

Strength-enhancing of Cationic Starch on Recycled Fibers via Layer-by-Layer Self-assembly

Hamidreza Rudi,^{a,*}Yahya Hamzeh,^b and Mousa M. Nazhad^c

The main objective in this study was to evaluate the possibility for the polyelectrolyte multilayer (PEM) assembly, selecting the cationic starch (CS) and anionic starch (AS) to increase the amount adsorption of cationic starch leading to modifying the bonding ability between recycled fibers. Experiments were conducted at neutral pH and 750 rpm stirring rate in Dynamic Drainage Jar (DDJ) for 10-minute deposition time to build 1 to 8 consecutive layers. The results have shown that CS/AS multilayers formation had significant influence on bonding ability between fibers. Tensile index increased from 15.62 N.m/g to 33.51 N.m/g at 5-layer assembly. Internal bonding between fibers showed a remarkable increase from 21.22 J/m² to 74.08 J/m² as well. Moreover, the most level of strength was obtained when cationic starch was the outermost layer. SEM images indicated that PEM formation makes the fiber surface rather rougher due to increase in adsorption that was not found in sheets made out of untreated fibers.

Keywords: Recycled Fibers - Polyelectrolyte Multilayers – Layer-by-Layer Technique – Cationic Starch – Anionic Starch –Paper strength

*Contact information: a: Department of Cellulose and Paper Technology, Faculty of New Technologies and Energy Engineering, Shahid Beheshti University, Zirab, Mazandaran, Iran; b: Department of Wood and Paper Science and Technology, Faculty of Natural Resources, University of Tehran, P.O. Box 31585-4314, Karaj, Iran.; c: Pulp and Paper Technology, Asian Institute of Technology, Thailand, *Corresponding author: h_rudi@sbu.ac.ir*

INTRODUCTION

Recycling of cellulosic fibers usually is associated with a significant loss of strength properties and bonding potential of the fibers (Hubbe and Zhang 2005; Garg and Singh 2006). This is mainly attributed to the greater fiber hornification and polysaccharide hardening (Hubbe *et al.* 2007; Rudi *et al.* 2012). Such phenomena tend to an irreversible losses of fiber re-wetting and inter-fiber bonding ability (Weise and Paulapuro 1996). In order to optimize the capability of the fiber to bond together, they are often subjected to a compression and shearing forces, i.e. “refining” (Paulapuro 2000) and an extensive refining action is mostly applied for recycled fibers (Hubbe 2006a).

Though the inter-fiber bonding properties and strength of paper can be substantially improved by refining (Seth *et al.* 1979), but it also tends to produce fines and decrease the rate at which water can be removed from the wet web of paper, limiting the rate of production (Bhardwaj 2004; Hubbe 2006a). Refining also tends to reduce the capability of the fibers to form strong inter-fiber bonds again when the recovered paper is made into recycled paper (pycraft and Howarth 1980; Weise 1998). Thus, a promising

approach is to add a polyelectrolyte, such as cationic starch, to enhance paper strength (Hubbe and Jowsey 1989; Ghosh 1994; Formento 1994).

Cationic starch increases the paper strength by increasing bond strength between fibers and creating an increased number of bonds between fibers (Moeller 1966). It has also been shown that the strength enhancement of paper is dependent on the amount of starch that can be adsorbed onto the fibers (Lindstrom 1984; Roberts *et al.* 1986; Hubbe 2006a). Furthermore, recent investigation have shown that it is possible to adsorb much higher amount of starch to the fibers by consecutively treating the fibers with polyelectrolyte multilayer (PEM) of cationic and anionic starch using a nanotechnology method called Layer-by-Layer, LbL, technique (Eriksson 2005; Pettersson 2006, Johansson 2009).

Recycling is one of the key areas in pulp and paper studies that can benefit from the polyelectrolyte layer-by-layer self-assembly on fiber surface to achieve desired properties (Podsiadlo *et al.* 2005; Wagberg *et al.* 2002; Eriksson *et al.* 2005; Zheng *et al.* 2006). This draws attention to apply LbL technique to modify the surface of recycled fibers, which can be changed with increase more adsorption of cationic starch.

Therefore, the purpose of present study was to explore the possibility of constructing bio-based PEM of cationic starch (CS) and anionic starch (AS) on recycled fiber. A further aim of this experimental approach was to establish a relationship between PEM formation and the amount starch adsorption, inter-fiber bonding ability and the paper strength.

EXPERIMENTAL

Materials

Fibers

Old corrugated container (OCC) as a sample of recycled fibers were collected from PPT laboratory, AIT, Thailand. Their contaminants were separated by hand, then turn into pieces approximately 25mm×25mm in size and soaked in tap water for at least 4h. The soaked papers were disintegrated for 30 minutes in a laboratory WEVERK Valley Beater according to SCAN-C 25:76. The pulp was therefore screened in a Voith Sulzer laboratory flat screen with slots 0.0008-inch (0.2 mm) in wide to divide the bundles and rejects from the fibers. Then, the screened pulp was fractionated by Bauer McNett fiber classifier according to SCAN-M 6:69, finally the fraction of pulp retained by wire sieve No. 200 as fines free pulp with freeness of about 655 ml CSF was used for following experiments.

Chemicals

Cationic starch (DS≈0.027) and anionic starch (DS≈0.145) used in this study, were kindly provided by Siam Modified Starch Co., Ltd. Cationic starch is usually stored as a powder, in the form of granules that are insoluble in water. So it must be gelatinized before use. Accordingly, based on the supplier instructions, it was first evenly dispersed in water and heated to 95°C under continuous mild stirring force for 30 minutes. After

cooling down to room temperature, the cationic starch solution was ready to use within 24 hours. The anionic starch was soluble in water, and used after complete solubilization in cold water.

Methods

LbL treatment

Cationic and anionic starch were consecutively layered onto the recycled pulp fibers. For each layering, certain amount of fiber suspension (500 ml containing 3g o. d. weight of fiber) was delivered into a 1 liter plastic beaker and then mixed with the ionic starches solutions by Britt Dynamic Drainage Jar (DDJ) apparatus, Electro-Craft®, Motomatic II model. The pulp fibers with zeta potential $\approx -16.9 \pm 4.45$ mV were firstly treated with 1% cationic starch, based on the oven dry weight of fibers. After mixing for 10 minute, the stock was washed with pure water on the Wattman filter paper No. 4 fitted in a Büchner funnel to remove weakly and physically adsorbed components. Then, the washed pulp was consecutively treated with 1% anionic starch, and washed again as above. This procedure was conducted to build up 1 to 8 layers of ionic starches. Determination of zeta potential of the surface of fibers was done after each stage by streaming potential method, SZP 06 BTG Müttek GmbH, using the standard screen electrode (308 μ m).

Sheet preparation and testing

Standard handsheets with grammage of 60 ± 3 g/m² and 16.5cm \times 16.5cm in size were made from both untreated and LbL-treated fibers by a KCL type laboratory sheet former, according to TAPPI T205 sp-95. The formed hand sheets were pressed two times at 400 kPa for 5 and 2 min, respectively and dried for 2h at 120°C. Handsheets were conditioned according to SCAN-P2:75 at constant temperature of 23 ± 1 °C and relative humidity 50 ± 2 % before testing. Paper properties including: thickness, apparent density, formation, roughness, tensile index, tensile energy absorption (TEA) and internal bonding (Scott type) were measured according to common SCAN and TAPPI methods. A LEO-440i scanning electron microscope (UK), in MTEC, Thailand, was also used to analyze the untreated pulp sheets formed from the untreated and LbL-treated recycled fibers.

RESULTS AND DISCUSSION

Effect of PEM forming on zeta potential of the fibers

Polyelectrolytes, such as cationic starch, often display high affinity adsorption behavior on cellulosic fibers (Gruber *et al.* 1996), leading to dramatic changes in electrokinetic behavior (Hubbe 2006b). Similarly, it is well known that one of the

important basics for the alternate deposition of polyelectrolytes onto cellulose fibers is the charge inversion at every deposition step (Xing *et al.* 2007).

In the present investigation, the zeta potential of the fibers has measured after each layering to confirm the possibility of PEM formation of ionic layers. Figure 1 represents consecutive variation of zeta potential for the CS/AS PEM during LbL treatment of recycled fibers. For example; the untreated recycled fibers present a negative zeta potential of about -16.9 ± 4.45 mV. By addition of cationic starch (DS \approx 0.027) in the first layer the zeta potential was measured around 17.2 ± 4.65 mV. In the second step of layering, depositing of anionic starches (DS \approx 0.145) the zeta potential has been inversed to the value of about -59.4 ± 1.55 mV. This negative charge has the potential to make the fibers more receptive to cationic starch (Marton and Marton 1976). Almost, the same successive charge inversion has occurred after adding of each ionic starches indicating the success of consecutive construction of the PEM of ionic starches onto the recycled fibers and the suitability of the existing layer for adsorption of next layer.

A noteworthy, as apparent from the figure 1, is the irregular variation of the charge inversion especially in final four layers. This effect was explained by the fact that the degree of substitution of the cationic polymer was much lower than that of the anionic counterpart (Wang *et al.* 2011). Therefore, adding of anionic starch possessing much higher DS (\approx 0.145) resulting in partially deterioration of the cationic layer having cationic starch (DS \approx 0.027). This is because for example, the measured zeta potential in 5th layer was a significant difference lower than did in third layer.

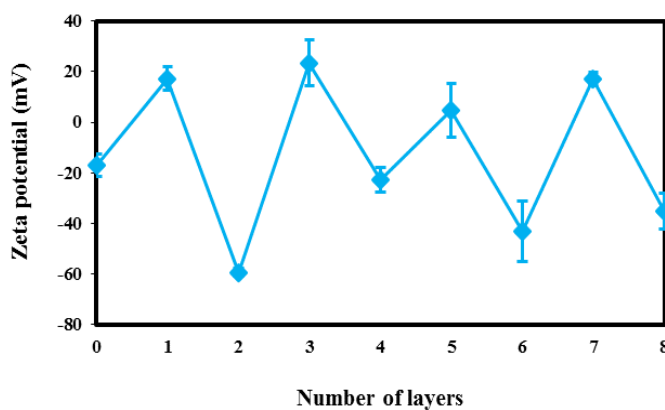


Fig. 1. Zeta potential changes during LbL multi-layering of ionic starches

Paper properties

Thickness, apparent density, roughness and formation

Paper thickness and density are two important structural properties which can be used to predict its physical and mechanical performance (Magnus *et al.* 2011). Figure 2 represents the variations of thickness and apparent density due to depositing of cationic starch in odd layers and anionic starch in even layers onto the recycled fibers. Unlike cationic starch as a frequently strength-increasing agent used in the wet-end of the paper machine (Johansson 2009), anionic pair, nor is as famous as cationic counterpart in pulp

and paper manufacturing, has functioned as a de-bonding agent in this study. Therefore, higher thickness and lower density were achieved after adding anionic starch compare to the previous step which cationic starch was used. Progressive decrease of thickness and contrarily, increase in paper density in successive layers indicates the possibility of forming PEM of ionic starches on the fibers leading to gradual increment in cationic starch adsorption.

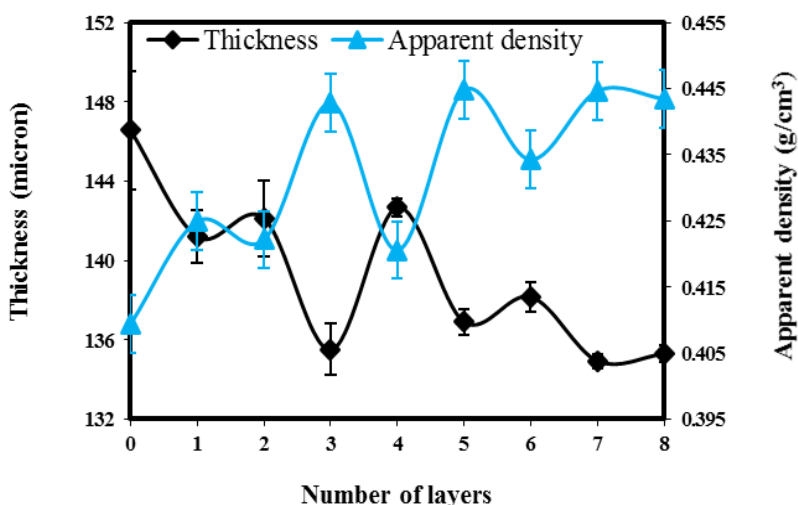


Fig. 2. Thickness and Apparent density changes during LbL multi-layering of ionic starches

Formation and Surface roughness

It has long been accepted that the different physical and mechanical properties of paper depend to some extent on formation, uniformity with which the fibers are distributed in the paper (Norman 1976). As seen in figure 3, though obtained data suggest that there may be a weak positive influence of PEM assembly on paper's uniformity. Within the accuracy of our results, we detected no significant difference between the measured formation values of sheets made of untreated and treated fibers. The reason for this was that only fine free recycled fibers was used in this study. Therefore, rough long untreated recycled fibers in agitated suspension can give rise to frequent inter-fiber collisions, mechanical entanglement and the formation of fiber flocs. But, optimizing addition of just 1% cationic starch charge in each odd-layering, seems to restrain mechanical-induced fiber flocculation tends to a minor improvement of paper's uniformity. In addition to formation, roughness is another important structural paper properties might be affected with the elongated fibers and formation of fiber flocs through the same reason explained as improving paper formation. Thereby, in consistent with thickness and density data, we detected to some extent lower roughness in the sheets made of PEM-treated fibers than did untreated ones (see Fig. 3).

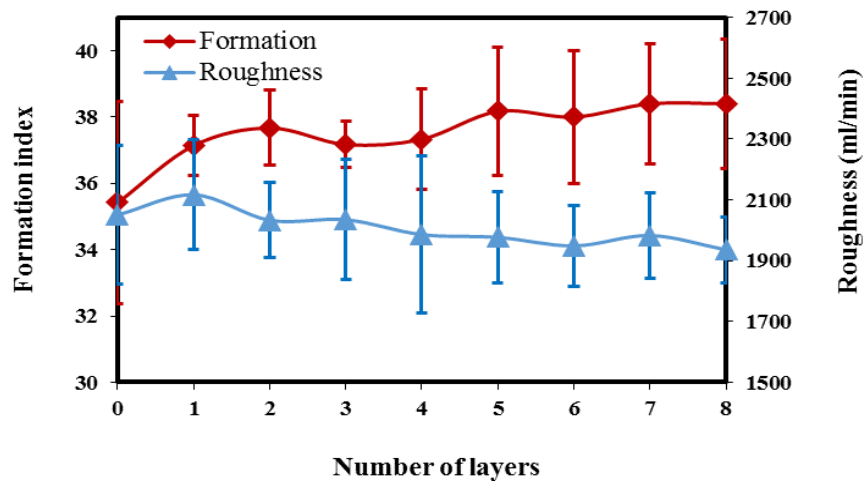


Fig. 3. Formation and Roughness changes during LbL multi-layering of ionic starches

Tensile index, TEA, Internal bonding (Scott bond)

The different strengths of paper prepared from CA/AS treated recycled fibers increased markedly with increasing numbers of deposited layers. For example, as shown in figure 4, tensile index enhanced from 15.62 ± 0.73 N.m/g to 33.51 ± 2.05 N.m/g showing an ascending rate of about 114% after five step layering. Tensile energy absorption, commonly termed as TEA, is a very important measure of the strength of paper (Ghasemian 2012), significantly increased from 18.66 ± 3.1 J/m² to the value of about 59.92 ± 5.09 J/m² depositing the same number of layer (see Fig. 4). Scott bond of paper depends on the number of bonds, the average area per bond and their specific strength (Koubaa and Koran 1995). Corresponding value was measured 21.22 ± 2.74 J/m² for untreated and did 74.08 ± 3.8 J/m² for PEM-treated fibers after three step treatment with ionic starches. Although, when the outer layer was anionic, Scott bond tended to decrease relative to resulted strength of the previous cationic layer (Fig. 5).

It can be attributed to the role of step-by-step increasing the amount adsorption within existing LbL process expected to yield increasing benefits on the bonding ability between fibers (Wagberg *et al.* 2002; Eriksson *et al.* 2005).

In certain cases the strengths were strongly influenced by the nature of the final deposited layer as seen in the section of explaining zeta potential variations. When cationic starch deposited onto the fibers, the most strengths were achieved (Eriksson *et al.* 2005). Oppositely, anionic starch has mostly lowered the strength of the papers.

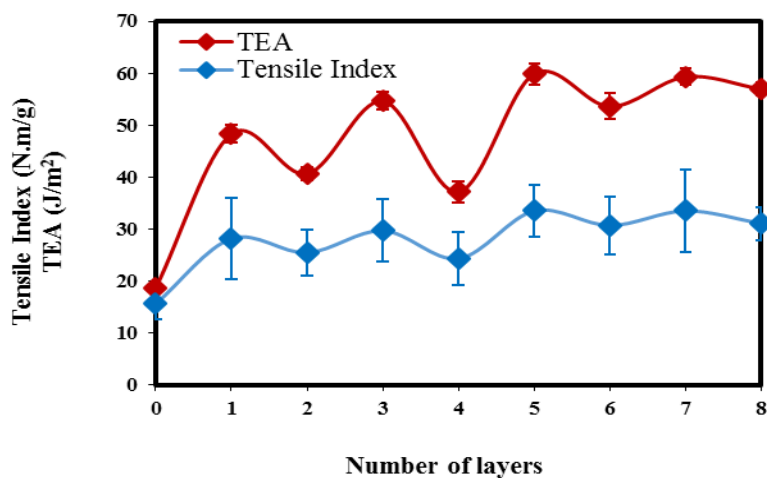


Fig. 4. Tensile index and TEA changes during LbL multi-layering of ionic starches

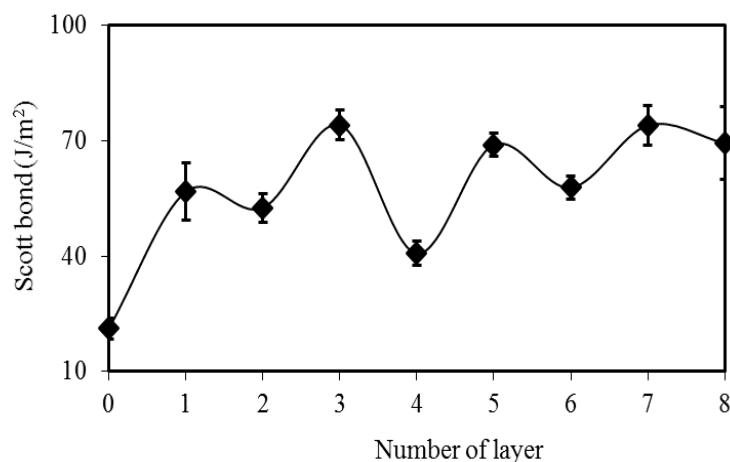


Fig. 5. Scott bond changes during LbL multi-layering of ionic starches

SEM Imaging

The objective of using Scanning Electron Microscopy (SEM) was to compare at the microscopic level the appearance differences between untreated and PEM-treated fibers. To do this, after making sheets with 10 g/m² basis weight from two types of treated and untreated fibers, the SEM images were analyzed. As depicted in Figure 6, the SEM images showing a distinguished appearance change of fiber surface after forming PEM of cationic starch (DS≈0.027) and anionic starch (DS≈0.145). These images indicated that PEM formation has led to gelatinization of the fiber surface with high amount of adhesive particles of cationic starch, in odd number layer, which makes the surface rather bumpy view that was not discovered in sheets made of relatively smooth untreated fibers. It can be expected that fibers with more gelatinized surface would have more flexible and adhesive properties producing well-bonded network of fibers and improving the paper strength.

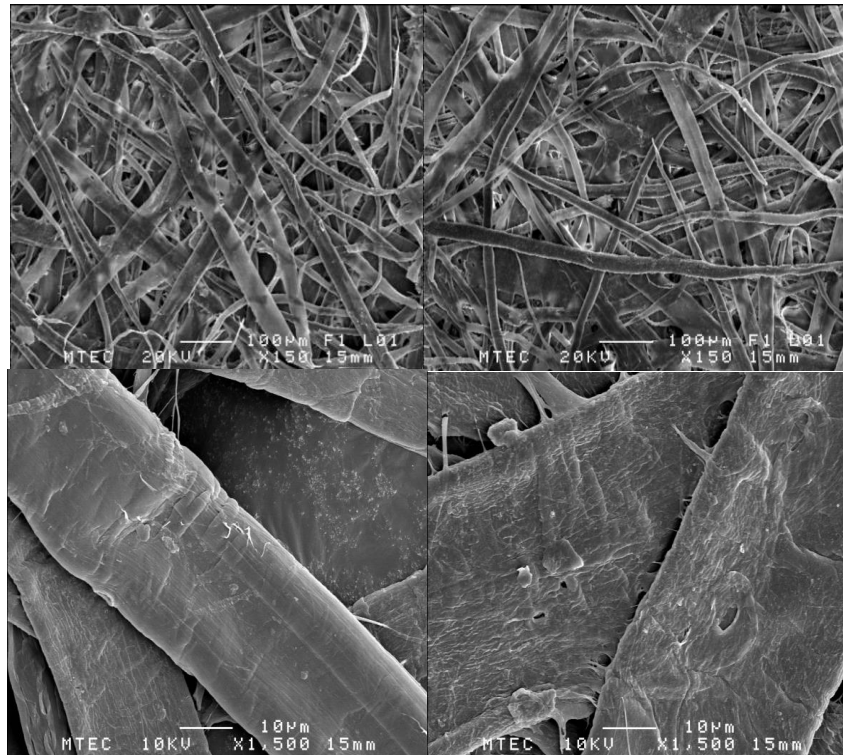


Fig. 6. SEM images of the surface of sheets (10 g/m^2 basis weight) made of untreated recycled fibers (left) and LbL-treated recycled fibers (right) with cationic starch ≈ 0.027 and anionic starch ≈ 0.145 .

CONCLUSIONS

1. Repeated charge inversion of the fibers at every step of layering indicated the possibility of forming PEM onto the recycled fibers.
2. Sheets made of PEM-treated fibers were less thick and had more density showing more interaction between fibers.
3. The inter-bonding ability indices such as tensile index, TEA and internal bonding improved significantly with multi-layering of cationic and anionic starch especially in three layer treatment without significant changed in formation and roughness of the papers.
4. SEM imaging of the treated and untreated fibers revealed that the PEM-treated fibers had a somewhat rougher surface, which definitely contributed to the gelatination of the surface due to an increase in starch adsorption, ultimately enhancing the formed papers.

REFERENCES CITED

- Bhardwaj, N. K., Duong, T. D., and Nguyen, K. L. (2004). Pulp charge determination by different methods: effect of beating/refining. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 236, 39–44.
- Eriksson, M., Pettersson, G., and Wagberg, L. (2005). Application of polymeric multilayers of starch onto wood fibers to enhance strength properties of paper. *Nordic Pulp & Paper Research Journal* 20(3), 270-276.
- Eriksson, M., Notley, S., and Wagberg, L., (2005). The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibres. *Journal of Colloids and Interface Science* 29, 38–45.
- Formento, J. C., Maximino, M. G., Mina, L. R., Srayh, M. I., and Martinez, M. J. (1994). Cationic starch in the wet end: Its contribution to interfiber bonding. *Appita Journal* 47(4), 305-308.
- Ghasemian, A., Ghaffari, M., and Ashori, A., (2012). Strength enhancing effect of cationic starch on mixed recycled and virgin pulps. *Carbohydrate Polymers* 87, 1269–1274.
- Ghosh, A. K., (1994). Enhancement of paper strength of container materials using wet end additives in an acidic system. *Appita Journal* 47(3), 227-237.
- Garg, M., and Singh, S. P., (2006). Reasons of strength loss in recycled pulp. *Appita Journal* 59(4), 274-279.
- Gruber, E., Grossmann, K., and Schempp, W., (1996). Interactions of synthetic cationic polymers with fibers and fillers; influence on adsorption. *Wochenbl. Papierfabr* 124(1), 4-11.
- Hubbe, M. A., and Zhang, M., (2005). *Recovered kraft fibers and wet-end dry-strength polymers*. Proc. TAPPI. Practical Papermakers Conf. TAPPI Press. Atlanta.
- Hubbe, M., (2006). Bonding between cellulosic fibers in the absence and presence of dry-strength agent- A review. *BioResource* 1(2), 739-788.
- Hubbe, M., (2006). Electrokinetic Potential of Fibers. *BioResources* 1, 116-149.
- Hubbe, M. A., Venditti, R. A., and Rojas, O. J., (2007). What happens to cellulosic fibers during papermaking and recycling? A review. *BioResources* 2 (4), 739-788.
- Howard, R. C., and Jowsey, C. J. (1989). The effect of cationic starch on the tensile strength of paper. *Journal of Pulp of Paper Science* 15(6), 225-229.
- Johansson, E., Lundstrom, L., Norgren, M., and Wagberg, L., (2009). Adsorption behavior and adhesive properties of biopolyelectrolyte multilayers formed from cationic and anionic starch. *Biomacromolecules* 10, 1768-1776.
- Koubaa, A., and Koran, Z., (1995). Measure of the internal bond strength of paper/board. *Tappi Journal* 78 (3), 103-111.
- Lindstrom, T., and Floren, T., (1984). The effects of cationic starch wet end addition on the properties of clay filled papers. *Svensk Papperstidn* 87 (12), 99-104.
- Lundstrom, H. L., Johansson, E., and Wagberg, L., (2010). Polyelectrolyte multilayers from cationic and anionic starch: Influence of charge density and salt concentration on the properties of adsorbed layers. *Starch* 62, 102-114.
- Magnus, G., Magnus, O., Soren, O., and Wagberg, L., (2011). Influence of beating and chemical additives on residual stresses in paper, *Nordic Pulp & Paper Research Journal* 26(4), 445-451.

- Marton, J., and Marton, T., (1976). Wet end starch: Adsorption of starch on cellulosic fibers. *Tappi Journal* 59(12), 121-124.
- Moeller, H. W., (1994). Cationic Starch as a Wet End Strength Additive. *Tappi Journal* 1966, 49(5), 211-214.
- Norman, B., and Wahren, D., (1976). *Mass Distribution of Sheet Properties of Paper*. Trans. BPBIF Symp. Fund. Props. Paper Related to Uses. Cambridge. 7-70.
- Paulapuro, H., (2000). Papermaking. *Part I: Stock Preparation and Wet End*. Papermaking Science and Technol. Ser. No. 8. Fapet Oy. Helsinki.
- Pettersson, G., Hogland, H., and Wagberg, L., (2006). The use of polyelectrolyte multilayers of cationic starch and CMC to enhance strength properties of papers formed from mixtures of unbleached chemical pulp and CTMP. Part II Influence of addition strategy, fibre treatment and fibre type. *Nordic Pulp & Paper Research Journal* 21(1), 122-128.
- Podsiadlo, P., Choi, S. Y., Shim, B., Lee, J., Cuddihy, M., and Kotov, N., (2005). Molecularly engineered nanocomposites: layer-by-layer assembly of cellulose nanocrystals. *Biomacromolecules* 6, 2914–2918.
- Pycraft, C. J. H., and Howarth, P., (1980). Does better paper mean worse waste paper? Paper. *Indian Journal of Technology* 21(12), 321-324.
- Roberts, J. C., Au, C. O., Clay, G. A., and Lough, C., (1986). The effect of C14-labelled cationic and native starches on dry strength and formation. *Tappi Journal* 69(10), 88-93.
- Rudi, H., Hamzeh, Y., Ebrahimi, G., Behrooz, R., and Nazhad, M. M., (2012). Influence of pH and conductivity on properties of paper made of polyelectrolyte multilayered recycled fibers. *Industrial and Engineering Chemistry Research* 51 (34), 11054–11058.
- Seth, R. S., Soszynski, R. M., and Page, D. H., (1979). Intrinsic edgewise compression strength of paper. *Tappi Journal* 62(12), 97-99.
- Wagberg, L., Forsberg, S., Johansson, A., and Juntti, P., (2002). Engineering of fibre surface properties by polyelectrolytes. *Journal of Pulp and Paper Science* 28, 222–9.
- Wang, Z., Hauser, P.J., Laine, J., and Rojas, O. J., (2011). Multilayers of Low Charge Density Polyelectrolytes on Thin Films of Carboxymethylated and Cationic Cellulose. *Journal of Adhesion Science and Technology* 25, 643–660.
- Weise, U., (1998). Hornification – Mechanisms and terminology. *Paperi ja Puu* 80(2), 110-115.
- Weise, U., Paulapuro, H., (1998). Relation between fiber shrinkage and hornification. *Prog. Paper Recycling* 7(3), 14-21.
- Xing, Q., (2007). Cellulose Fiber-Enzyme Composites Fabricated through Layer-by-Layer Nanoassembly. *Biomacromolecules* 8, 1987-1991.
- Zheng, Z., McDonald, J., Khillan, R., Grozdits, G., and Lvov, Y., (2006). Layer-by-layer nanocoating of lignocellulose fibres for enhanced paper properties *Journal of Nanoscience and Nanotechnology* 6, 624–32.

Article Submitted: August 13, 2014; Peer review completed: September 20, 2014;
Revised version received and accepted: October 15, 2014; Published: December 9, 2014.