Carbohydrate Polymers 114 (2014) 500–505

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

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

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ARTICLE INFO

Article history:
Received 6 April 2014
Received in revised form 19 July 2014
Accepted 22 August 2014
Available online 30 August 2014

Keywords:
Cellulose fibre
Layer-by-layer
Polyelectrolyte complex
Wet web strength
Wet strength
Water vapour transmission rate

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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http://dx.doi.org/10.1016/j.carbpol.2014.08.053
0144-8617/

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) ($M_w \sim 90{,}000$ 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