



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



Andrew Marais^{a,*}, Simon Utsel^a, Emil Gustafsson^b, Lars Wågberg^{a,b,*}

^a Division of Fibre Technology, School of Chemical Science and Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

^b The Wallenberg Wood Science Centre, School of Chemical Science and Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

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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 SiO₂ 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.

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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

* Corresponding author. Tel.: +46 8 790 82 96; fax: +46 8 790 61 66.
E-mail address: marais@kth.se (A. Marais).

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; Rennecker 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 $\mu\text{eq/g}$) 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 $\beta(1-4)$ -linked N-acetyl-D-glucosamine and D-glucuronic acid, linking other units with $\beta(1-3)$ 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, & Chabreck, 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 $\mu\text{S/cm}$. 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 $\mu\text{eq/g}$ (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

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