It was rinsed with Millipore quality water and dried with N_2 gas. The cleaned QCM-D crystal was dipped in a solution of 1% polyethyleneimine for 5 min, rinsed with de-ionized water and dried with N_2 gas. The NFC suspension (0.2%) was dropped on the cationically modified surface of the crystal mounted on a chuck of the spin coater. Once NFC was dropped to the surface, the crystal started to spin at 3500 rpm for 1 min. The film was cured in an oven for 4 hours at 105 °C.

QCM-D is a unique technique for monitoring adsorption and film properties, giving frequency and dissipation data. The resonant frequency of the crystal is decreased as the adsorbed mass, Δm, is increased. If the adsorbed mass is evenly distributed, rigidly attached and small compared to the mass of the crystal, the change in the frequency (Δf) is related to the adsorbed mass per unit surface, Δm, by the Sauerbrey equation (Sauerbrey 1959), which is shown in Eq. 1,

$$\Delta m = - C\Delta f/n \qquad (1)$$

where n is an overtone number, C is a constant that describes the sensitivity of the device to changes in mass, and 0.177 mg m^{-2} for the AT-cut 5 MHz crystals used in this study.

When the driving power to the crystal is switched off, there is a decay in the oscillation due to frictional losses in the crystal in the adsorbed layer and in the surrounding solution. The energy dissipation is characterized by dissipation factor D (Höök *et al.* 1998), which is shown in Eq. 2,

$$\mathrm{D} = \mathrm{E}'/2\pi\mathrm{E} \qquad (2)$$

where E' is the energy dissipated during one oscillation and E is the total energy stored in the quartz oscillator.

After mounting the crystal, on which the NFC film was built, in the QCM cell, it was exposed to an aqueous buffer solution containing the same salt concentration (100 mM NaCl) and pH as used for the preparation of the complex or polymer solution to ensure a stable baseline for the frequency and energy dissipation. The adsorption experiments were then started by exchanging the buffer with the polymer solution. Residual polymer was removed after 30 min. by the addition of the aqueous buffer solution. Qsoft software (Q-Sense AB, Västra Frölunda, Sweden) was utilized to record the changes in the properties of the adsorbed polymer layer at four different overtones during the adsorption process. Of these, the third overtone data was used for evaluation due to its stability. The concentration of the polymer solution was 100 mg l^{-1} in all experiments. All QCM-D experiments were conducted at a constant temperature of 24.0 °C.

Surface imaging

The surface change of the model cellulose surface after polymer adsorption was studied by means of atomic force microscopy with the tapping mode (Nanoscope IV, Multimode SPM, Veeco Inc., Santa Barbara, CA, USA). All experiments in which standard rectangular non-contact silicon cantilevers (RTESP, Veeco Probe Centre Inc., Santa Barbara, CA, USA) were used were conducted under ambient conditions (23 °C and 50% relative humidity).

Determination of charge density

The charge density of starches and PAE was determined with a streaming current detector (PCD III MÜTEK GmbH, Herrsching, Germany) by polyelectrolyte titration. The volume of polyelectrolyte consumed for 0 mV of streaming potential of the samples was used to calculate the charge density. The charge density (q) was calculated by following equation:

$$q = \frac{V.n}{m} \tag{3}$$

where V is the volume of polyelectrolyte titrant (mL), n is titrant concentration (eq/ml), m is amount of polymer or aqueous sample (g or mL). Charge densities of polymer and suspension were calculated in meq/g and meq/mL units, respectively. P-DADMAC and polyethylenesulphonate sodium salt (PES-Na) purchased from MÜTEK GmbH were used as a cationic titrant and an anionic titrant, respectively (Suty and Luzakova 1998).

Determination of aldehyde content

The 30 mL of NFC suspension (0.1%) was disintegrated and its pH was set to 4.5 using 0.5 N HCl. Hydroxyl amine hydrochloride (20 mL) was added to NFC solution and reaction was continued for a day. The pH of hydroxyl amine hydrochloride was adjusted to 4.5 before addition. NFC slurry was titrated by 0.1 N of NaOH until pH was stabilized at 4.5. Aldehyde content was calculated according to Eq. 4,

$$\text{Aldehyde content (mmol/g)} = V.N/w \tag{4}$$

where V is the consumed NaOH amount during titration (mL), N is the normality of NaOH (mol/L), and w is the dry basis mass of NFC (g) (Sirvio *et al.* 2011).

Determination of carboxyl content

The amount of carboxyl groups was determined by conductometric titration. NFC (0.1 g) was disintegrated in 250 mL deionized water, and 15 mL of 0.01 M HCl was added to suspension. After mixing for 10 min., NFC suspension was titrated with 0.1 M NaOH. The carboxyl content was determined from titration curves using Eq. 5,

$$\text{Carboxyl content (mmol/g)} = V.N/w \tag{5}$$

where V is consumed NaOH amount during titration (mL), N is normality of NaOH (mol/L), and w is dry basis of NFC (g) (Saito *et al.* 2007).

Complex size

The average size of the complex particles were determined with Dynamic Light Scattering (DLS) using a Zetasizer Nano ZS particle characterization system (Malvern Instruments Ltd, Worcester, UK).

Molecular weight

The molecular weights of the starches were determined using a Ubbelohde capillary viscometer at 25 °C. Samples with different concentrations were prepared in 1 M KOH. Specific viscosity was calculated by using the drain time of the sample and solvent using. Average molecular weight M_w was calculated from intrinsic viscosity $[\eta]$ using the Mark-Houwink equation (Eq. 3),

$$[\eta] = \mathrm{KM_W}^{\mathrm{a}} \tag{3}$$

where K and a were used as 1.18 10^{-5} dl/g and 0.89 for all measurements, respectively (Ahmad *et al.* 1999).

FTIR spectrum

The chemical structures of starches were evaluated with a Perkin Elmer spectrophotometer (Spectrum One FT-IR, MA, USA) equipped with UATR. Scans (16 scans in point) were performed in the spectral range of 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. The results were collected and treated with Spectrum One software (Spectrum One, version 5.3, MA, USA).

Handsheet preparation and tensile strength measurement

The unbeaten softwood kraft pulp was diluted to 0.5% consistency and after adjusting pH to 7.0 ± 0.3, the chemical additive (PAE, cationic starch or complexes) at different ratios, between 0 and 50 mg/g based on dry fiber, was added to the fiber suspension. After 10 min of mixing at 750 rpm, 400 mL of suspension was used to obtain a handsheet on a Rapid Köthen sheet former (Mülheim an der Ruhr, Germany) according to TAPPI T205 sp-02 (2006). The formed wet sheet was dried at 93 °C at a pressure of 90 kP for 10 min. The tensile strength of paper in both dry and wet form were measured on a Zwick Z2.5 Model Universal device, according to TAPPI T494 om-01 (2006) and TAPPI T456 om-10 (2010) standards, respectively.

RESULTS AND DISCUSSION

Properties of Starches and their Complexes

Because of selective oxidation with TEMPO/NaBr/NaClO, the carbonyl and carboxyl groups are expected to be introduced to C_6 of glucopyranosyl units. It was targeted to produce higher aldehyde functionality with lower carboxyl groups to provide a starch with the properties of a wet strength additive. After oxidation, the content of the aldehyde and carboxyl groups were determined as 0.5 mmol/g and 0.1 mmol/g, respectively. This oxidation resulted in a viscosity decrease due to the disruption of the α-D-(1-4) and α-D-(1-6) glycosidic bonds, as well as converting primary hydroxyls to carbonyl groups. As shown in Table 1, parallel to knowledge stated above, the molecular weight and cationic charge density decreased significantly. In addition to breaking linkages and removing molecules becoming smaller by the cleaning procedure after oxidation, the generation of carboxyl groups also caused a decrease in the total cationic charge amount of starch. Figure 1 shows characteristic peaks in the FTIR spectrum of the different starches. The bands at 1732 cm^{-1} indicated vibrations due to the stretching vibrations of C-H and C=O in the -CHO group. The band at 1640 cm^{-1} was assigned to the aldehyde and carboxyl group of starch. These two peaks appeared after oxidation of cationic starch. The peak of C-C bonds in –CHO group appeared at 1336 cm^{-1}. The peak at 2930 cm^{-1} was attributed to C-H stretches associated with hydrogen atoms of the aldehyde group and CH_2. The bands at 1080 cm^{-1} and 1150 cm^{-1} were ascribed to C-O bond stretching of the C-OH group, which indicates a breakage of the glycosidic bonds and thus, resulted in a decrease in molecular weight (Chang *et al.* 2010; Zhang *et al.* 2004).

Table 1. Charge Density, Intrinsic Viscosity, and Molecular Weight of PAE, Cationic Starch, CAS, and AAS

Polymer	Charge Density (meq/g)	$[\eta]$ (dL/g)	M_w (kDa)
Cationic starch	+0.77	1.65	604.7
CAS	+0.44	0.04	9.4
AAS	-0.50	0.09	23.8
PAE	+0.80	ND	ND
ND: Not determined			

Different cationic complexes were produced by mixing AAS with CAS or AAS with PAE at different charge ratios (q-/q+) ranging from 0.4 to 1.2. The complex concentrations and addition rate (or dosage rate) were adjusted to 0.5 g/L and 50 mL/min, respectively.

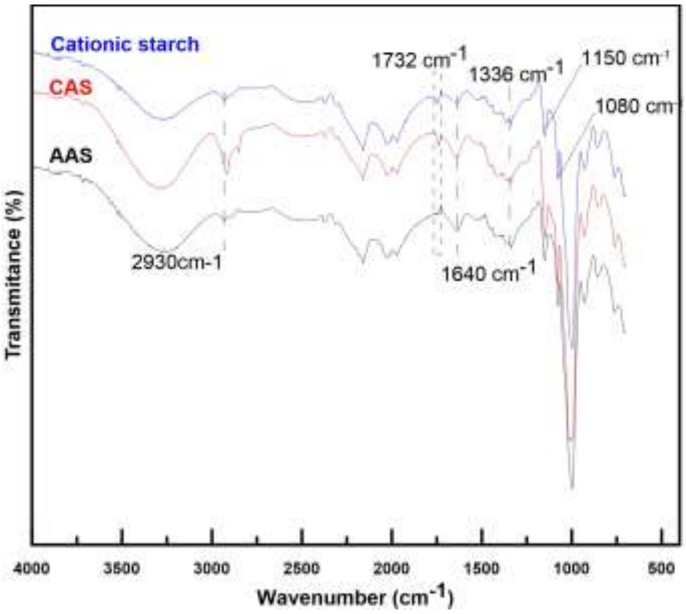

Fig. 1. FTIR spectra for cationic starch, CAS, and AAS

Figure 2a and 2b show size and charge density of complexes at different charge ratios. Complexes of CAS and AAS exhibited larger size than those of the PAE and AAS couple. Due to lower charge density of CAS, its complexes with AAS resulted in a bigger size. The helical and branched structure of starch molecules also play a role in the complex size. As seen in Fig. 2b, PECs produced at 1 charge ratio (q-/q+) had “0 meq/g” charge density due to the 1:1 stoichiometric coupling. With approximately 1:1 mixing, there was no macroscopic aggregation (Fig. 2a). In comparison to the PAE complexes produced with CMC (Gardlund *et al.* 2003), the complex sizes were stable and in the same size range. Because AAS was added slowly (50 ml/min) to the cationic polymer (CAS or PAE) during complex production, the excess cationic charge was always present until the complex solution reached a 1:1 charge ratio. Complex particles are produced during the initial addition of anionic starch and strongly stabilized with cationic charges. Most likely, complexation at further AAS addition could not result in particle formation as much as the initial mixing. The production parameters and properties of complexes used in adsorption experiments and paper tests are shown in Table 2.

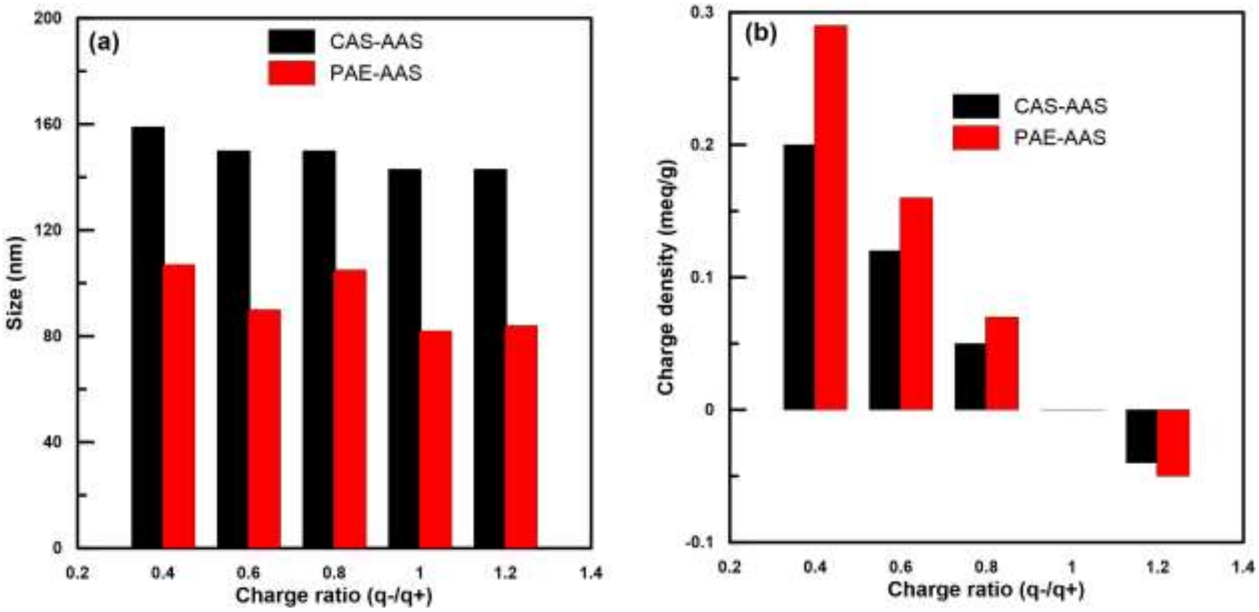

Fig. 2. Complex size (a) and charge density (b) as a function of charge ratios

Table 2. The Production Parameters and Properties of Complexes

Complexes	Cat. PE	An. PE	q^-/q^+	Dosage rate (mL/min)	Mix. rate (rpm)	Con. (g/L)	Av. Size (nm)	Charge density (meq/g)
SC1	CAS	AAS	0.4	50	750	0.5	159	0.20
SC2	CAS	AAS	0.8	50	750	0.5	150	0.05
PC1	PAE	AAS	0.4	50	750	0.5	107	0.25
PC2	PAE	AAS	0.8	50	750	0.5	105	0.08

SC, starch complex; PC, polymer complex; PE, polyelectrolyte

Adsorption on cellulose model film

The adsorption properties of CAS, PAE, and their complexes with AAS on cellulose model film prepared from NFC were studied by QCM-D. The data from these experiments give important information about polymer adsorption and the polymer layer on the surface. Frequency change due to the material adsorption onto the crystal sensor can be converted to the adsorbed amount of polymer according to the Sauerbrey equation. In Fig. 3a, adsorbed amount of CAS was higher than that of its complex (SC1). This was an unexpected result because polyelectrolytes with lower cationic charge density is adsorbed to an anionic surface more than the polyelectrolyte with higher charge density due to the 1:1 stoichiometric interaction. Differently from cationic starch, aldehyde starch can participate in the building of hemiacetal and acetal bonds between aldehyde groups and hydroxyl groups (Espy 1995). In the case of aldehyde groups on both oppositely charged starches, homo-crosslinking take place during complex formation and thus, the number of available hydroxyl and aldehyde groups decrease. Because electrostatic interactions and hydrogen bonding play roles during adsorption of cationic starch, a decrease in the number of free aldehyde and hydroxyl group caused to less adsorption to surface. As shown in the dissipation figure, CAS formed a thicker and softer layer than SC1. Although the complex adsorption was 2.5 times less than CAS adsorption, the difference in energy dissipation was not much as adsorption. This result suggests that the complex had a larger size and bound more water in the surrounding layer.

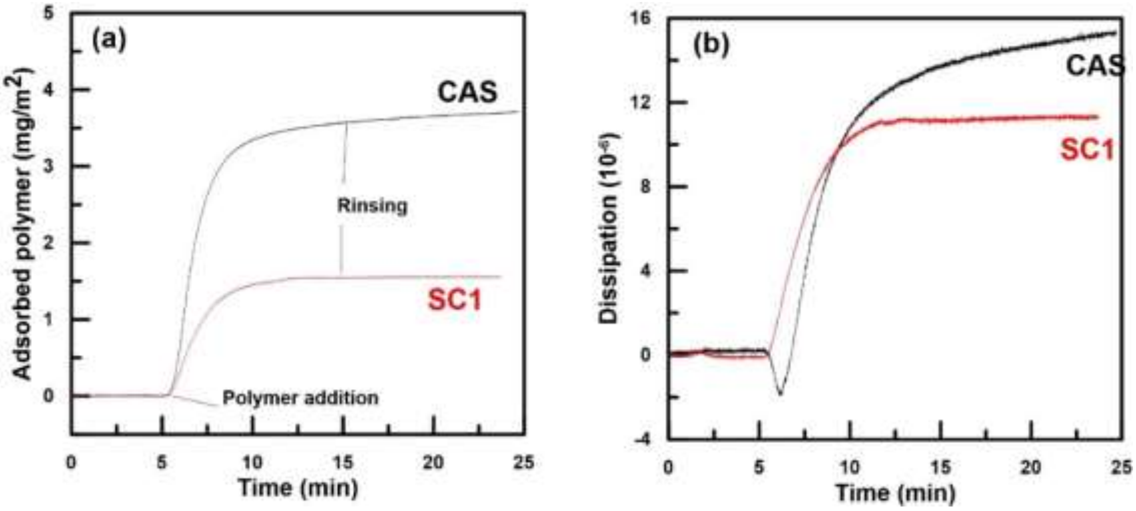

Fig. 3. Adsorption of CAS and its complex (SC1) on NFC model film studied by QCM-D (a: Adsorbed polymer and b: Dissipation value)

Figure 4 shows the adsorbed mass and dissipation value of PAE and its complex (PC1) on cellulose model film. As shown in Fig. 4a, the adsorbed amount of PAE was less than that of its complex because PAE has a higher charge density. The azetidinium groups formed by linking epichlorohydrine to polyamidoamine backbone gives cationic charges (Espy 1995). The complexation reaction takes place between these cationic groups and carboxylic acid groups of AAS. In addition to electrostatic interaction, acetal bonds between aldehyde groups and hydroxyl groups, as well as amidol bonds between oxygen and amines promote interaction through the starch/PAE and NFC network. The dissipation value of PC1 layer was higher because the bigger complex size and higher water interaction, especially with the presence of hydroxyl and aldehyde groups on starch.

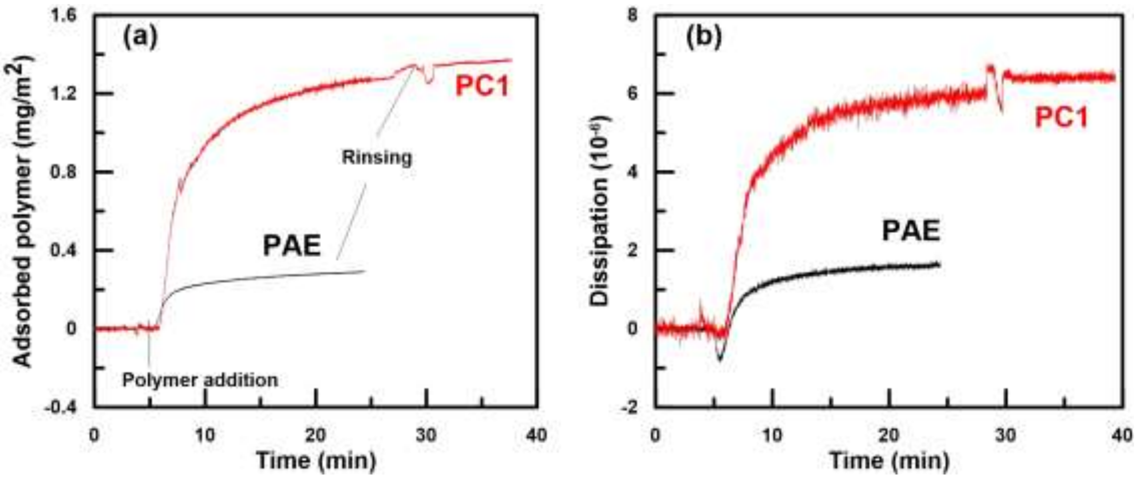

Fig. 4. Adsorption of PAE and its complex (PC1) on NFC model film studied by QCM-D (a: Adsorbed polymer and b: Dissipation value)

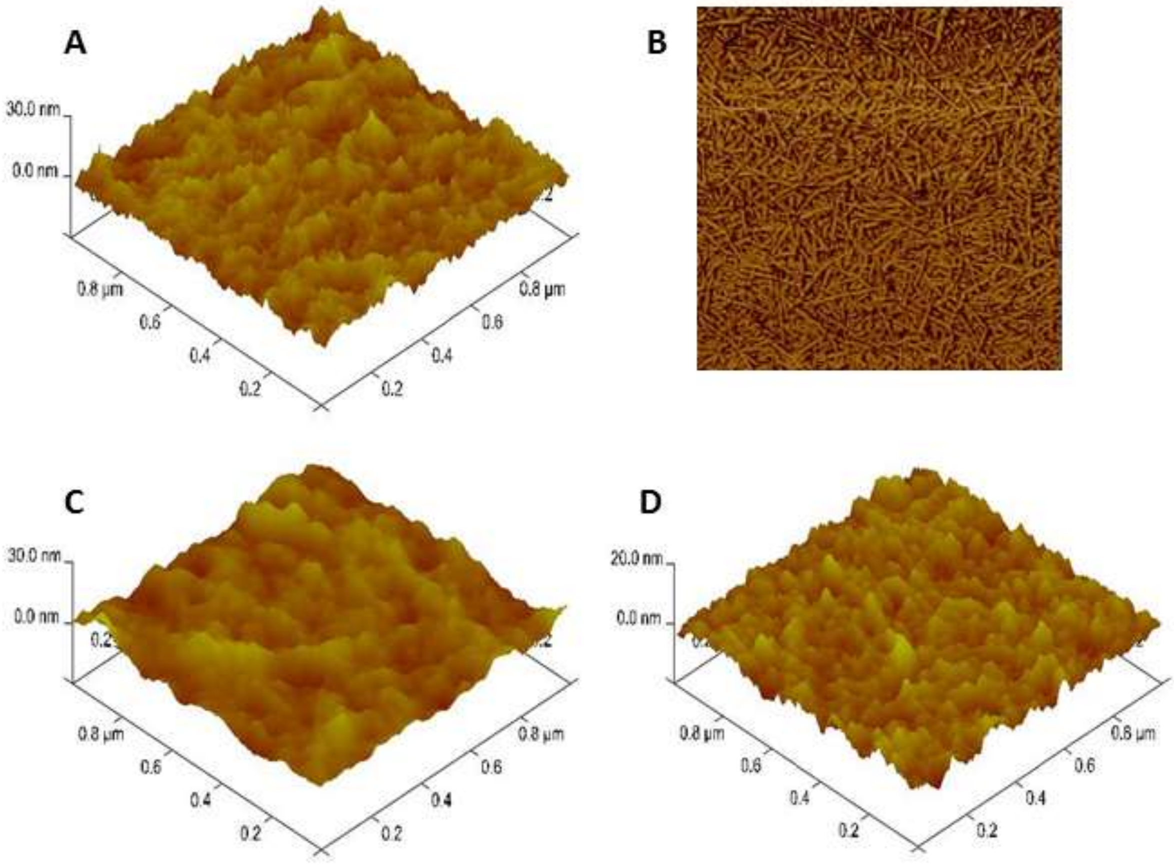

Fig. 5. AFM images of NFC surface before and after complex adsorption (A: NFC surface height mode 3D image, B: NFC phase mode, C and D: After adsorption of complexes SC1 and PC1, respectively)

It is clear from the AFM image (Fig. 5c) that the complex of CAS and AAS (SC1) filled the gaps on the NFC layer and made the surface flatten, as can be seen in Fig. 5a and 5b. However, the complex of PAE and AAS (PC1), which had a smaller size, could not fill the gaps between fibrils as much as SC1 (Fig. 5d).

Strength improvement of paper

Figure 6 shows the efficiency of cationic aldehyde starch and its complexes with AAS in both dry and wet strength of paper. The initial positive change of dry tensile strength due to the CAS addition was higher than its complexes (SC1 and SC2), as can be seen in Fig. 6a. However, complexes became more effective after 3 mg/g due to higher adsorption on the fibre surface. The initial dry strength change was parallel to the QCM-D results, which showed higher CAS adsorption compared to its complex. Higher adsorption could provide more hydrogen and acetal bonds addition to electrostatic interaction between fibres. Starch molecules adsorbed on fibre surfaces, binding them together like cement and thus, the dry strength of paper was enhanced *via* increasing molecular bonding area and bond number at fibre/fibre contact points (Robert 2004). By adding aldehyde functional groups to a glucose unit, starch also enhances the wet strength of paper (Espy 1995). The complex of cationic and anionic polyelectrolytes enhances dry strength better than single addition and layer-by-layer addition of the same polyelectrolytes at the same polymer addition (Ankerfors *et al.* 2009).

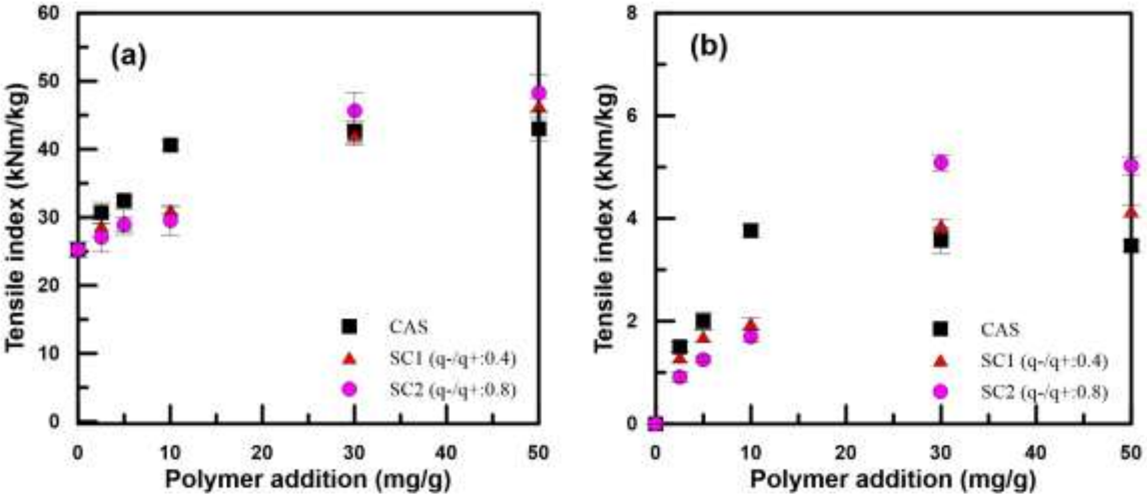

Fig. 6. Dry (a) and wet strength (b) improvement of paper depending on addition amount of CAS and its complexes with AAS

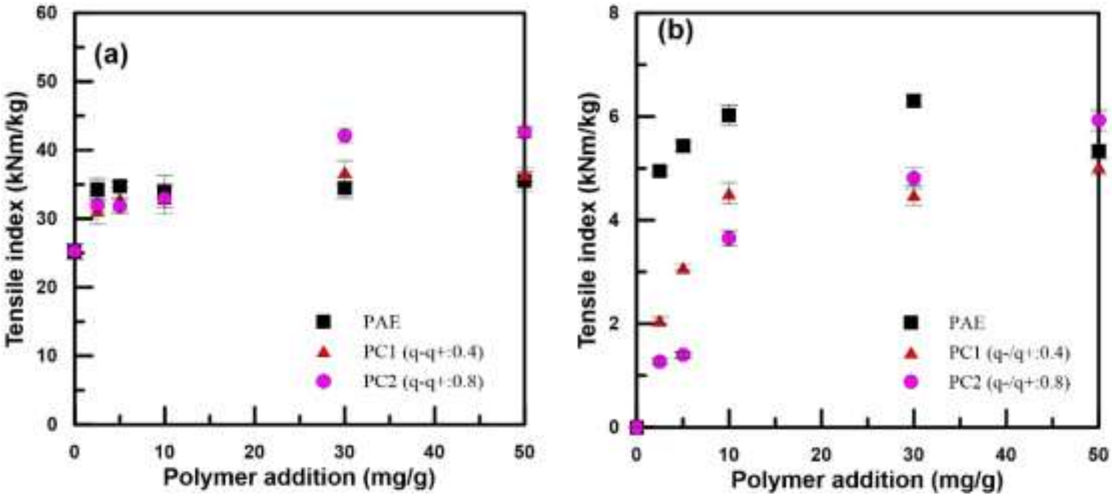

Fig. 7. Dry (a) and wet strength (b) improvement of paper depending on addition amount of PAE and its complexes with AAS

When the paper produced without a wet strength additive was soaked in water, it lost its strength. On this basis, it had a shear-sensitive network. Temporary wet strength polymers, such as aldehyde starch and glyoxylated cationic polyacrylamide, provide enough strength to paper for the initial exposure to water because of acetal and amidol bonds in the fibre network and a self-crosslinking mechanism (Espy 1995). As shown in Fig. 6b, CAS increased wet strength to 3.8 kNm/kg, *i.e.*, 9.5% relative increase for wet strength, which is enough to provide temporary wet strength for toilet papers. Once polymer addition increased to 30 mg/g, complexes gave better performance. SC2 (0.8 charge ratio) improved wet strength better than SC1 (0.4 charge ratio). An increase in charge ratio (0.4 to 0.8) means that the amount of AAS in the complex production doubled. This causes a decrease in charge density resulting in decreasing adsorption.

It is clear in Fig. 7a that single PAE addition to the paper provided about 35 kNm/kg dry tensile index, which was less than CAS performance. However, PAE gave higher wet strength to paper, as can be seen in Fig. 7b. As mentioned before, PAE has a different chemical structure and groups, especially azetidinium groups, which can bind to the carboxyl group of cellulose with covalent bonds and making a stronger fibre-fibre network (Roberts 1996). This also contributed to the dry strength of paper, but its complex with aldehyde starches increased dry strength more due to the formation of acetal/amidol bonds. However, dry tensile index increased at higher polymer concentrations, *i.e.*, higher AAS addition. The wet strength of paper decreased when the PAE/starch complex was used. Even if PAE has been used highly effective for enhancing wet strength of tissue papers for more than half a century, more re-pulpable paper that has a relatively lower wet strength can be produced by using the complex of PAE and AAS.

CONCLUSIONS

1. The cationic aldehyde starch (CAS), polyamidoamine epichlorohydrine (PAE), and their complexes with anionic aldehyde starch (AAS) were compared regarding the adsorption behaviour and performance as a strength enhancer for paper. QCM-D results showed that CAS adsorption on NFC film was higher than its complex with a 0.4 charge ratio (q-/q+), while PAE adsorption was lower than its complex. This decrease for the CAS-AAS complex was attributed to decrease in available hydroxyl and carbonyl groups, which were able on cellulose by hydrogen and acetal bonds.
2. The tensile index of paper containing was lower when the starch complexes was added at a low concentration. When more starch complex was added to the fibre suspension, its performance exceeded CAS’s performance.
3. The PAE-AAS complex gave better performance in dry tensile index only at higher concentrations, and complexation with AAS caused a reduction in PAE efficiency in wet tensile index.
4. CAS complex had higher performance in improving dry strength compared to PAE complex and gave moderate wet strength, which was less than PAE performance.

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REFERENCES CITED

Ahmad, F. B., Williams, P. A., Doublier, J. L., Durand, S., and Buleon, A. (1999). "Physico-chemical characterisation of sago starch," *Carbohydrate Polymers* 38(4), 361-370. DOI: 10.1016/S0144-8617(98)00123-4

Ankerfors, C., Lingström, R., Wagberg, L., and Ödberg, L. (2009). "A comparison of polyelectrolyte complexes and multilayers: Their adsorption behaviour and use for enhancing tensile strength of paper," *Nordic Pulp & Paper Research Journal* 24(1), 77-86. DOI: 10.3183/NPPRJ-2009-24-01-p077-086

Bertolini, A. C. (2010). *Starches-Characterization, Properties and Applications,* Taylor & Francis, Abingdon, UK.

Biesheuvel, P. M. and Cohen, M. A. (2004). "Electrostatic free energy of weakly charged macromolecules in solution and intermacromolecular complexes consisting of oppositely charged polymers," *Langmuir* 20(7), 2785-2791. DOI: 10.1021/la036204l

Chang, P. S., Park, K. O., Shin, H. K., Suh, D. S., and Kim, K. O. (2008). "Physicochemical properties of partially oxidized corn starch from bromide-free TEMPO-mediated reaction," *Journal of Food Science* C173, 73. DOI: 10.1111/j.1750-3841.2008.00682.x

Chang, P. R., Jian, R., Zheng, P., Yu, J., and Ma, X. (2010). "Preparation and properties of glycerol plasticized-starch (GPS)/cellulose nanoparticle (CN) composites," *Carbohydrate Polymers* 79(2), 301-305. DOI: 10.1016/j.carbpol.2009.08.007

Chiu, C., and Solarek, D. (2009). *Starch: Chemistry and Technology,* J. B. Miller and R. Whistler (eds.), Academic Press, Elsevier, USA.

Cimecioglu, A. L., and Thomaides, J. S. (2003). "Polysaccharide aldehydes prepared by oxidation method and used strength additives in papermaking," United States Patent 6586588.

Clerck, P. D. (2009). *Applications of Wet-End Paper Chemistry,* I. Thorn and C.O. Au (eds.), Springer, Netherlands.

Dautzenberg, H. and Rother, G. (2003). "Response of polyelectrolyte complexes to subsequent addition of sodium chloride: Time-dependent static light scattering studies," *Macromolecular Chemistry and Physics* 205(1), 114-121. DOI: 10.1002/macp.200350083

Espy, H. H. (1995). "The mechanism of wet-strength development in paper: A review," *Tappi Journals* 78(4), 90.

Fiedorowicz, M. and Para, A. (2006). "Structural and molecular properties of dialdehyde starch," *Carbohydrate Polymers* 63(3), 360-366. DOI: 10.1016/j.carbpol.2005.08.054

Fredheim, G. E. and Christensen, B. E. (2003). "Polyelectrolyte complexes: Interactions between lignosulfonate and chitosan," *Biomacromolecules* 4(2), 232-239. DOI: 10.1021/bm020091n

Gardlund, L., Wagberg, L., and Gernandt, R. (2003). "Polyelectrolyte complexes for surface modification of wood fibres: II. Influence of complexes on wet and dry strength of paper," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 218(1-3), 137-149. DOI: 10.1016/S0927-7757(02)00588-5

Gardlund, L., Forrsström, J., Andreasson, B., and Wagberg, L. (2005). "Influence of polyelectrolyte complexes on strength properties of papers made from unbleached kraft pulps with different yields," *Nordic Pulp & Paper Research Journal* 20(1), 36-42. DOI: 10.3183/NPPRJ-2005-20-01-p036-042

Holik, H. (2006). *Handbook of Paper and Board,* Wiley-Vch Verlag GmbH & Co. KGaA, Weinheim, Germany.

Höök, F., Rodahl, M., Brzezinski, P., and Kasemo, B. (1998). "Energy dissipation kinetics for protein and antibody-antigen adsorption under shear oscillation on a quartz crystal microbalance," *Langmuir* 14(4), 729-734. DOI: 10.1021/la970815u

Hubbe, M. A., Moore, S. M., and Lee, S. Y. (2005). "Effects of charge ratios and cationic polymer nature on polyelectrolyte complex deposition onto cellulose," *Industrial and*

Engineering Chemistry 44(9), 3068-3074. DOI: 10.1021/ie048902m

Johansson, E., Lundström, L., Norgren, M., and Wågberg, L. (2009). "Adsorption behavior and adhesive properties of biopolyelectrolyte multilayers formed from cationic and anionic starch," *Biomacromolecules* 10(7), 1768-1776. DOI: 10.1021/bm900191s

Kovacevic, D., Borkovic, S., and Pozar, J. (2007). "The influence of ionic strength, electrolyte type and preparation procedure on formation of weak polyelectrolyte complexes," *Colloid and Surfaces A* 302(1-3), 107-112. DOI: 10.1016/j.colsurfa.2007.02.007

Kulkarni, A. D., Vanjari, Y. H., Sancheti, K. H., Patel, H. M., Belgamwar, V. S., Surana, S. J., *et al.* (2016). "Polyelectrolyte complexes: mechanisms, critical experimental aspects, and applications," *Artificial Cells, Nanomedicine, and Biotechnology An International Journal* 44(7), 1615-1625. DOI: 10.3109/21691401.2015.1129624

Lundström, L., Lindgren, J., Svensson, E., Sennerfors, E., and Wågberg, L. (2009). "The adsorption of polyelectrolyte multilayers (PEM) of starch on mechanical pulps for improved mechanical paper properties," *Nordic Pulp & Paper Research Journal* 24(4), 459-468. DOI: 10.3183/NPPRJ-2009-24-04-p459-468

Malay, Ö., Yalçın, D., Batıgün, A., and Bayraktar, O. (2008). "Characterization of silk fibroin/hyaluronic acid polyelectrolyte complex (PEC) films," *Journal of Thermal Analysis and Calorimetry* 94(3), 749-755. DOI: 10.1007/s10973-008-9368-5

Maurer, H. W. (2009). *Starch: Chemistry and Technology*, J. B. Miller and R. Whistler (eds.), Academic Press, Elsevier, USA.

Mazumder, M. A. J., Shen, F., Burke, N. A. D., Potter, M. A., and Stöver, H. (2008). "Self-cross-linking polyelectrolyte complexes for therapeutic cell encapsulation," *Biomacromolecules* 9(9), 2292-2300. DOI: 10.1021/bm800580c

Ondaral, S., Ankerfors, C., Ödberg, L., and Wågberg, L. (2010). "Surface-induced rearrangement of polyelectrolyte complexes: Influence of complex composition on adsorbed layer properties," *Langmuir* 26(18), 14606-14614. DOI: 10.1021/la1022054

Pal, S., Mal, D., and Singh, R. P. (2005). "Cationic starch: An effective flocculating agent," *Carbohydrate Polymers* 59(4), 417-423. DOI: 10.1016/j.carbpol.2004.06.047

Roberts, J. C. (1996). *The Chemistry of Paper*, The Royal Society of Chemistry, United Kingdom.

Robert, P. (2004). "On the design of polymers for increased paper dry strength - A review," *Appita Journal: Journal of the Technical Association of the Australian and New Zealand Pulp and Paper Industry* 57(3), 181-190.

Saito, T., and Isogai, A. (2006). "Introduction of aldehyde groups on surfaces of native cellulose fibers by TEMPO-mediated oxidation," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 289(1-3), 219-225. DOI: 10.1016/j.colsurfa.2006.04.038

Saito, T., Kimura, S., Nishiyama, Y., and Isogai, A. (2007). "Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose," *Biomacromolecules* 8(8), 2485-2491. DOI: 10.1021/bm0703970

Sauerbery, G. (1959). "Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung," *Zeitschrift für Physik* 155(2), 206-222. DOI: 10.1007/BF01337937

Silva, C. L., Pereira, J. C., Ramalho, A., Pais, A. A. C. C., and Sousa, J. J. S. (2008). "Films based on chitosan polyelectrolyte complexes for skin drug delivery: Development and characterization," *Journal of Membrane Science* 320(1-2), 268-279. DOI: 10.1016/j.memsci.2008.04.011

Sirvio, J., Hyvakko, U., Liimatainen, H., Niinimaki, J., and Hormi, O. (2011). "Periodate oxidation of cellulose at elevated temperatures using metal salts as cellulose activators," *Carbohydrate Polymers* 83(3), 1293-1297. DOI: 10.1016/S0927-7757(98)00322-7

Suty, S., and Luzakova, V. (1998). "Role of surface charge in deposition of filler particles onto pulp fibres," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 139(3), 271-278. DOI: 10.1016/S0927-7757(98)00322-7

TAPPI T205 sp-02 (2006). “Forming handsheets for physical tests of pulp,” TAPPI Press, Atlanta, GA.

TAPPI T494 om-01 (2006). “Tensile properties of paper and paperboard,” TAPPI Press, Atlanta, GA.

TAPPI T456 om-10 (2010). “Tensile breaking strength of water-saturated paper and paperboard (“wet tensile strength”),” TAPPI Press, Atlanta, GA.

Thünemann, A. F., Müller, M., Dautzenberg, H., Joanny, J. F., and Löwen, H. (2004). *Polyelectrolytes with Defined Molecular Architecture II*, M. Schmidt (ed.), Springer-Verlag, Germany.

Yi, X. Zhang, S., and Ju, B. (2013). “Preparation of water-soluble oxidized starch with high carbonyl content by sodium hypochlorite,” *Starch* 66(1-2), 115-123. DOI: 10.1002/star.201300037

Zhang, X., Shi, F., Yu, X., Liu, H., Fu, Y. *et al.* (2004). “Polyelectrolyte multilayer as matrix for electrochemical deposition of gold clusters: Toward super-hydrophobic surface,” *Journal of American Chemical Society* 126(10), 3064-3065. DOI: 10.1021/ja0398722

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