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Cellulose fibre networks reinforced with carboxymethyl cellulose/chitosan complex layer-by-layer

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ABSTRACT

An eco-friendly and full-polysaccharide polyelectrolyte complex system was developed to enhance the wet and dry tensile strength of cellulose fibre networks. Cellulose fibres were treated by carboxymethyl cellulose (CMC) in pulp suspension. Paper sheets made from CMC-treated fibres were further modified via the layer-by-layer (LbL) deposition of CMC/chitosan (CS) complex. The effect of number of CMC/CS layers on the strength properties of cellulose fibre networks (both under wet and dry conditions) was studied and sample structure was investigated by scanning electron microscopy (SEM). Water vapour transmission rate (WVTR) of CMC/CS-treated samples was also examined. The observed changes in the strength properties of treated samples were explained based on the competition between the rate of diffusion of CS to the fibre–fibre bond areas and the rate of disassociation of fibre–fibre interactions during the LbL deposition process.

1. Introduction

Cellulose is the most abundant biopolymer on earth, as well as a biodegradable and renewable resource. Cellulose fibres obtained from plant materials have been used in papermaking for thousands of years (Hansson, Östmark, Carlmark, & Malmström, 2009). Mechanical properties of paper are significantly affected by the strength of joints between cellulose fibres (Davison, 1972). Fibre–fibre joints can be improved by increasing the molecularly bonded area, enhancing the strength of bonds in this area, or both. Mechanical treatment of fibres, e.g. beating and refining, is commonly used to increase the fibre–fibre bonded area (Emerton, 1957). However, to further improve the strength properties of paper, especially for wet-web strength (i.e. strength of never-dried paper) and wet strength (i.e. strength of rewetted paper), strength additives are needed to enhance the adhesion between adjacent cellulose fibres. This may be achieved, for example, by introducing functional groups onto the surface of cellulose fibres and subsequent cross-linking reaction in fibre suspension and/or during the drying process.

Several polymeric wet strength additives have been reported in the literature, such as polyamidoamine–epichlorohydrin (PAE) (Keim, 1960), urea-formaldehyde (Britt, 1943), melamine–formaldehyde (Devore & Fischer, 1993), glyoxal polyacrylamide (Alince, Vanerek, de Oliveira, & van de Ven, 2006), polyvinylamine (Miao, Leduc, & Pelton, 2008), poly(maleic acid) (Yang & Xu, 1998; Zhou, Luner, & Caluwe, 1995), poly(vinyl alcohol) (Xu, Yang, & Den, 2006), and cationic poly(vinyl alcohol) (Fatehi & Xiao, 2008). These polyelectrolytes are able to be adsorbed onto the fibre surface through ion exchange process and participate in cross-linking reactions (Wågberg, 2000). Among the above wet strength additives, PAE is the most commonly used agent (Boden, Lundgren, Stensio, & Gorzynski, 1997). It has been reported that wet strength of paper could be improved by 900–1400% with 2–6% PAE addition (on dry fibres) (Obokata & Isogai, 2007).

In recent years, environmental concerns are driving the need for developing new eco-friendly wet strength additives that reduce the dependence on petroleum-derived chemicals. Accordingly, several polyelectrolytes derived from natural polymers have been developed and examined for their wet-web strength performance, including cationic starch (Laleg & Pikulik, 1993), chitosan (CS) (Muzzarelli, 1977; Rinaudo, 2006) and carboxymethyl cellulose (CMC) (Watanabe, Gondo, & Kitao, 2004). Such polyelectrolytes are able to adsorb on the surface of fibres in aqueous solutions and increase fibre-to-fibre interactions by increasing the number of bonds between fibres (Scott, 1996). For example, it has been

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reported that the wet-web strength of paper made of bleached kraft pulp improved by about 50% at 50% solids content upon 2% cationic aldehyde starch addition (Laleg & Pikulik, 1991). In a separate study, CMC-treated cellulose fibres were cross-linked overnight by adipic acid dihydrazide in pulp suspensions and an increase of ~500% was achieved in wet-web strength at 40% solids content (Reddy, Li, & Yang, 2009).

An alternative approach to improve the strength of paper is the use of polyelectrolyte complex systems. Oppositely charged polyelectrolyte pairs, such as PAE/CMC (Gärdlund, Wågberg, & Gernandt, 2003; Gernandt, Wågberg, Gärdlund, & Dautzenberg, 2003), CMC/polyvinylamine (Feng, Pouw, Leung, & Pelton, 2007) and CMC/CS (Fatehi, Kititerakun, Ni, & Xiao, 2010; Fatehi, Qian, Kititerakun, Rirksomboon, & Xiao, 2009), were studied and reported to be effective wet strength additives. This technique has been widely used for layer-by-layer (LbL) self-assembly for surface modification through constructing multilayers with tailored composition and properties on solid surface (Zhang et al., 2004). In particular, polyallylamine hydrochloride/polyacrylic acid complex LbL self-assembly has been employed to modify the surface of cellulose fibres to enhance the fibre–fibre joints in paper sheets (Eriksson, Torgnysdotter, & Wågberg, 2006).

In this work, we aim to develop an alternative approach to enhance the strength properties of cellulose fibre network through LbL self-assembly. The eco-friendly CMC/CS complex was deposited via dip-coating on wet paper sheets, rather mixing with the cellulose fibres in pulp suspensions. This treatment resulted in a significant improvement in wet-web strength, wet strength, and dry strength of cellulose fibre network. The mechanism of this improvement is discussed and the effect of the number of CMC/CS layers on the mechanical properties and water vapour transmission rate of modified cellulose fibre networks is investigated.

2. Experimental

2.1. Materials

Standard Eucalyptus hardwood bleached Kraft pulp was purchased from NIST (Aracruz Celulose S.A., Brazil). Chitosan (CS) with a low molecular weight (deacetylation ≥ 75%), carboxymethyl cellulose sodium salt (CMC) (M_w ~ 90,000 g/mol), calcium chloride ($CaCl_2$) and acetic acid were purchased from Sigma-Aldrich (Canada). All experiments and cleaning steps were performed using water treated by a Milli-Q Plus purification system (Millipore) with a pH of 6.3 and a resistivity of 18.2 M Ω cm.

2.2. Preparation of CMC-treated cellulose fibres and paper sheets

Aqueous pulp suspension (2 g dried pulp) was prepared in a pulp disintegrator and then treated with CMC following the general recipe reported in the literature (Laine, Lindstrom, Nordmark, & Risinger, 2000). Briefly, 0.12 g of CMC was initially dissolved in water at 1 wt.% concentration and added to 100 g of pulp suspension (2 wt.%) under constant stirring, together with 6 mL of 1 M $CaCl_2$. The mixture was heated at boiling temperature for 2 h in a glass flask equipped with a condenser to prevent water evaporation. The CMC-treated cellulose fibres were washed twice to remove excess CMC by filtering and re-dispersing them in Milli-Q water. A 0.1 wt.% suspension of CMC-treated cellulose fibres was used for making paper sheets with grammages of 25 g/m^2, 50 g/m^2 and 100 g/m^2 using a British handsheet making machine according to Tappi standard T205. After pressing each sheet between blotters at 350 kPa for 5.5 min to partially remove water, fresh wet sheets were used for LbL deposition of CMC/CS complex. Control samples containing untreated cellulose fibres were also prepared under similar conditions.

2.3. LbL deposition of CMC/CS complex

Wet CMC-treated cellulose fibre sheets were first immersed into a solution of positively charged CS (2.5 mg/mL) for 10 min, and washed using Milli-Q water for 15 min. The washing step was repeated for three times to remove excess CS. It should be noted that although chitosan itself is insoluble in water, protonated chitosan is water soluble (Fatehi et al., 2009, 2010). Subsequently, the sheets were immersed into a solution of negatively charged CMC (2.5 mg/mL) for 10 min and washed again to remove excess CMC. The above steps were repeated successively until the desired number of CMC/CS layers was attained. All CMC/CS-treated samples were finished with the CS deposition as the last treatment step. These samples were labeled as $(CMC/CS)_x$, where x indicated the number of CMC/CS layers. For wet-web tensile tests, the treated sheets were cut into even strips (25 mm wide) and allowed to dry under controlled conditions (23 °C, 50% relative humidity) until the desired solids content (i.e. dryness) was achieved. For all other test, the strips were conditioned for 48 h prior to testing at 23 °C, 50% relative humidity.

2.4. Characterization and measurements

Samples were characterized using scanning electron microscopy (SEM, JSM-6610LV, JEOL, Japan). Prior to SEM observations, the sample was coated with gold using an SPI sputter coater for enhanced conductivity.

The tensile index of samples was measured using a SinTech universal testing machine according to TAPPI T 494 and T 456. For each sample, five strips with a span of 100 mm were tested at an elongation rate of 14 mm/min. For wet tensile index, i.e. tensile index of rewetted sample, dry samples were re-wetted for 30 min in Milli-Q water and were partially dried in air prior to testing until the desired solids content was reached.

The water vapour transmission rate (WVTR) of cellulose fibre network was determined gravimetrically according to ASTM E-96-97 method. The specimen was mounted on top of a metal cup to form an air gap of approximately 6 mm between surface of the sample and the desiccant. The desiccant was 10 g of anhydrous calcium chloride that created a relative humidity of ~0% below the specimen. The cup was weighed at 1 h intervals and a plot of weight loss versus time was used to determine WVTR from the steady-state region. Three specimens were tested for each sample and the average values were reported.

3. Results and discussion

3.1. Effect of chitosan deposition on tensile index of wet webs

A series of CS solutions with concentrations ranging from 10 mg/mL to 0.31 mg/mL in 1% acetic acid were prepared and used for the dip coating of CMC-treated samples. Fig. 1 shows the tensile index of wet webs (never-dried paper sheets) at 30% solids content, i.e. containing 70% water, as a function of the concentration of CS solution. It can be seen that the tensile index for the control sample (i.e. made of untreated fibres) was relatively low (0.65 N m/g) and did not change significantly after soaking in CS solutions. This suggests that in the absence of CMC, CS chains did not deposit efficiently on fibres and hence did not improve the fibre–fibre bonding. In the case of CMC-treated sheets prior to dipping in CS solution, the wet-web tensile index at 30% solids content was 0.47 N m/g that was less than that of the control sample. This may be due to the charge repulsion caused by the presence of CMC on the fibre

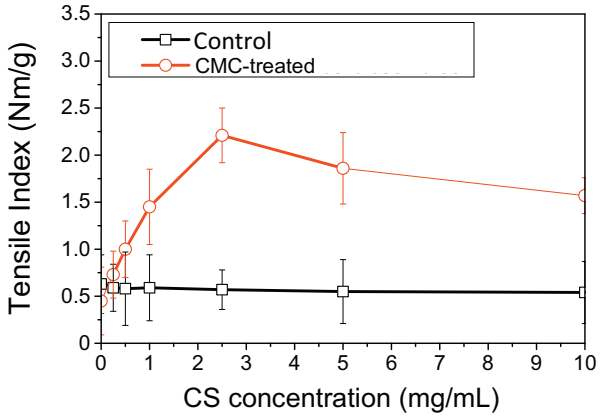
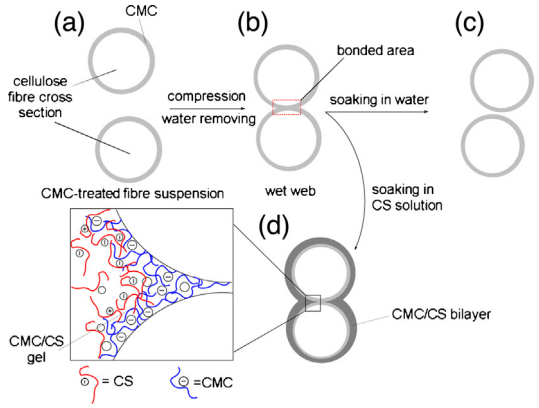


Fig. 1. Tensile index of CMC-treated and control samples at 30% solids after soaking in CS solutions.



Scheme 1. Proposed mechanism for the improvement of fibre–fibre bond by CMC/CS bilayer deposition.

surfaces. Such interactions could enhance the diffusion of water molecules into the bonded area and hence interrupt the fibre–fibre joints. Upon soaking CMC-treated sample in CS solution, the wet-web tensile index increased and reached a maximum of 2.3 N m/g at a CS concentration of 2.5 mg/mL. This peak value of wet-web tensile index was 280% higher than that of the control sample made of untreated cellulose fibres.

The above result suggests that the concentration of CS solution is an important factor to achieve optimum enhancement in the wet-web tensile index of samples. This phenomenon can be explained by the nature of the CS deposition. As illustrated in Scheme 1, it is proposed that fibre–fibre adhesion is governed by the competition between the deposition of CS to 'weld' the bonded area and the disassociation of fibre–fibre interactions. Once CMC-treated samples are soaked in water, fibre–fibre interactions (predominantly hydrogen bonds) are interrupted and cellulose fibres will be increasingly separated by water molecules (Scheme 1(c)) resulting in a relatively low wet-web tensile index. The fibre–fibre adhesion can be improved by introducing polymers; such as CS, that are long enough to reach adjacent cellulose fibres and 'bridge' between them (McKenzie, 1984). The competition between the rate of deposition of CS and the rate of disassociation of fibre–fibre interactions results in an optimum CS concentration, at which the improvement of fibre–fibre adhesion is maximized. At a low concentration of CS, there is insufficient amount of CS near cellulose fibres to weld the bonded area in a timely fashion and to prevent the excessive separation of fibres. Once fibre separation at the bonded area exceeds a critical value, CS chains are no longer able to effectively bridge between them and weld the joints. On the other hand, at very high

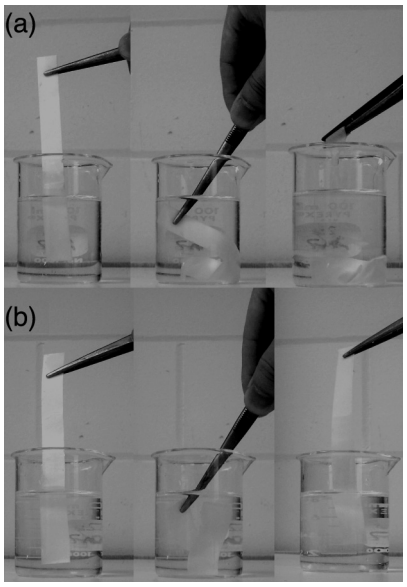


Fig. 2. Photographs showing CMC-treated samples (a) immersed in Milli-Q water, and (b) immersed in CS solution (2.5 mg/mL). From left to right: immediately before immersion, immediately after immersion, after 10 min soaking.

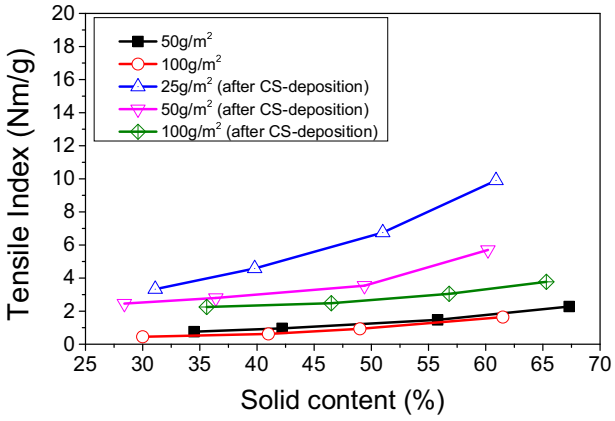


Fig. 3. Tensile index of CMC-treated cellulose fibre networks with various paper grammages as a function of solids content. The concentration of CS solution is 2.5 mg/mL.

CS concentrations, the high viscosity of the solution will reduce the diffusion rate of CS chains that will also lead to the reduction in the deposition rate of CS at the joints and hence weakening of the fibre–fibre bonds.

Fig. 2 demonstrates the role of CS in improving the wet-web strength of CMC-treated samples. As seen in Fig. 2a, CMC-treated sheets disintegrated readily after 10 min soaking in Milli-Q water. However, soaking the sample in CS for 10 min resulted in a significant enhancement in the wet strength and the sample maintained its physical integrity (Fig. 2b).

The effect of CS-deposition on wet-web tensile index of CMC-treated samples was dependent on the paper grammage. Fig. 3 shows the effect of solids content on the wet-web tensile index of samples with different grammages. Without CS treatment, wet-web tensile index of untreated samples with grammages of 100 g/m^2 and 50 g/m^2 were similar and increased by six folds to 2.5 N m/g as the solids content raised from 30% to about 67%. It should be noted that the attempt to measure wet-web tensile index of untreated sheets with a grammage of 25 g/m^2 failed due to their weak structure and disintegration during handling. However, after soaking in CS solution, the effect of sheet grammage on the

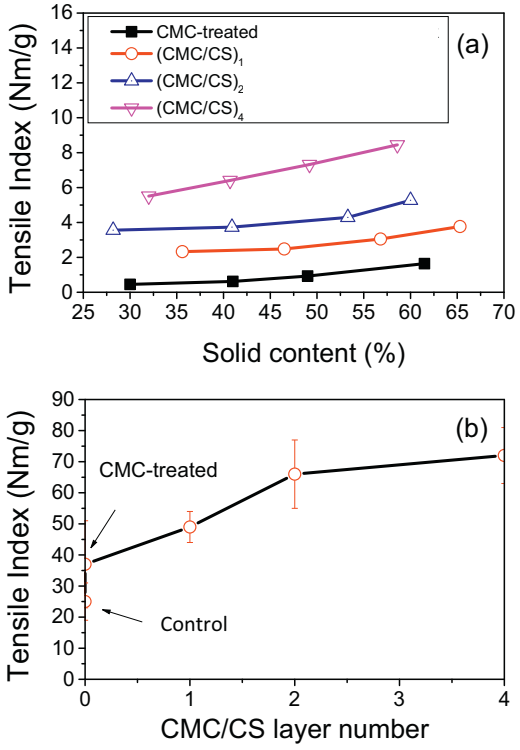


Fig. 4. (a) Wet-web tensile index as a function of solids content and number of CMC/CS layers, and (b) dry tensile index as a function of the number of CMC/CS layers.

wet-web tensile index became noticeable. At a given solids content, wet-web tensile index increased by increasing sheet grammage. The wet-web tensile indices at 40% solids content were 4.8 N m/g, 3.4 N m/g and 2.5 N m/g for sheet grammage of 25 g/m^2, 50 g/m^2 and 100 g/m^2, respectively. That is, tensile index at 40% solids for the 25 g/m^2 sample was 92% higher than that of 100 g/m^2 sample. This is likely due to the thicker structure of 100 g/m^2 sample that reduces the rate of diffusion and hence concentration of CS inside the sheet. As discussed earlier, reduction in CS availability at the vicinity of fibre–fibre bond areas could reduce the ability of CS to bridge between the fibres and weld the joints, hence compromise the beneficial effect of CS on the wet-web tensile index.

3.2. Effect of CMC/CS complex layer number on strength properties

Fig. 4a shows the effect of CMC/CS layer number on wet-web tensile index of samples. It can be seen that tensile index increased with increasing the layer number of CMC/CS complex. At 50% solids, the increase in the wet-web tensile index were 150%, 300% and 650% for $(CMC/CS)_1$, $(CMC/CS)_2$ and $(CMC/CS)_4$, respectively, in comparison with the CMC-treated sample. As seen in Fig. 4b, the tensile index of dry sheets exhibited a similar trend and increased with the number of CMC/CS layers. The values of dry tensile index for control and CMC-treated samples were 26 N m/g and 37 N m/g, and 66 N m/g, respectively. The observed increase in the tensile strength of dry sheets containing CMC is in good agreement with the results reported in the literature (Watanabe et al., 2004). Dry tensile index increased 81%, 154% and 177% for $(CMC/CS)_1$, $(CMC/CS)_2$ and $(CMC/CS)_4$, respectively, in comparison with that of the control sample. The improvement in the dry strength may be due to the formation of covalent bonds during the drying process as a result of imine and aminal linkages between CS and cellulose fibres as well as amide bonds between CMC and CS (DiFlavio et al., 2007; El-Ghaffar & Hashem, 2010). These covalent linkages will further benefit the fibre–fibre joints and ultimately the strength properties of cellulose fibre networks.

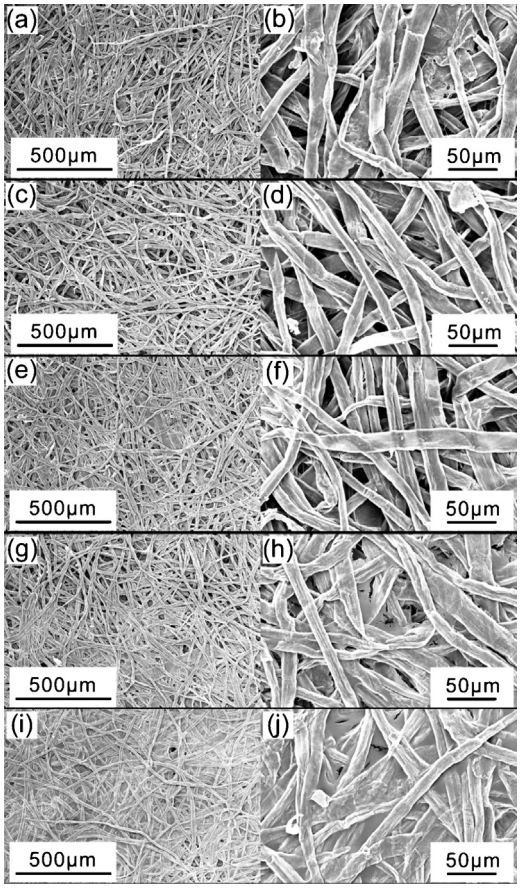


Fig. 5. SEM images of control (a and b), CMC-treated (c and d), $(CMC/CS)_1$ (e and f), $(CMC/CS)_2$ (g and h), and $(CMC/CS)_4$ (i and j) samples.

SEM images of control sample, CMC-treated sample and multilayer CMC/CS treated samples are provided in Fig. 5. Comparing Fig. 5a and c, it can be seen that CMC treatment resulted in a looser sheet structure. This might be due to increase in the charge density of fibre surface caused by CMC presence that resulted in higher charge repulsion (Laine et al., 2000). However, as shown in Fig. 5c–j, with increasing the number of layers and hence the amount of CMC/CS there appears to be more bridging and bonding between fibres. This observation is consistent with the higher tensile index of CMC/CS-treated samples, as discussed earlier. Close examination of Fig. 5 also shows that with increased number of layers, the CMC/CS complex forms a thin film on the surface. This observation suggests that the LbL deposition method developed in this study differs from conventional polyelectrolyte bilayer deposition techniques since the amount of CMC/CS complex used here is much larger than what is used for conventional LbL assembly that is usually at nanoscale (Wee & Hong, 2013). This might be related to the high solubility of CMC/CS complex which forms gel rather than precipitating in the process solution. It is due to this unique property that the CMC/CS is highly efficient in improving fibre–fibre bonding.

The wet tensile index of samples also increased with increasing the number of CMC/CS layers (Fig. 6). At 50% solids content, the wet tensile indices of $(CMC/CS)_1$, $(CMC/CS)_2$, and $(CMC/CS)_4$ were 200%, 750% and 1100% larger than that of control sample, respectively. This may be again attributed to the increasing amount of CMC/CS complex in the sheet structure which reinforced the fibre–fibre adhesion. It is worth mentioning that the CMC-treated sample

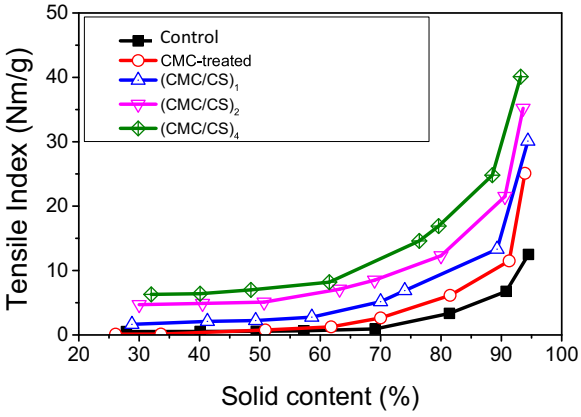


Fig. 6. Effect of LbL deposition of CMC/CS on the wet tensile index as a function of solids content.

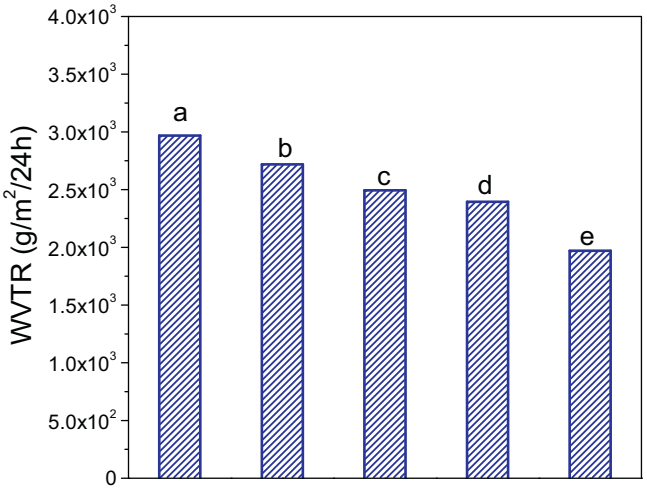


Fig. 7. WVTR of samples before and after CMC/CS treatment: (a) control sample, (b) CMC-treated sample, (c) $(CMC/CS)_1$, (d) $(CMC/CS)_2$, and (e) $(CMC/CS)_4$.

(i.e. without CS addition) exhibited a similar wet tensile index compared to the control sample up to a solids content of 60%. At higher solids contents, the reinforcing effect of CMC in enhancing the wet strength property of the sheet became noticeable.

3.3. Effect of CMC/CS complex layer number on water vapour transmission rate (WVTR)

Both CMC treatment and LbL deposition of CMC/CS reduced the WVTR of the samples. As seen in Fig. 7, WVTR was about 2970 g/m^2/24 h for control sample and 2750 g/m^2/24 h for CMC-treated sample. This finding suggests that CMC not only enhanced the fibre–fibre adhesion, but also increased the bonded area, which resulted in the reduction of pore volume and lowering of WVTR. Similarly, with increasing the number of CMC/CS layers, WVTR progressively decreased. $(CMC/CS)_1$, $(CMC/CS)_2$, and $(CMC/CS)_4$ exhibited 17%, 20% and 33% lower WVTR compared to the control sample, respectively. This is expected since as seen in Fig. 5, with increasing the amount of CMC/CS complex, sample surface was increasingly covered by CMC/CS film hence reducing the sheet porosity.

4. Conclusions

LbL deposition of full-polysaccharide polyelectrolyte complex (CMC/CS) on wet paper sheets can significantly enhance the wet and dry strength properties of paper. Cellulose fibres were treated by CMC to increase the negative charge density of fibre surface and used to form paper sheets. These samples were further dip coated with multiple layers of CMC/CS complex. The observed enhancement in the strength properties of CMC-treated cellulose fibre networks after dipping in the CS solution is believed to be governed by the competition between the deposition of CS and the disassociation of fibre–fibre interactions in the bonded area. Using LbL deposition method, samples containing up to four layers of CMC/CS complex were prepared in this work. Wet-web strength, dry strength and wet strength of samples were enhanced with increasing the CMC/CS layer number. Compared to the control (untreated) sample, the wet-web tensile index of CMC/CS treated sheets at 50% solids was improved by up to 650%, while the dry tensile index and the wet tensile index increased by 177% and 1100%, respectively. LbL deposition of CMC/CS also resulted in reduced water vapour transmission rate by up to 33%. This study provides a useful approach to prepare high-performance value-added specialty wood–fibre based products.

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References

Alince, B., Vanerek, A., de Oliveira, M. H., & van de Ven, T. G. M. (2006). The effect of polyelectrolytes on the wet-web strength of paper. *Nordic Pulp and Paper Research Journal*, *21*, 653–658.

Boden, L., Lundgren, M., Stensio, K. E., & Gorzynski, M. (1997). Determination of 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol in papers treated with polyamidoamine–epichlorohydrin wet-strength resins by gas chromatography mass spectrometry using selective ion monitoring. *Journal of Chromatography A*, *788*, 195–203.

Britt, K. W. (1943). High-wet-strength paper. USA patent 2325302.

Davison, R. W. (1972). Weak link in paper dry strength. *Tappi Journal*, *55*, 567.

Devore, D. I., & Fischer, S. A. (1993). Wet-strength mechanism of polyaminoamide–epichlorohydrin resins. *Tappi Journal*, *76*, 121–128.

DiFlavio, J., Pelton, R., Leduc, M., Champ, S., Essig, M., & Frechen, T. (2007). The role of mild TEMPO–NaBr–NaClO oxidation on the wet adhesion of regenerated cellulose membranes with polyvinylamine. *Cellulose*, *14*, 257–268.

El-Ghaffar, M. A. A., & Hashem, M. S. (2010). Chitosan and its amino acids condensation adducts as reactive natural polymer supports for cellulase immobilization. *Carbohydrate Polymers*, *81*, 507–516.

Emerton, H. W. (1957). *Fundamentals of the beating process. The theory of the development in pulps of papermaking characteristics by mechanical treatment*. Kenley, UK: British Paper and Board Industry Research Association.

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

Fatehi, P., Kititerakun, R., Ni, Y., & Xiao, H. (2010). Synergy of CMC and modified chitosan on strength properties of cellulosic fiber network. *Carbohydrate Polymers*, *80*, 208–214.

Fatehi, P., Qian, L., Kititerakun, R., Rirksomboon, T., & Xiao, H. (2009). Complex formation of modified chitosan and carboxymethyl cellulose and its effect on paper properties. *Tappi Journal*, *8*, 29–35.

Fatehi, P., & Xiao, H. (2008). The influence of charge density and molecular weight of cationic poly(vinyl alcohol) on paper properties. *Nordic Pulp and Paper Research Journal*, *23*, 285–291.

Feng, X., Pouw, K., Leung, V., & Pelton, R. (2007). Adhesion of colloidal polyelectrolyte complexes to wet cellulose. *Biomacromolecules*, *8*, 2161–2166.

Gärdlund, L., Wågberg, L., & 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*, 137–149.

Gernandt, R., Wågberg, L., Gärdlund, L., & Dautzenberg, H. (2003). Polyelectrolyte complexes for surface modification of wood fibres: I. Preparation and characterisation of complexes for dry and wet strength improvement of paper. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *213*, 15–25.

Hansson, S., Östmark, E., Carlmark, A., & Malmström, E. (2009). ARGET ATRP for versatile grafting of cellulose using various monomers. *ACS Applied Materials and Interfaces*, *1*, 2651–2659.

Keim, G. I. (1960). Wet-strength paper and method. USA patent 2926116.

Laine, J., Lindstrom, T., Nordmark, G. G., & Risinger, G. (2000). Studies on topochemical modification of cellulosic fibres—Part 1. Chemical conditions for the

attachment of carboxymethyl cellulose onto fibres. *Nordic Pulp and Paper Research Journal*, *15*, 520–526.
Laleg, M., & Pikulik, I. I. (1993). Modified starches for increasing paper strength. *Journal of Pulp and Paper Science*, *19*, J248–J255.
Laleg, M., & Pikulik, I. I. (1991). Web strength increase by a cationic aldehyde starch. In *1991 Papermakers conference*.
McKenzie, A. W. (1984). The structure and properties of paper. Part XXI: The diffusion theory of adhesion applied to interfiber bonding. *Appita Journal*, *37*, 580.
Miao, C., Leduc, M., & Pelton, R. (2008). The influence of polyvinylamine microgels on paper strength. *Journal of Pulp and Paper Science*, *34*, 69–75.
Muzzarelli, R. A. (1977). *Chitin*. Oxford: Pergamon Press.
Obokata, T., & Isogai, A. (2007). The mechanism of wet-strength development of cellulose sheets prepared with polyamideamine–epichlorohydrin (PAE) resin. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *302*, 525–531.
Reddy, N., Li, Y., & Yang, Y. (2009). Wet cross-linking gliadin fibers with citric acid and a quantitative relationship between cross-linking conditions and mechanical properties. *Journal of Agricultural and Food Chemistry*, *57*, 90–98.
Rinaudo, M. (2006). Chitin and chitosan: Properties and applications. *Progress in Polymer Science*, *31*, 603–632.
Scott, W. E. (1996). *Dry strength additives principles of wet end chemistry*. Atlanta, GA: TAPPI Press.
Wågberg, L. (2000). Polyelectrolyte adsorption onto cellulose fibres: A review. *Nordic Pulp and Paper Research Journal*, *15*, 586–597.
Watanabe, M., Gondo, T., & Kitao, O. (2004). Advanced wet-end system with carboxymethyl-cellulose. *Tappi Journal*, *3*, 15–19.
Wee, B. H., & Hong, J. D. (2013). A method for fabricating an ultrathin multilayer film composed of poly(*p*-phenylenevinylene) and reduced graphene oxide on a plastic substrate for flexible optoelectronic applications. *Advanced Functional Materials*, *23*, 4657–4666.
Xu, G. G. Z., Yang, C. Q. X., & Den, Y. L. (2006). Mechanism of paper wet strength development by polycarboxylic acids with different molecular weight and glutaraldehyde/poly(vinyl alcohol). *Journal of Applied Polymer Science*, *101*, 277–284.
Yang, C. Q., & Xu, Y. (1998). Paper wet performance and ester crosslinking of wood pulp cellulose by poly(carboxylic acid)s. *Journal of Applied Polymer Science*, *67*, 649–658.
Zhang, X., Shi, F., Yu, X., Liu, H., Fu, Y., Wang, Z., et al. (2004). Polyelectrolyte multilayer as matrix for electrochemical deposition of gold clusters: Toward super-hydrophobic surface. *Journal of the American Chemical Society*, *126*, 3064–3065.
Zhou, Y. J., Luner, P., & Caluwe, P. (1995). Mechanism of crosslinking of papers with polyfunctional carboxylic acids. *Journal of Applied Polymer Science*, *58*, 1523–1534.