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Towards a super-strainable paper using the Layer-by-Layer technique

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ABSTRACT

The Layer-by-Layer technique was used to build a polyelectrolyte multilayer on the surface of pulp fibres. The treated fibres were then used to prepare paper sheets and the mechanical properties of these sheets were evaluated as a function of the number of bi-layers on the fibres. Two different systems were studied: polyethyleneimine (PEI)/nanofibrillated cellulose (NFC), and polyallylamine hydrochloride (PAH)/hyaluronic acid (HA). Model experiments using dual polarization interferometry and SiO_2 surfaces showed that the two systems gave different thicknesses for a given number of layers. The outer layer was found to be a key parameter in the PEI/NFC system, whereas it was less important in the PAH/HA system. The mechanical properties of the sheets made from the PAH/HA treated fibres were significantly greater than those made from untreated fibres, reaching 70 Nm/g in tensile index and 6.5% in strain at break. Such a modification could be very useful for 3D forming of paper, opening new perspectives in for example the packaging industry, with a renewable and biodegradable product as a potential substitute for some of the traditional oil-based plastics.

1. Introduction

The depletion of petroleum resources has led to a greater environmental awareness, giving rise to a significant amount of research aimed at finding alternatives to oil-based products. Due to their low cost, good barrier properties and shaping ability, petroleum-based polymers such as polyethylene (PE) or polypropylene (PP) have been widely used in the packaging industry. Nevertheless, in addition to being produced from non-renewable resources, these polymers are not biodegradable. A plausible and interesting bio-based alternative to these oil-based products could be specially treated paper. However, although it is widely used in packaging materials, paper cannot be used to form stable 3D-structures to the same extent as PP or PE since the stretch at break of regular papers is below 5%, in addition to the fact that regular paper has unacceptable barrier properties. Therefore it is necessary to make paper more extensible to compete with plastics in the packaging industry. The notion of a stretchable paper is not new: already in the late nineteenth century, before the development of plastics, sizing was invented and developed as a possible way to increase paper stretchability (Nonnenmacher, 1898). Later, throughout the twentieth century, many technologies aiming at obtaining a stretchable paper were patented: for example, fluting rolls were used to modify the structure of the paper web (Sherman, 1941). Another technology was the doctor blade, which led to a wrinkling of the paper web (Widmer, 1928). This creping process is still used in hygiene papers. More recently, a micro-creping technique was developed to produce paper with high strainability (Annable, 2004). Trani and Cariolaro (1996) and Trani, Sterner, and Cariolaro (2005) have also developed a new technique based on the presence of two rolls made of different materials and geometries and driven at different speed to create a structural modification of the paper sheet, leading to a highly stretchable final material. However, these techniques, which involve a structural modification of the fibrous network, may require logistic modification on the paper machine and slow down the papermaking process. The creping technique also increases the strain at break at the cost of the stress at break of the paper. An appealing alternative to these earlier techniques is a chemical modification of the fibre surface prior to the classic papermaking process. Such a treatment could be a good way of reaching high strainability without disturbing the papermaking process. Charged polymers have been used for a long time in the papermaking industry to improve the properties of standard paper grades or to allow the addition of low cost, low strength components to the papermaking furnish while maintaining an acceptable paper quality.

Different types of polyelectrolytes have been used for years in the paper industry for different purposes, particularly cationic polyelectrolytes which interact efficiently with the carboxyl groups on the fibres (Lindstrom, Wagberg, & Larsson, 2005; Wagberg, 2000). This entropy-driven process leads to a modification of the

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properties of the fibres and thus influences properties such as the wet web strength, formation, retention, dry and wet strength etc. of paper made from the treated fibres (Bates, Beijer, & Podd, 1999; Davison, 1980; Gimaker and Wagberg, 2009; Lindstrom and Floren, 1987; Moeller, 1966). Among the most commonly used polyelectrolytes in the paper industry are cationic starch (Wagberg and Bjorklund, 1993), poly-diallyl dimethyl ammonium chloride (pDADMAC) and cationic polyacrylamides (C-PAM) (Lindstrom and Soremark, 1976). Recent studies have demonstrated that the adsorption of a monolayer of a cationic polymer such as polyvinylamine (PVAm) or polyallylamine hydrochloride (PAH) on the surface of the pulp fibres has a significant effect on the dry strength of the resulting paper (Marais and Wagberg, 2012; Rathi and Biermann, 2000). The Layer-by-Layer (LbL) deposition technique for introducing oppositely charged polyelectrolytes onto a charged surface, as described by Decher (1997), has opened up totally new possibilities for the modification of wood fibre surfaces (Agarwal, Lvov, & Varahramyan, 2006; Renneckar and Zhou, 2009; Wagberg, Forsberg, Johansson, & Juntti, 2002). A large amount of research has also recently been devoted to polyelectrolyte multilayers and their properties and the applications are numerous: optics, biomedical devices etc. (Hammond, 2004; Yoo et al., 2006). Applied to pulp fibres, this method may provide a significant improvement in both strength and strain at break of paper materials (Lingstrom and Wagberg, 2008; Wagberg et al., 2002) and it may be an alternative to the energy-consuming mechanical beating of the fibres, provided that paper strength is the most important aspect of the paper quality. Different polyelectrolytes have been evaluated (Eriksson, Notley, & Wagberg, 2005; Lingstrom and Wagberg, 2008; Lvov, Grozdits, Eadula, Zheng, & Lu, 2006; Wagberg et al., 2002), but so far the number of polyelectrolytes tested for fibre modification has been limited and in the present work it has been considered important to evaluate the use of polyelectrolytes and nanoparticles that exhibit both a linear and a super-linear growth (Decher and Schlenoff, 2003) in the thickness of the multilayers as a function of layer number, in order to evaluate how this affects the development of paper properties.

The interest around nano-fibrillated cellulose (NFC) has recently dramatically increased due to the need for more sustainable materials, coupled with developments to make the production of NFC feasible on the industrial scale (Ankerfors, 2012). NFC is a renewable and bio-based biomaterial made from wood fibres that are homogenized to liberate the fibrils from the fibre matrix. This treatment can be preceded by a carboxymethylation step, making the fibre easier to defibrillate, and giving rise to a highly charged final material (typically about 500 μeq/g) and with nanometric dimensions (Wagberg et al., 2008).

Hyaluronic acid (HA) is an interesting natural polyelectrolyte that can be used for the formation of LbLs at solid/liquid interfaces (Buhler and Boue, 2004; Boudou, Crouzier, Ren, Blin, & Picart, 2010). It is a linear, high molecular mass biopolymer made of a disaccharide repeating unit consisting of β(1-4)-linked N-acetyl-D-glucosamine and D-glucoronic acid, linking other units with β(1-3) bonds to form the polymer chain. It is present for example in the synovial liquid, in the human eye, and it is a polysaccharide of considerable interest due to its unique properties (stiffness of the polymer chains, hydrophilicity, rheology, lubrication ability). It is commonly used in biomedical applications such as in ophthalmology, drug delivery and surgery (Lapcik, De Smedt, Demeester, & Chabrecek, 1998; Laurent and Fraser, 1992).

In the present work, HA was used together with PAH as a fibre modification additive to build up a multilayer on lignocellulosic pulp fibres, using the LbL deposition technique. Another system involving polyethyleneimine (PEI) and NFC was investigated, since this system is known to form water-rich visco-elastic multilayer structures (Aulin, Varga, Claesson, Wagberg, & Lindstrom, 2008). Paper sheets were prepared from these treated fibres and the mechanical properties were studied. The fibre modification treatments were preceded by model experiments including LbL formation on silicon oxide surfaces in order to characterize the formation of the multilayers and their properties as a function of layer number and salt concentration.

2. Experimental

2.1. Materials

2.1.1. Fibres

The fibres used in this study were provided by SCA Forest Products (Östrand Pulp Mill), Sundsvall, Sweden, as dry sheets of a kraft pulp from softwood, digested to a kappa number of 44 and then bleached according to a totally chlorine-free (TCF), (OO)Q(OP)(ZQ)(PO), bleaching sequence (where O stands for oxygen, Q for chelating agent, P for hydrogen peroxide and Z for ozone). In order to separate the fibres, the dry sheets were disintegrated following the ISO 5263:1995 Standard. A washing procedure was then used to remove metal ions as well as dissolved colloids such as carbohydrates, lignin or extractives. The fibres were first converted to their protonated form; the pH of the suspension was adjusted to 2 with 1 M HCl and the suspension was stored for 30 min. It was then dewatered and washed with deionized water until the conductivity of the filtrate was below 5 μS/cm. Thereafter, the fibres were converted to their sodium form; 0.1 M $NaHCO_3$ was added and the pH was adjusted to 9 with 1 M NaOH. After a storage time of 30 min, the suspension was then dewatered and rinsed with deionized water, as in the first step. The dewatered fibres were stored in a refrigerator at 5 °C until they were used.

Fibres from an unbleached pulp were also used. This pulp was a specially prepared, laboratory-digested kraft pulp delivered by SCA AB, Sundsvall, Sweden, with a kappa number of 75 (hereinafter denoted K75). The preparation of the pulps has earlier been described in more detail by Gimaker, Ostlund, Ostlund, and Wagberg (2011). They were not subjected to mechanical beating and washed according to the protocol explained previously.

2.1.2. Polyelectrolytes

Two different systems were investigated: PEI/NFC and PAH/HA. The PEI was provided by Acros Organics (U.S.), as a 50 wt% aqueous solution, with a molecular weight of 60 kDa. Both PAH and HA were provided by Sigma–Aldrich. The molecular weight of PAH was 15 kDa and HA had a molecular weight of about 1.6 MDa. The NFC was kindly provided by Innventia AB, Stockholm, Sweden, as a 2.0 wt% suspension and it was prepared according to an earlier described procedure (Wagberg et al., 2008). After careful preparation, this NFC consisted of nanoparticles with a cross-section of approximately 5 nm and a length of approximately 1 μm and, according to conductometric titration, this material had a charge of 515 μeq/g (Wagberg et al., 2008).

2.2. Methods

2.2.1. Polyelectrolyte multilayers on the fibres

In order to determine the amounts of polymer to be added in the different LbL treatment steps, a two-step procedure was used. Initially, the amount of polyelectrolyte that could be adsorbed as a first layer on the fibres was evaluated by determining the adsorption isotherm of the cationic polymer on the pulp fibres following a method described by Winter, Wagberg, Odberg, and Lindstrom (1986), with an adsorption time of 10 min and a NaCl concentration of 10 mM. In order to circumvent endless adsorption studies, the amount of polyelectrolyte to be added in the consecutive steps in the fibre treatments was determined through model studies using

Dual Polarization Interferometry (DPI) since this type of model study has earlier been shown to be appropriate for predicting the formation of multilayers on fibres (Eriksson et al., 2005). From these measurements, the relationship between the saturation adsorption in the different layers was established and this was then used to add an appropriate amount of polyelectrolytes in the different steps of fibre modification. The actual amount of polymer adsorbed onto the fibre at saturation was determined via nitrogen analysis as described later. The multilayers were formed on the pulp fibres by a procedure in which the cationic polymer was added to a 3.6 g/L fibre suspension under mechanical stirring. The adsorption time was 10 min. After the adsorption, 1 L of the fibre suspension was taken out and used for the sheet-making. The remaining suspension was dewatered to remove the excess polymers, but no further washing was performed, and the fibres were kept in the never-dried state throughout the procedure. Water was thereafter added to form a new 3.6 g/L fibre suspension to which the anionic polymer was added. The same sequence was repeated to give the desired number of bilayers. For systems with added salt, the required amount of salt was added to the suspension from a concentrated solution (5 M NaCl). No exact pH control was used but, due to the buffering capacity of the fibre suspensions and polymer systems used, the pH was close to 6.5 for the PAH/HA system and to 9.0 for the PEI/NFC system.

2.2.2. Dual Polarization Interferometry

A Dual Polarization Interferometer Analight Bio200 from Farfield Sensors Ltd (Manchester, UK) was used to study the PAH/HA and PEI/NFC assemblies with a continuous flow of 100 μL/min (Swann, Peel, Carrington, & Freeman, 2004). All the samples had a concentration of 100 mg/L. Nitrogen-doped silica chips were used as deposition substrates. The salt concentration in the systems with added salt was 10 mM of NaCl.

2.2.3. Sheet preparation

A Rapid Köthen apparatus (PTI, Vorchdorf, Austria) was used to prepare sheets with a grammage of 120 g/m^2 from the treated and untreated fibres according to the ISO 5269-2:2004 Standard. The sheets were dried under restrained conditions at 93 °C for 15 min and at a pressure of 95 kPa below atmospheric pressure. The moisture content of the paper samples (conditioned at 50% HR) was not affected by the LbL treatment, and was determined to be 7.1 (±0.2) %.

2.2.4. Nitrogen analysis

Samples (pieces of ca. 10 mg) were taken from each sheet for elemental nitrogen determination (test performed on an ANTEK MultiTek by PAC, Houston, Texas, USA). In this method, the instrument provides a number of counts that can further be translated into the mass of polymer, using appropriate calibration. For the PEI/NFC system, the calculation was direct, but for the PAH/HA system, two calibration curves were needed (one for each polymer) since each layer was composed of a nitrogen-containing polymer. The calculated adsorbed amounts correspond to the values for the external layer, which was further matched with the corresponding calibration curve, assuming that no polymer was desorbed in the different steps. The calibrations for each of the three polymers are summarized in Supporting Information.

2.2.5. Tensile strength

The sheets were conditioned at 23 °C and 50% relative humidity prior to testing. Dry tensile strength measurements were conducted on a horizontal tensile tester (PTI Vorchdorf, Austria) following the SCAN P:67 Standard.

2.2.6. Z-strength

The strength of paper in the thickness direction was investigated according to a method developed at Innventia AB, Stockholm, Sweden (Andersson and Fellers, 2010). In this method, a sandwich structure is prepared, where a plastic laminate and a tissue are applied on each side of the paper sample. The structure is then glued onto a metallic sample holder using a fast curing glue, and this holder is then mounted on the testing apparatus. During the test, the stress and strain are recorded, and the stress at break, expressed in kPa, is the z-strength value.

3. Results

3.1. Adsorption of polyelectrolyte multilayers onto pulp fibres

As described earlier, the DPI technique was used to establish the ratio of the components to be added to the system in order to form the multilayers on the fibres, knowing the amount of polymer to add on the first layer from adsorption isotherms. The results obtained from adsorption isotherms showed that the fibres could adsorb much higher amounts of polyelectrolyte with the addition of 10 mM NaCl (2.5 mg/g of PAH and 16.0 mg/g of PEI, whereas it was as low as 0.6 mg/g of PAH and 1.2 mg/g of PEI without added salt). The results of the DPI measurements are shown in Fig. 1. The two systems investigated in this study showed two different film thickness responses. The PEI/NFC system showed a linear increase in thickness as the number of layer was increased and the addi-

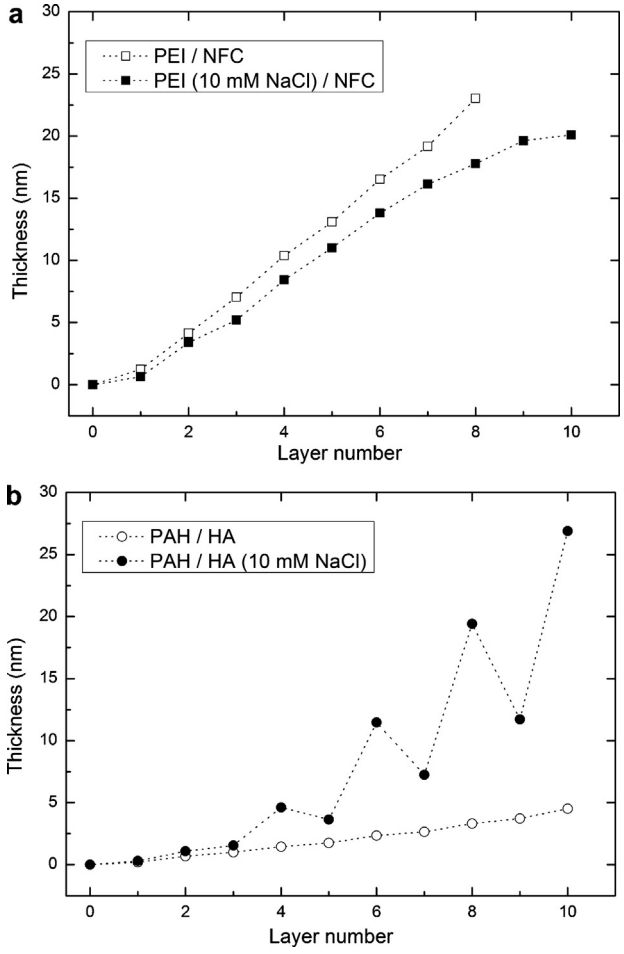

Fig. 1. Results of the DPI measurements showing the film thickness for (a) PEI/NFC and (b) PAH/HA, with and without added salt.

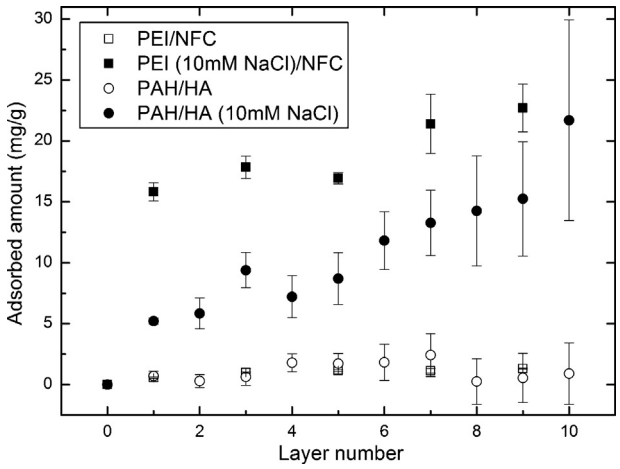

Fig. 2. Total actual amounts of polymer adsorbed, determined by nitrogen analysis, as a function of the layer number for the PEI/NFC and PAH/HA systems, both with and without added salt.

tion of salt did not change this trend. In the case of the PAH/HA system, however, the presence of salt dramatically affected the build-up of the multilayer structure and a non-linear behaviour was observed. In this system, the adsorbed amount of polymer was dependent on the salt concentration. The film thickness increased from 5 nm to 27 nm after 5 bilayers when 10 mM NaCl was added.

The actual amount of polymer adsorbed onto the fibres was determined by nitrogen analysis. Fig. 2 shows that the addition of salt greatly affects the amount of polymer adsorbed. In the absence of added salt, a low adsorption was observed, and there was no significant increase in the adsorbed amount with increasing number of layers. In the presence of added salt, there was a dramatic increase in the adsorbed amount, although the behaviour was different in the two systems. In the PAH/HA system the amount adsorbed increased with an increased number of layers, whereas in the case of the PEI/NFC system, the increase in adsorbed amount becomes very low after the first layer.

3.2. *Mechanical properties of papers from treated and untreated fibres*

Tensile tests were carried out for sheets made from treated and non-treated fibres to evaluate the impact of the LbL deposition on the surface of fibres prior to the sheet making. The results are presented in Fig. 3. An interesting pattern can be seen in the case of the PEI/NFC system with 10 mM salt: both the tensile index and the strain at break increase and decrease alternately following the addition of PEI and NFC respectively. With PEI as the outer layer, the tensile strength increases from 25 Nm/g to 42 Nm/g, whereas it reaches only 35 Nm/g with NFC as the outer layer. These improvements are reached already with 5 layers, after which a levelling off is observed. For the PAH/HA system, the improvement does not follow an alternating pattern and, in this case, the outer layer does not have the same influence on the properties of the paper. A total of five PAH/HA bilayers gave a considerable increase in both tensile index and strain at break. The tensile index increased to 70 Nm/g, and the strain at break increased from 2.0% to 6.5%, which means an increase of a factor three in both tensile index and strain at break. This improvement in the mechanical properties of the sheets made from LbL-treated fibres can also be seen in the stress-strain curves in Fig. 4, which show that each layer, regardless of whether it was anionic or cationic in nature, provided a notable gain in mechanical properties for the PAH/HA system. The alternating

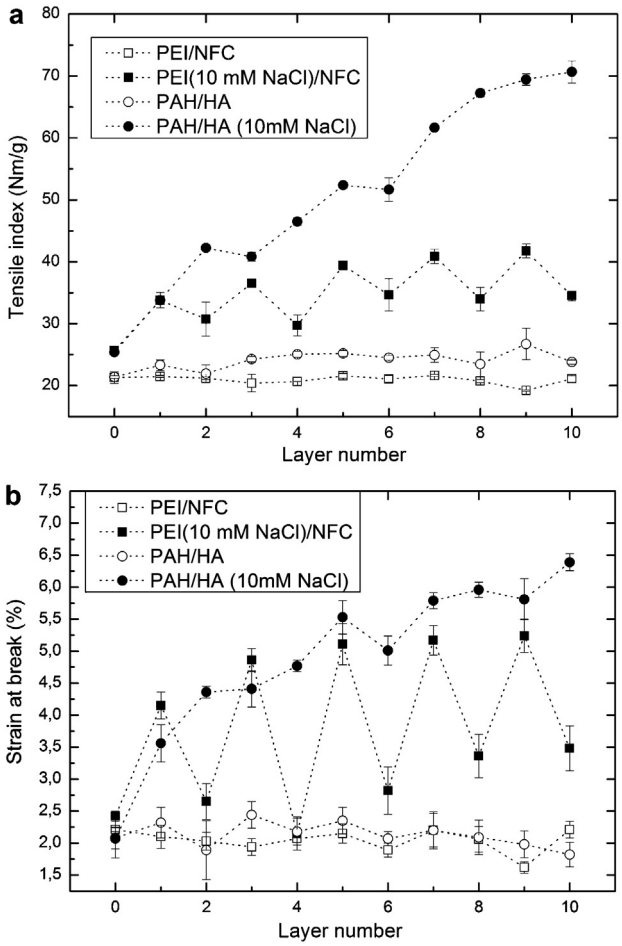

Fig. 3. (a) Tensile index and (b) strain at break as a function of layer number for PEI/NFC and PAH/HA systems with and without added salt.

behaviour in the PEI/NFC system is also depicted by the stress-strain curves, where all the curves for a structure with NFC as the outer layer (even numbers) are gathered in a lower stress and strain region than those for a structure with PEI as the outer layer (odd numbers).

For sheets prepared from the K75 unbleached kraft pulp, the PAH/HA system did not exhibit the same relative improvement in the strain at break. However, as shown in Fig. 5a, the tensile index increased to 125 Nm/g, but both the tensile index and the strain at break levelled off after 2 bilayers.

Another interesting aspect of this treatment is its effect on the z-strength of the papers, i.e. the strength of the paper when subjected to a load in the thickness direction. This property is crucial in both converting (i.e. bending and creasing) and printing processes, particularly in offset printing, where high viscosity inks with a high tack value are used. The z-strength, or z-direction tensile strength (ZDTS) was evaluated for papers made from the unbleached kraft pulp. Fig. 5b shows that the PAH/HA treatment led to a large improvement in internal cohesion of paper, from 750 kPa for the unmodified sheet to 2250 kPa for the sheet made from fibres treated with five bilayers. This behaviour was expected since during the sheet-making process, it was increasingly difficult to peel-off the samples from the blotting paper after drying with increasing the number of layers. It is also worth noting that the z-strength showed a steady improvement as a function of layer number whereas the tensile index levelled off after 2 bilayers.

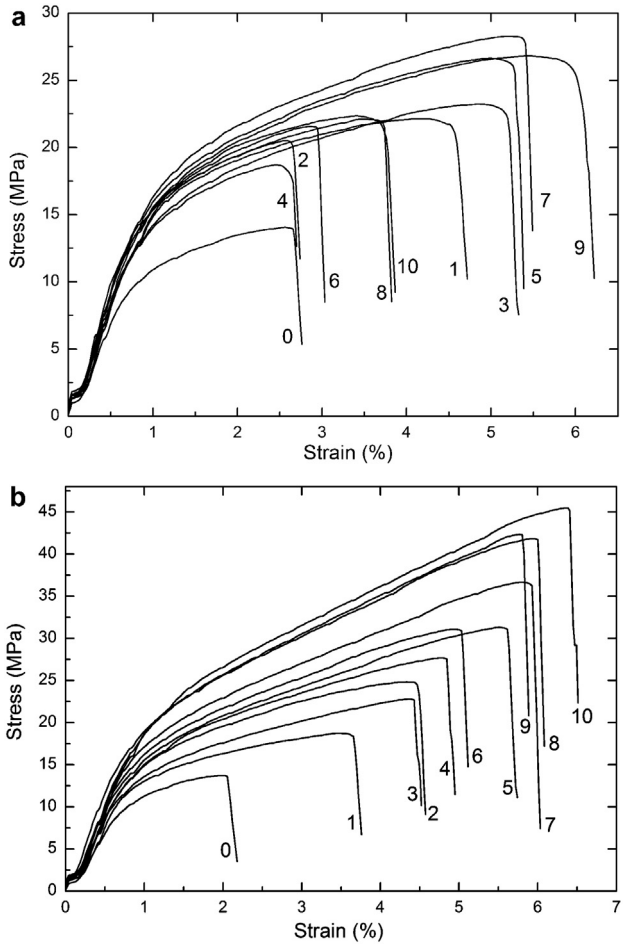

Fig. 4. Stress vs. strain curves for (a) PEI/NFC and (b) PAH/HA systems, both with 10 mM NaCl. The number assigned to each curve corresponds to the layer number.

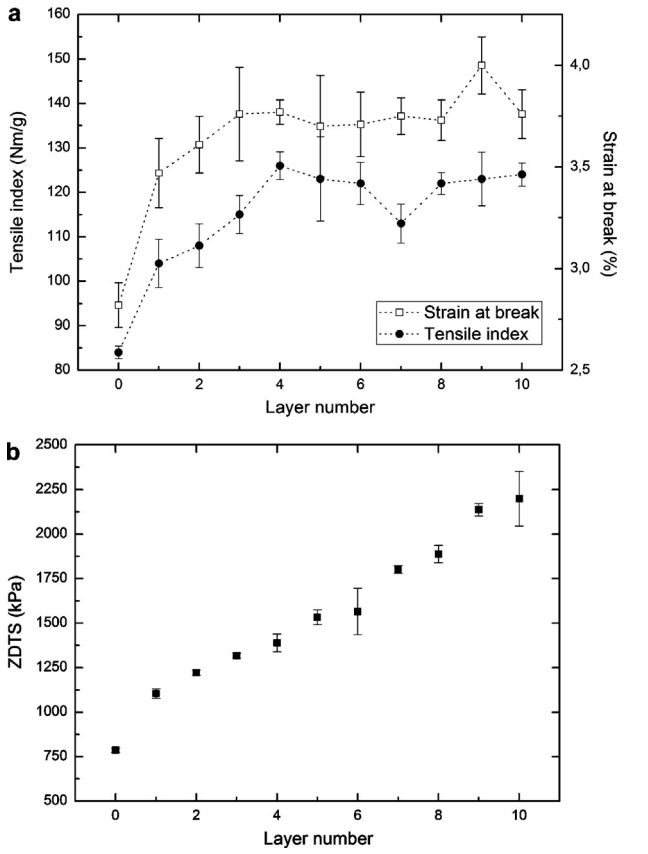

Fig. 5. (a) Tensile index and strain at break and (b) z-strength as a function of the layer number for sheets made from unbleached kraft pulp fibres treated with the PAH/HA system with 10 mM NaCl.

4. Discussion

Recent investigations by Eriksson et al. (2005, 2006) have shown that the build-up of a multilayer system composed of PAH and polyacrylic acid (PAA) on the same fibres as those used in the present study led to an increase in the tensile strength. However, in the best case (in which the pH was adjusted to 7.5 and 3.5 during the adsorption of PAH and PAA respectively), the adsorbed amount of PAH was up to 35 mg/g (after the deposition of 7 layers) and such a modification gave rise to an increase in tensile index from 20 Nm/g to 50 Nm/g. In Fig. 6, the tensile index is plotted as a function of the adsorbed amount of polymer for both the PAH/HA and PEI/NFC systems in the present study. An adsorbed amount of polymer as low as 15 mg/g was sufficient to increase the tensile index of the paper sheets from 20 Nm/g to 70 Nm/g for the PAH/HA system. This shows that the polymers investigated in the present study were very efficient strength-enhancing additives. The same observation can be made regarding the strain at break. However, for the PEI/NFC system, an adsorbed amount of 17 mg/g of PEI gave rise to a less significant increase, from 20 Nm/g to 40 Nm/g, showing that this combination was not as efficient as the system incorporating hyaluronic acid.

In order to understand the influence of the multilayers on the strength of paper, the molecular organisation in the fibre–fibre joints must be considered. Two features are crucial in order to form a fibre–fibre joint providing both strength and stretchability to paper. These are (a) a solid anchoring of the polymers at the surface of the fibre, and (b) ductile properties in the multilayer film, which means that the film has a yield point lower than the fibre wall, and that the different layers in the film interpenetrate. The diagram in Fig. 7 depicts these two aspects.

A solid anchoring of the first polymeric layer to the fibre surface can be achieved by both charge interactions and partial penetration of the polymer chains into the fibre wall. In this work, PAH and PEI with relatively low molecular masses (15 kDa and 60 kDa respectively) were used as the first layer. In the case of PAH, the radius of gyration of polymer chains in a 10 mM NaCl medium has

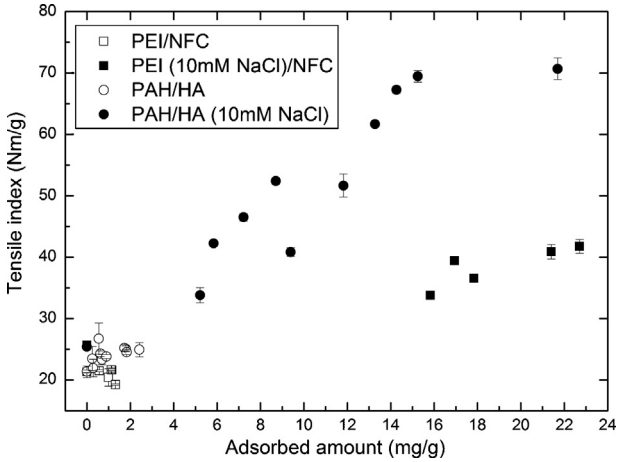

Fig. 6. Tensile index as a function of the amount of adsorbed polyelectrolyte for the PAH/HA and PEI/NFC systems, with and without added salt.

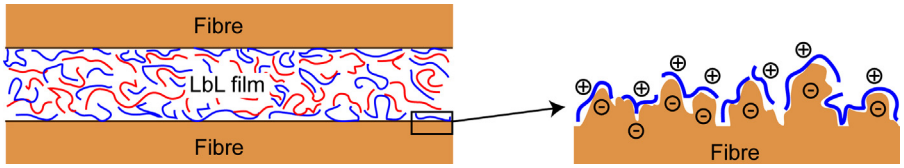

Fig. 7. Diagram of a fibre-fibre joint between two LbL-treated fibres with an enlargement of the fibre/LbL film interface, showing the anchoring of the polymer at the fibre surface, and the intermixing within the LbL film.

been reported to be 7 nm (Gimaker and Wagberg, 2009), and the pore radius of a bleached kraft pulp fibre is of the order of 10 nm (Andreasson, Forsstrom, & Wagberg, 2003). It is thus possible for a polymer chain to penetrate the outer layers of the fibre wall, ensuring a good anchoring of the layer, from which the build-up of the structure is initiated. However, in the case of the PEI/NFC system, the high aspect ratio of the fibrils may prevent penetration of the polymer into the fibre wall, and this may be the reason why the adsorbed amount of PEI is much higher for the first layer (for which PEI can penetrate the fibre wall to a certain extent) than for the subsequent layers (where the stiff nanofibrils have blocked the pores). The porous structure of the fibre wall combined with the high aspect ratio of the NFC might also explain why the results obtained from the DPI (Fig. 1) are different from the results provided by nitrogen analysis (Fig. 2) in the case of the PEI/NFC system without added salt, since the silica wafers used in the DPI measurements are non porous, whereas the fibres are highly porous and the build-up might be prevented by both the lack of mobility (due to the absence of added salt) and the fact that the pores are blocked by the fibrils (Kovacevic, van der Burgh, de Keizer, & Stuart, 2002).

The amount of polymer adsorbed per unit surface area can be estimated according to a method by Lindstrom and Soderberg (1986), where the hydrodynamic specific surface area for a bleached softwood kraft pulp was determined to be 1.37 m^2/g. However, considering that the polyelectrolyte penetrates the fibre wall to some extent, the specific surface area can be estimated to be of the order of 10 m^2/g by examination of labelling studies by Gimaker and Wagberg (2009). Assuming a density of 1000 kg/m^3, and considering an adsorbed amount of 20 mg/g, the thickness of the LbL deposition can be estimated to be about 2 nm. This shows that the deposition could not be considered to be a film if it was only a flat and homogeneous system. In our case, HA permits the build-up of a 3D structure and this confers film properties to the deposition. In addition, according to the DPI results, the structures investigated in this study (five bilayer-structures) had a thickness of over 20 nm, and they can therefore be considered to be films, since the thickness from which a multilayer structure starts to exhibit film properties, as demonstrated by the use of the strain-induced elastic buckling instability for mechanical measurements (SIEBIMM) technique, has been evaluated to be about 20 nm by Johansson and Wagberg (2011) and by Cranston et al. (2011). Another fundamental aspect for the achievement of a film with good mechanical properties is the intermixing of the polymer chains. Fig. 3 shows that the tensile index was higher when PEI was adsorbed in the outermost layer than when NFC was in the outermost layer. As pointed out by Johansson, Blomberg, and Wagberg (2009), the stiffness of the polymer chains determines the intermixing capacity and thus the final properties of the multilayer film. The stiff fibrils (NFC) are therefore responsible for a reduced intermixing in the layers, giving rise to a final structure with lower mechanical properties. In the PAH/HA system, the low molecular mass polymer chains of PAH and the higher molecular mass HA may provide an intermixing which increases the mechanical properties of the film and the PAH/HA films may therefore be more visco-elastic, i.e. have a lower modulus and higher strain at break. It is important to seek a more fundamental understanding of the mechanical properties of the film since those determine the behaviour of the fibre-fibre joints upon loading and thereby the mechanical properties of paper on a macroscale. A more thorough investigation of the mechanical properties of these two systems is currently being conducted in the laboratory of the authors. The impact of LbL-treated pulp fibres on the final paper material, as well as on the fibre-fibre joints, was studied by Eriksson, Torgnysdotter, and Wagberg (2006). The fibre joint strength was shown to increase by a factor of three following the deposition of a PAH/PAA multilayer. This improvement in the joint strength gave rise in turn to a higher tensile index. Since the polymers used in the present study have been shown to be more efficient, it may be argued that the deposition of a PAH/HA film on the surface of the fibres led to the formation of a fibrous network with more robust fibre-fibre joints. The very high strain at break obtained with a PAH/HA multilayer is probably associated with the presence of HA since such a large improvement was not found with the PAH/PAA system (Eriksson et al., 2005). HA is well-known for its ability to form hydrogen bonds (Lapcik et al., 1998) but it is also probable that the PAH/HA system will form 3D-structures at the interface with 10 mM NaCl, and this may be important for the development of strength properties.

5. Conclusions

This study has shown that highly stretchable paper could be obtained by deposition of a polyelectrolyte multilayer film onto the surface of pulp fibres prior to the sheet making. The system based on polyethyleneimine and nanofibrillated cellulose was sensitive to the outer layer, emphasizing the importance of the mobility of the chains in the build-up of a multilayer. The use of the biopolymer hyaluronic acid as anionic layer together with the cationic polyallylamine led to a paper with a tensile index and a strain at break both increased by a factor of three. This improvement was obtained with an adsorbed amount of polymer as low as 15 mg/g, emphasizing the efficiency of this combination of polymers. The strength in the z-direction was also dramatically increased, although the LbL treatment had no such effect on an unbleached pulp. This LbL treatment could pave the way for new chemical surface treatments within the papermaking industry, since it is a very easy and relatively inexpensive method providing a dramatic change in the properties of the final material. The production of stretchable paper could be of major importance in the packaging industry, where polymers made from non-renewable resources are still dominating, although the environmental consciousness is growing.

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Appendix A.

See Fig. A1.

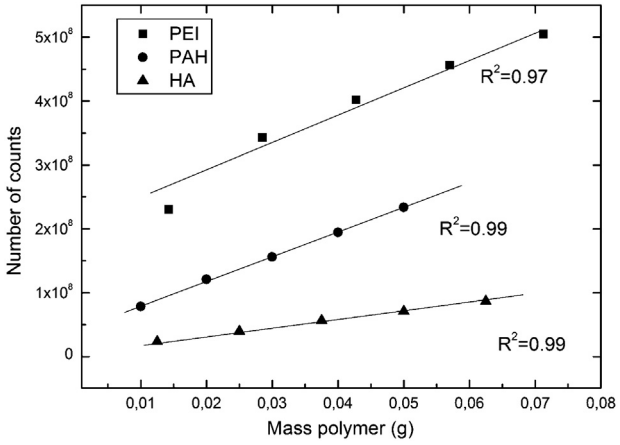

Fig. A1. Nitrogen analysis calibration curves for PEI, PAH and HA.

References

Ankerfors, M. (2012). Microfibrillated cellulose: Energy-efficient preparation techniques and key properties. Stockholm, Sweden. ISBN 978-91-7501-464-7.

Agarwal, M., Lvov, Y., & Varahramyan, K. (2006). Conductive wood microfibres for smart paper through layer-by-layer nanocoating. *Nanotechnology*, *17*, 5319–5325.

Andersson, C., & Fellers, C. (2010). Evaluation of the stress-strain properties in the thickness direction – Particularly for thin and strong papers. In *Progress in Paper Physics Seminar* FPInnovation, Montreal.

Andreasson, B., Forsstrom, J., & Wagberg, L. (2003). The porous structure of pulp fibres with different yields and its influence on paper strength. *Cellulose*, *10*(2), 111–123.

Annable, P. A. (2004). Process of making microcreped wipers. US Patent 6,797,226.

Aulin, C., Varga, I., Claesson, P. M., Wagberg, L., & Lindstrom, T. (2008). Buildup of polyelectrolyte multilayers of polyethyleneimine and microfibrillated cellulose studied by in situ dual-polarization interferometry and quartz crystal microbalance with dissipation. *Langmuir*, *24*(6), 2509–2518.

Bates, R., Beijer, P., & Podd, B. (1999). Wet strengthening of paper. In L. Neimo (Ed.), *Papermaking Chemistry*. Helsinki, Finland: Fapet Oy, 288–301.

Boudou, T., Crouzier, T., Ren, K., Blin, G., & Picart, C. (2010). Multiple functionalities of polyelectrolyte multilayer films: New biomedical applications. *Advanced Materials*, *22*(4), 441–467.

Buhler, E., & Boue, F. (2004). Chain persistence length and structure in hyaluronan solutions: Ionic strength dependence for a model semirigid polyelectrolyte. *Macromolecules*, *37*(4), 1600–1610.

Cranston, E. D., Eita, M., Johansson, E., Netrval, J., Salajkova, M., Arwin, H., et al. (2011). Determination of Young's modulus for nanofibrillated cellulose multilayer thin films using buckling mechanics. *Biomacromolecules*, *12*(4), 961–969.

Davison, R. W. (1980). *Theory of dry strength development. Dry strength additives*. Atlanta: TAPPI Press.1–31.

Decher, G. (1997). Fuzzy nanoassemblies: toward layered polymeric multicomposites. *Science*, *277*(5330), 1232–1237.

Decher, G., & Schlenoff, J. B. (2003). *Multilayer thin films – Sequential assembly of nanocomposite materials*. Wiley-VCH.

Eriksson, M., Notley, S. M., & Wagberg, L. (2005). The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibres. *Journal of Colloid and Interface Science*, *292*(1), 38–45.

Eriksson, M., Torgnysdotter, A., & Wagberg, L. (2006). Surface modification of wood fibers using the polyelectrolyte multilayer technique: Effects on fiber joint and paper strength properties. *Industrial & Engineering Chemistry Research*, *45*(15), 5279–5286.

Gimaker, M., Ostlund, M., Ostlund, S., & Wagberg, L. (2011). Influence of beating and chemical additives on residual stresses in paper. *Nordic Pulp & Paper Research Journal*, *26*(4), 445–451.

Gimaker, M., & Wagberg, L. (2009). Adsorption of polyallylamine to lignocellulosic fibres: Effect of adsorption conditions on localisation of adsorbed polyelectrolyte and mechanical properties of resulting paper sheets. *Cellulose*, *16*(1), 87–101.

Hammond, P. T. (2004). Form and function in multilayer assembly: New applications at the nanoscale. *Advanced Materials*, *16*(15), 1271–1293.

Johansson, E., Blomberg, E., & Wagberg, L. (2009). Adhesive interaction between polyelectrolyte multilayers of polyallylamine hydrochloride and polyacrylic acid studied using atomic force microscopy and surface force apparatus. *Langmuir*, *25*(5), 2887–2894.

Johansson, E., & Wagberg, L. (2011). Tailoring the mechanical properties of starch-containing layer-by-layer films. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *394*(0), 14–22.

Kovacevic, D., van der Burgh, S., de Keizer, A., & Stuart, M. A. C. (2002). Kinetics of formation and dissolution of weak polyelectrolyte multilayers: Role of salt and free polyions. *Langmuir*, *18*(14), 5607–5612.

Lapcik, L., De Smedt, S., Demeester, J., & Chabrecek, P. (1998). Hyaluronan: preparation, structure, properties, and applications. *Chemical Reviews*, *98*(8), 2663–2684.

Laurent, T. C., & Fraser, J. R. (1992). Hyaluronan. *The FASEB Journal*, *6*(7), 2397–2404.

Lindstrom, T., & Floren, T. (1987). The effect of filler particle size on the dry-strengthening effect of cationic starch wet-end addition. *Nordic Pulp and Paper Research Journal*, *4*(4), 142–145.

Lindstrom, T., & Soderberg, G. (1986). On the mechanism of sizing with alkylketene dimers – Part I. Studies on the amount of alkylketene dimer required for sizing of different pulps. *Nordic Pulp and Paper Research Journal*, *1*(1), 26–33.

Lindstrom, T., & Soremark, C. (1976). Adsorption of cationic polyacrylamides on cellulose. *Journal of Colloid and Interface Science*, *55*(2), 305–312.

Lindstrom, T., Wagberg, L., & Larsson, T. (2005). On the nature of joint strength in paper: A review of dry and wet strength resins used in paper manufacturing. In *13th Fundamental Research Symposium* (pp. 457–562).

Lingstrom, R., & Wagberg, L. (2008). Polyelectrolyte multilayers on wood fibers: Influence of molecular weight on layer properties and mechanical properties of papers from treated fibers. *Journal of Colloid and Interface Science*, *328*(2), 233–242.

Lvov, Y. M., Grozdits, G. A., Eadula, S., Zheng, Z., & Lu, Z. (2006). Layer-by-layer nanocoating of mill broken fibers for improved paper. *Nordic Pulp and Paper Research Journal*, *21*(5), 552–557.

Marais, A., & Wagberg, L. (2012). The use of polymeric amines to enhance the mechanical properties of lignocellulosic fibrous networks. *Cellulose*, *19*(4), 1437–1447.

Moeller, H. W. (1966). Cationic starch as a wet-end strength additive. *Tappi*, *49*(5), 211–214.

Nonnenmacher, F. (1898). Sizing. Patent number: US 599726 A 18980301.

Rathi, M. S., & Biermann, C. J. (2000). Application of polyallylamine as a dry strength agent for paper. *Tappi Journal*, *83*(12).

Renneckar, S., & Zhou, Y. (2009). Nanoscale coatings on wood: Polyelectrolyte adsorption and layer-by-layer assembled film formation. *ACS Applied Materials & Interfaces*, *1*(3), 559–566.

Sherman, J.C. (1941). Stretchable paper. Patent number: US2245014.

Swann, M. J., Peel, L. L., Carrington, S., & Freeman, N. J. (2004). Dual-polarization interferometry: an analytical technique to measure changes in protein structure in real time, to determine the stoichiometry of binding events, and to differentiate between specific and nonspecific interactions. *Analytical Biochemistry*, *329*(2), 190–198.

Trani, G., & Cariolaro, N. (1996). Method for producing yieldable paper and plant for implementing the method. WO Patent WO/1996/031,647.

Trani, G., Sterner, M., & Cariolaro, F. (2005). Method for producing extensible paper, plant for implementing the method, product obtained by the method, and paper material obtained from the product. WO Patent WO/2005/100,686.

Wagberg, L. (2000). Polyelectrolyte adsorption onto cellulose fibres – A review. *Nordic Pulp and Paper Research Journal*, *15*(5), 586–597.

Wagberg, L., & Bjorklund, M. (1993). Adsorption of cationic potato starch on cellulosic fibres. *Nordic Pulp and Paper Research Journal*, *8*(4), 399–404.

Wagberg, L., Decher, G., Norgren, M., Lindstrom, T., Ankerfors, M., & Axnas, K. (2008). The build-up of polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes. *Langmuir*, *24*(3), 784–795.

Wagberg, L., Forsberg, S., Johansson, A., & Juntti, P. (2002). Engineering of fibre surface properties by application of the polyelectrolyte multilayer concept. Part I: Modification of paper strength. *Journal of pulp and paper science*, *28*(7), 222–228.

Widmer, H.G. (1928). Process and mechanism for producing stretchable paper. Patent number: US 1676759.

Winter, L., Wagberg, L., Odberg, L., & Lindstrom, T. (1986). Polyelectrolytes adsorbed on the surface of cellulosic materials. *Journal of Colloid and Interface Science*, *111*(2), 537–543.

Yoo, P. J., Nam, K. T., Qi, J., Lee, S. K., Park, J., Belcher, A. M., et al. (2006). Spontaneous assembly of viruses on multilayered polymer surfaces. *Nature Materials*, *5*(3), 234–240.