

Effect of Cationic Hemicellulosic Fractions from Corncob Obtained by Graded Ethanol Precipitation on Recycled Paper Strength

Xiaoting Zhang,^a Yushuang Zhao,^a Zehong Chen,^a Shuangshuang Jing,^a Hao Zhuo,^a Yijie Hu,^a Linxin Zhong,^{a,*} Xinwen Peng,^{a,*} and Runcang Sun^{a,b}

This study investigated how various hemicellulosic fractions extracted from corncob, which have different chemical structures, affect paper strength properties when derivatized and used as paper strengthening agents. Four hemicellulosic fractions with different molecular weights and heteropolymer branching were extracted from corncob *via* a selective precipitation process; afterwards, the fractions were then chemically modified to obtain cationic hemicelluloses, which were used as strengthening agents for recycled pulp papermaking. These cationic hemicellulosic fractions improved the mechanical strengths of handsheets composed of recycled fibers and paper machine white water fines; however, the level of improvement was different among the fractions. Cationic hemicellulosic fractions showed a better improvement on the strength of handsheets without fines than that of the handsheets with fines. Especially, cationic hemicellulosic fraction obtained from 30% ethanol aqueous medium had the highest molecular weight and the highest substitution degree and thus showed the best enhancement in the mechanical strength of handsheets. Hence, this work demonstrates how to utilize hemicelluloses efficiently as strength agents for recycled pulp papermaking.

Keywords: Cationic hemicelluloses; Recycled pulp fiber; Graded ethanol precipitation; Paper strength

Contact information: a: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China; b: Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing, China; *Corresponding authors: lxzhong0611@scut.edu.cn; fexwpeng@scut.edu.cn

INTRODUCTION

Much research has been conducted with recycling various materials to minimize natural resource shortages and environmental emissions. In the papermaking industry, recycling waste paper as a fiber source represents an essential way to reduce the depletion of forest and energy resources, in addition to reducing environmental pollution. The mechanical strength of paper made from recycled waste paper fibers is lower than that from virgin fibers; this phenomenon is attributed to the hornification of recycled fibers during repeated cycles of drying and repulping during papermaking (Bhardwaj *et al.* 2005; Salgueiro *et al.* 2016). In order to improve the mechanical properties of paper made from recycled fibers, strengthening additives are often added to the slurry of recycled pulp during the papermaking process.

Widely used strengthening aids for papermaking include starch (Mohamed *et al.* 2010; Tan *et al.* 2011), polyacrylamide (Wang and Jing 2014), polyvinyl acetate (PVA) (Hamzeh *et al.* 2013a; Hamzeh *et al.* 2013b), and hemicelluloses (Fatehi *et al.* 2010; Salgueiro *et al.* 2016). Among these functional polymers, strengthening agents derived from the hemicelluloses are especially attractive because these polysaccharides can be obtained easily from various forest

wastes or agriculture resources, as well as from the pulp mill (as by-products during chemical pulping). Furthermore, hemicelluloses are natural polysaccharides that constitute 20% to 40% of most lignocellulosic plants; its abundance is only second to cellulose and it can be extracted by hot water or by select solvents (Kong *et al.* 2014). Hemicelluloses are branched and have an amorphous structure with various functional groups (*e.g.*, hydroxyl, acetoxy, carboxyl, and methoxyl groups), which can interact with similar functional groups contained in cellulose fibers to enhance fiber-to-fiber bonding. Wang *et al.* (2015) prepared glucomannans that had been carboxymethylated as a paper strength additive; this additive improved the mechanical strength properties of paper handsheets. Oxidized hemicelluloses are also promising paper strength additives. Song and Hubbe (2014a) prepared β -D-glucans oxidized by the TEMPO-mediated process, which were then added to pulp slurries to enhance paper strength of laboratory-made paper handsheets. Etherification of hemicelluloses with cationic functional groups enhanced the solubility of the modified polysaccharides, and created cationic or amphoteric heteropolymers (Ren *et al.* 2007a). Deuschle *et al.* (2014) prepared cationic xylans, derived from oat spelt and wheat, as papermaking additives to enhance paper strength; cationic xylans from oat spelt afforded better paper strength improvement. Song and Hubbe (2014b) also prepared cationic β -D-glucans as a dry-strength additive for paper. These literature examples indicate that chemically modified hemicelluloses have a promising application as effective paper strengthening agents. To the best of our knowledge, however, the use of hemicelluloses or their derivatives as a papermaking additive to improve recycled paper strength has not been reported in the literature.

Hemicelluloses are a group of plant polysaccharides with different compositions, structures, molecular weights, and physicochemical properties. However, it is unknown how these polysaccharide factors affect paper strength when this heteropolymer is used as a papermaking additive. In this work, four hemicellulosic fractions with different molecular weights and degrees of polymer branching were extracted from corncob *via* a selective precipitation process using ethanol; these fractions were chemically modified and examined as paper strength aids for recycled paper production. The results from this study will demonstrate that these fractionated and derivatized hemicellulosic fractions can improve mechanical strength of laboratory handsheets made from recycled fibers to different degrees. The degree of paper strength improvement was dependent upon the physicochemical properties of the hemicellulosic fractions. Hemicelluloses obtained from 30% ethanol solution fraction, which were then cationized, were shown to enhance the mechanical strengths of handsheets made from recycled newsprint the most.

EXPERIMENTAL

Materials

Corn cob was obtained from a farm in Shandong Province, China. The waste newspaper pulp (China) and fines (fines contain 88% ash and 12% inorganic fillers) were obtained from Guangzhou Paper Group Ltd. The fines were obtained by filtering paper machine white water through a 200-mesh screen. Sodium hydroxide (NaOH) and 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (CHMAC) were purchased from Aladdin (China).

Methods

Fractionation of hemicelluloses by graded ethanol precipitation

A 3000 mL Erlenmeyer flask with 1950 mL distilled water was heated to 75 °C. To this flask was added, while stirring, 15 mL glacial acetic acid, 26 g sodium chlorite, and 60 g bone-dried (b. d.) corncob power. Another 15 mL glacial acetic acid and 26 g sodium chlorite were added to the flask after 1 h of reaction; the mixture was allowed to react for another hour at 75 °C. Subsequently, the flask was placed into an ice water bath to stop the reaction. The solid product was filtered, washed with water five times, and air-dried to obtain the holocellulose fraction.

Hemicelluloses were obtained from the holocellulose fraction by extracting the above air-dried solid with 10% KOH solution (at solids-to-liquor ratio of 1 g-to-20 mL) for 16 h at room temperature. Upon the completion of the KOH extraction, the mixture pH was adjusted to 5.5 with the addition of an acetic acid solution; the hemicelluloses precipitated at this step were recovered by filtration. The obtained solid was washed with 70% ethanol and freeze-dried to obtain the hemicellulosic fraction designated as H_{pH5.5}. The supernatant from filtration was mixed with a 35% ethanol solution until a final ethanol concentration of 15% was obtained. The hemicelluloses precipitated from this step were then recovered by filtration, washed with 70% ethanol, and freeze-dried to obtain the hemicellulosic fraction designated as H_{15%}. Similarly, the hemicellulosic fractions designated as H_{30%} and H_{75%} were obtained by precipitating subsequent supernatants from filtration with 30% and 75% ethanol solutions, respectively.

Synthesis of the cationic hemicellulosic derivatives

Cationic hemicelluloses were synthesized in a three-neck round-bottom flask fitted with a mechanical stirrer and a reflux condenser. A hemicellulosic fraction (0.66 g) was dispersed in 20 mL distilled water and heated to 60 °C for 20 min; afterwards, 0.48 g NaOH was added to the flask and stirred for 20 min at 60 °C. Subsequently, 2.17 g CHMAC was added while stirring. The reaction mixture was stirred for 5 h at 60 °C. Afterwards, the solution was cooled to room temperature and then neutralized with 0.1 M HCl. A precipitate was obtained from the neutralized solution by the addition of 80% ethanol solution. The resulting precipitate was filtered from the supernatant, and the solid was washed thoroughly with 95% ethanol to remove spent reagents. The purified product was first air-dried for 12 h and then dried in an oven at 45 °C for 24 h. The cationic hemicellulosic fractions from H_{pH5.5}, H_{15%}, H_{30%}, and H_{75%} were designated as CH_{pH5.5}, CH_{15%}, CH_{30%}, and CH_{75%}, respectively.

Determination of degree of substitution (DS) of cationic hemicellulosic fractions

The nitrogen and carbon contents of the cationic hemicellulosic derivatives were measured using a Vario EL II Elemental Analyzer (Elementar; Hanau, Germany). The degree of substitution (DS) was calculated from the ratio of nitrogen to carbon content of cationized hemicelluloses according to the following equation:

$$DS = (60 \times N) / (14 \times C - 72 \times N) \quad (1)$$

where *N* and *C* are the mass percentages of nitrogen and carbon from the elemental analysis (Ren *et al.* 2009).

Preparation and testing of paper handsheets

CH_{pH5.5}, CH_{15%}, CH_{30%}, and CH_{75%} were individually dissolved in water to generate 0.5% (w/v) solutions. Then the solutions were added into well-dispersed recycled pulp slurries, in the

absence and presence of paper machine white water fines, while stirring. Handsheets with a grammage of $60 \text{ g}\cdot\text{m}^{-2}$ were prepared according to TAPPI T 205 standard. The concentrations of cationic hemicellulosic fractions were 0.5%, 1.0%, 1.5%, and 2.0% (based on the b.d. mass of the pulp). Formed handsheets were placed in a constant temperature and humidity room ($23 \text{ }^\circ\text{C}$ and 50% relative humidity) for 24 h before testing. The tensile, tear, and burst strength properties of the handsheets were measured in accordance to TAPPI Standard Test Methods.

High-performance anion-exchange chromatography (HPAEC)

The neutral sugars in the hemicelluloses were determined by high-performance anion-exchange chromatography (HPAEC) using a Dionex ICS-3000 HPLC (Dionex; Sunnyvale, CA, USA) fitted with a gradient pump (GP-50), an amperometric detector (ED-50), an auto sampler (AS-50), and a DionexCarboPac™PA-20 column ($4\times 250 \text{ mm}$). The method was slightly modified from Sluiter *et al.* (2011): Neutral sugars were liberated by the hydrolysis of hemicellulosic fractions with 10% H_2SO_4 for 2.5 h at $105 \text{ }^\circ\text{C}$. After hydrolysis, the sample was diluted 50-fold, filtered, and injected into the HPLC. HPLC separations were performed using a 5 mM NaOH isocratic eluent (carbonate free and purged with nitrogen) for 20 min, which was then followed by a 0 to 75 mM sodium acetate gradient in 5 mM NaOH for 15 min at a constant flow rate of 0.5 mL/min. Then the HPLC column was washed with 200 mM NaOH to remove carbonate for 10 min, and followed by 5 min elution with 5 mM NaOH to re-equilibrate the column prior to the next injection. The total analysis time was 50 min. Calibrations were performed with standard solutions of L-arabinose, D-glucose, D-xylose, D-glucose, D-mannose, and D-galactose.

Gel permeation chromatography (GPC)

The weight-average molecular weights (M_w) of the hemicellulosic fractions and their corresponding derivatives were estimated by gel permeation chromatography (GPC) on a PL aquagel-OH 50 column ($300\times 7.7 \text{ mm}$; Polymer Laboratories Ltd.; Church Stretton, England) calibrated with pullulan polysaccharide standards (M_w of 738, 12,200, 100,000, and 16,00,000 (Polymer Laboratories Ltd.)). A flow rate of 0.5 mL min^{-1} was maintained in the chromatography column. The eluent was 0.02 M NaCl in 0.005 M sodium phosphate buffer. A differential refractive index detector (Knauer; Berlin, Germany) was used for the detection of eluted polymer fractions. The column oven temperature was maintained at $30 \text{ }^\circ\text{C}$. Cationic hemicellulosic samples were dissolved into 0.02 M NaCl in 0.05 M sodium phosphate buffer at a concentration of 0.1% prior to being applied to the chromatographic column.

FT-IR and zeta-potential analyses

Fourier transform infrared (FT-IR) spectra were recorded using a Vector 33 instrument (Bruker BioSpin GmbH; Rheinstetten, Germany) with a scan range of $400 \text{ to } 4000 \text{ cm}^{-1}$ and a resolution rate of 1 cm^{-1} . KBr discs containing 1% finely-grounded samples were used for FT-IR spectral scans. Surface charge of the pulp fibers and fines with cationic hemicellulosic fractions were measured using a SZP-06 Müttek zeta-potential analyzer (BTG Instruments GmbH; Wessling, Germany) based on the streaming potential method (Cadena *et al.* 2009). Prior to zeta-potential measurements, a pulp slurry of 1% consistency was made with deionized water, and cationic hemicellulosic fractions were added to the slurry at 0.5%, 1.0%, 1.5%, or 2.0% (based on b.d. pulp).

SEM analysis

The surface morphologies of the handsheets surfaces were examined using a LEO 530V scanning electron microscope (SEM) (LEO Electrón Microscopía Ltd.; Cambridge, UK) after gold sputtering to avoid charging effects.

RESULTS AND DISCUSSION**Sugar Composition of Hemicellulosic Fractions**

The chemical compositions of the four hemicellulosic fractions in terms of neutral sugar units are given in Table 1. For all samples, xylose was the predominant neutral sugar unit (63.1 to 91.2%). Among these samples, H_{pH5.5} had the highest xylose content, while H_{75%} had the least amount of xylose content; H_{15%} and H_{30%} had similar xylose levels. These results indicated that as the ethanol concentration for precipitation increased, the amount of branched hemicelluloses isolated increased. Arabinose was the second most abundant sugar unit isolated; its content increased from 7.7 to 20.9% as the ethanol concentration for precipitation increased. Small amounts of glucose (0.78 to 8.01%) and galactose (0.39 to 8.01%) were also identified in these fractions, and mainly existed in the precipitated fraction that used the highest ethanol concentration (H_{75%}). The ratio of arabinose-to-xylose (Ara/Xyl), which indicates the degree of branching, was very low (0.084) for H_{pH5.5}, whereas it increased to 0.33 for H_{75%} as the ethanol concentration for precipitation was increased to 75%. This suggests that the H_{pH5.5} fraction was the least branched, while the H_{75%} had the highest amount of branching. The side branch groups were composed of arabinose, glucose, and galactose (Peng *et al.* 2011). This observation can be explained as follows. Hemicellulosic fractions possessing low degree of polymer branching had lower solubilities in solutions that contained low ethanol levels; on the other hand, hemicellulosic fractions possessing more side chains could only be precipitated by using solutions containing high ethanol concentrations (Roels *et al.* 1999; Bian *et al.* 2010).

Table 1. Neutral Sugar Components in the Hemicellulosic Fractions

Neutral Sugar (%)	H _{pH 5.5}	H _{15%}	H _{30%}	H _{75%}
Xylose	91.16	81.26	82.82	63.12
Arabinose	7.66	10.53	11.84	20.87
Glucose	0.78	5.31	4.02	8.01
Galactose	0.39	2.90	1.32	8.01
Ara/Xyl ratio	0.084	0.13	0.14	0.33

Molecular Weight and Water Solubility of Hemicellulosic Fractions

The molecular weights of the hemicellulosic fractions and their cationic derivatives were determined by GPC. The weight-average (M_w) and number-average (M_n) molecular weights, as well as polydispersity index (M_w/M_n) of the various fractions are presented in Table 2. The M_w values of unmodified hemicellulosic fractions ranged from 7,830 to 25,330 g·mol⁻¹, which were higher than those of the corresponding derivatized hemicellulosic fractions, which were from 5,830 to 18,330 g·mol⁻¹, respectively. M_w and M_n increased when the ethanol concentration used for precipitation was increased from 0 to 30%; the M_w and M_n values decreased slightly when ethanol content used for precipitation was increased from 30 to 75%. These observations indicated

that polysaccharide degradation occurred during the alkaline quaternization process. Underivatized and cationized hemicellulosic fractions with the highest molecular weight were obtained when a 30% ethanol solution was used for precipitation.

Table 2. Weight-Average Molecular Weight (M_w), Number-Average Molecular Weight (M_n), and Polydispersity Index (M_w/M_n) of the Various Hemicellulosic Fractions and Their Corresponding Derivatives

Property	Underivatized Hemicelluloses Fractions				Cationic Hemicelluloses Fractions			
	H _{pH5.5}	H _{15%}	H _{30%}	H _{75%}	CH _{pH5.5}	CH _{15%}	CH _{30%}	CH _{75%}
M_w (mol·g ⁻¹)	7827	23,293	25,327	20,491	5827	17,793	18,327	15,491
M_n (mol·g ⁻¹)	4668	9764	14,668	12,448	2168	6764	10,968	8448
M_w/M_n	1.68	2.39	1.73	1.65	2.69	2.63	1.67	1.84

As shown in Fig. 1a, as ethanol concentration used for precipitation increased, the residual solid decreased, which indicated that the water solubility of the isolated fractions improved. The fraction precipitated by 75% ethanol had the highest water solubility due to the high degree of branching of the polysaccharides (Li *et al.* 2016). The aqueous solubility of cationized hemicellulosic fractions also showed a similar trend (Fig. 1b) as the corresponding underivatized samples. The cationic hemicellulosic fractions had a better water solubility than their corresponding underivatized fractions.

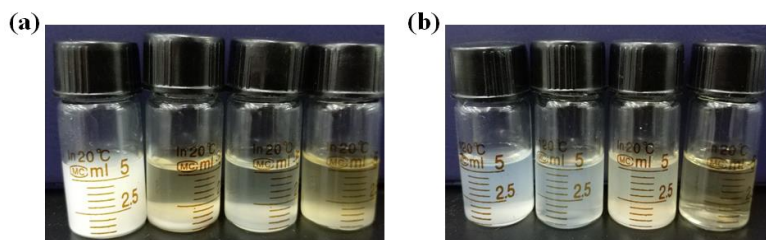


Fig. 1. Photographs of underivatized (a) and cationized (b) hemicellulosic fractions dissolved in water at a concentration of 0.5% (samples from left to right are H_{pH5.5} or CH_{pH5.5}, H_{15%} or CH_{15%}, H_{30%} or CH_{30%}, H_{75%} or CH_{75%}, respectively).

Degree of Substitution

Table 3. Elemental Analyses and DSs of Cationic Hemicellulosic Fractions

Samples	C (%)	H (%)	N (%)	DS
CH _{pH5.5}	40.32	7.05	2.45	0.38
CH _{15%}	41.67	7.76	2.47	0.37
CH _{30%}	37.38	7.29	2.43	0.42
CH _{75%}	40.68	7.13	2.51	0.39

Table 3 presents the amount of cationization of the hemicellulosic fractions in terms of their elemental analysis and their degree of substitution (DS). There were no appreciable differences in the hydrogen and nitrogen contents among these samples; however, there were some small differences in the carbon contents among the samples. The DS for CH_{pH5.5}, CH_{15%}, CH_{30%}

and CH_{75%} were 0.38, 0.37, 0.42, and 0.39, respectively. These results implied that there were no notable differences among the samples in terms of their cationization. It is hypothesized that all hemicellulosic fractions are very soluble in water in the presence of alkali; the high solubility of the fractions would then expose the hydroxyl groups of the polysaccharides to react with CHMAC.

FT-IR Spectra Analysis

The FT-IR spectra of the hemicellulosic fractions and their derivatives are shown in Fig. 2. The absorption at 3468 cm⁻¹ is attributed to the stretching of -OH groups (Ren *et al.* 2007a). The C-H stretching vibration gave signals at 2920 cm⁻¹ (Ren *et al.* 2008). The band at 1646 cm⁻¹ is attributed to the bending mode of the absorbed water. The -CH₂ stretching vibrations are observed at 1469 cm⁻¹. The stretching vibrations around 1040 cm⁻¹ and 893 cm⁻¹ can be ascribed to the C-O-C and the β-glycosidic bonds, respectively (Peng *et al.* 2011). Clearly, after the cationic modification of the hemicelluloses, the absorbance intensity of the ether bond at approximated 1040 cm⁻¹ was enhanced. Moreover, an increase in the intensity of the 1416 cm⁻¹ band, which is assigned to the C-N stretching vibration, was observed. In addition, the symmetric -CH vibration bands at 2916 and 2874 cm⁻¹ also increased, which implied that -CH₃ groups in CHMAC were successfully grafted onto the hemicellulosic fractions (Ren *et al.* 2006, 2007b).

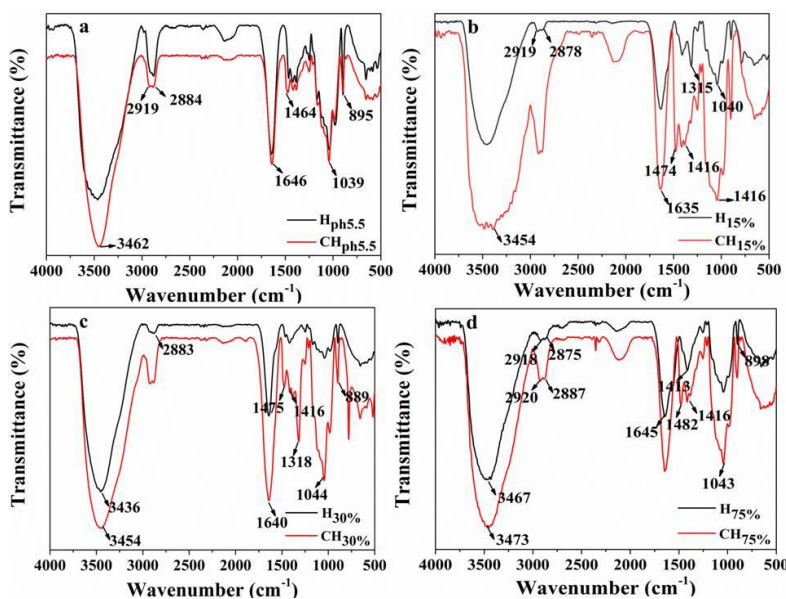


Fig. 2. FT-IR spectra of H_{pH5.5} and CH_{pH5.5} (a), H_{15%} and CH_{15%} (b), H_{30%} and CH_{30%} (c), H_{75%} and CH_{75%} (d)

Zeta Potential

Paper machine white water fines affect the structure and mechanical strength of paper. These fines fill the interstices and bridge the gaps between fibers, which in turn affect the mechanical properties and the quality of the resulting paper. In the papermaking process, lots of fines are lost with white water. In this study, paper handsheets were also made with the addition of white water fines to represent more realistically the papermaking process at the paper machine. Zeta potential is a process parameter of central importance in the retention and drainage of the pulp slurry at the paper machine. Drainage is affected by the interactions among the pulp fibers,

fine particles, and dispersed polymers in the aqueous slurry. The measured zeta potentials of recycled pulp slurries with and without fines in the presences of various cationic hemicellulosic fractions are given in Table 4. The zeta potentials of the recycled pulp slurries with and without fines were -27.3 mV and -27.6 mV, respectively; these values became less anionic with the addition of cationic hemicellulosic fractions, particularly at 1.0% and 1.5% dosage levels. At the relatively high dosages of 1.5% and 2.0%, the electrostatic charge neutralization caused by CH_{30%} and CH_{75%} were lower than those caused by CH_{pH5.5} and CH_{15%}. Among the various cationized fractions, CH_{15%} had the best electrostatic charge neutralization effect.

Table 4. Zeta-Potential of Recycled Pulp Fibers with and without White Water Fines in the Presences of Various Cationic Hemicellulosic Fractions at Various Dosages

Dosage	CH _{pH5.5} (mV)	CH _{15%} (mV)	CH _{30%} (mV)	CH _{75%} (mV)
0%	-27.6			
0.5%	-25.3	-24.4	-21.3	-22.6
1.0%	-15.7	-13.5	-12.8	-14.5
1.5%	-6.7	-4.7	-7.3	-9.6
2.0%	-1.8	1.4	-2.3	-4.3
0% + fines	-27.3			
0.5% + fines	-21.0	-24.7	-18.2	-22.9
1.0% + fines	-13.6	-13.0	-14.3	-15.6
1.5% + fines	-6.7	-4.7	-7.4	-9.8
2.0% + fines	-1.7	1.7	-1.6	-4.8

The Mechanical Properties of Handsheets

Figure 3 shows the effect of adding various cationized hemicellulosic fractions, at different dosage levels, on the tensile index strength of recycled pulp handsheets without fines addition. The tensile index of the control without any additive was 27.9 N·m·g⁻¹ (Fig. 3a); the addition of cationic hemicellulosic fractions appreciably increased the tensile index. The tensile indices of handsheets with 0.5 wt% (basing on the dry weight of recycled fiber) of CH_{pH5.5}, CH_{15%}, CH_{30%}, and CH_{75%} were 28.0, 28.9, 30.5, and 32.5 N·m·g⁻¹ (Fig. 3a-3d), which represented increases of 0.46%, 3.66%, 9.49%, and 16.60%, respectively, over the control. As the dosage of cationic hemicellulosic fractions increased, the tensile index showed a more noticeable increase. At a dosage of 2.0%, the tensile indices of the handsheets with CH_{pH5.5}, CH_{15%}, CH_{30%}, and CH_{75%} increased by 22.5%, 20.4%, 26.8%, and 24.4%, respectively, versus the control.

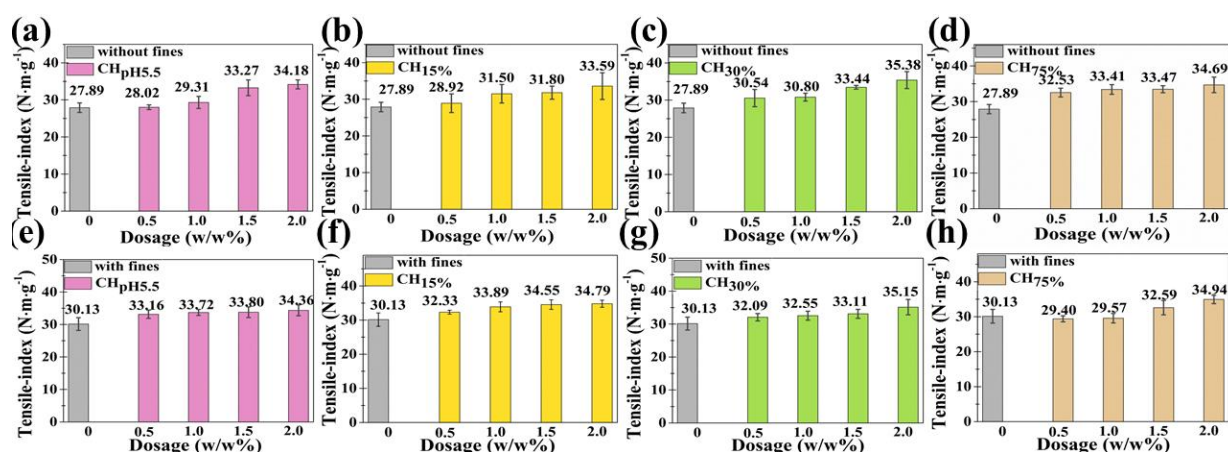


Fig. 3. Influence of various cationic hemicellulosic fractions, at different dosages, on the tensile indices of handsheets in the absence and presence of fines and the error bars represent standard deviation

The cationic hemicellulosic derivatives have a strong interaction with the anionic-charged fibers by neutralizing the repulsive charges of ionized carboxyl groups on the fibers with the ammonium groups from the derivatized hemicellulosic fractions. Hence, the mechanical properties of the handsheets were enhanced. Additionally, the physical properties of paper were affected by the hydrogen bonding among fibers. Hence, the mechanical strengths of handsheets were improved by the addition of cationic hemicelluloses, which promoted hydrogen bonding among the various carbohydrate components. The CH_{30%} addition resulted in the highest improvement of tensile index strength at a 2% dosage.

Additionally, fines from paper machine white water were added to the recycled pulp to determine their impacts on tensile index strength. Figures 3e to 3h show the effect of 5% fines addition on tensile index in the absence and presence of various cationic hemicellulosic fraction additions. The tensile index of the control with fines (without cationic hemicellulosic fraction addition) was 30.1 N·m·g⁻¹ (Fig. 3e), which was higher than the initial control without fines (27.9 N·m·g⁻¹, Fig. 3a). This observation indicated that the addition of small amounts of fines could improve the tensile strength of the recycled pulp handsheets. As shown in Fig. 3e-3h, the addition of 0.5% cationic hemicellulosic fractions resulted in tensile indices of 33.2, 32.3, 32.1, and 29.4 N·m·g⁻¹ for CH_{pH5.5}, CH_{15%}, and CH_{30%}, which represented increases of 10.0%, 7.3%, 6.5%, and minus 2.42%, respectively. At a 2% cationic hemicellulosic fraction dosage, the tensile indices increased by 14.0%, 15.4%, 16.6%, and 15.9% for the handsheets with CH_{pH5.5}, CH_{15%}, CH_{30%} and CH_{75%}, respectively. CH_{30%} was observed to be the best additive among the derivatized hemicellulosic fractions to improve handsheets tensile strength with fines at a high dosage (2%). As compared with the handsheets without fines, the handsheets with fines showed smaller tensile strength gains, which may be attributed to the fines adsorbing some of the derivatized hemicelluloses.

Figure 4a indicates that the burst index of handsheets without fine addition was 1.81 kPa·m²·g⁻¹; the addition of 0.5 to 1.5% CH_{pH5.5} did not appreciably improve the burst index, whereas a 2% CH_{pH5.5} addition did show a notable improvement. Figure 4b indicates that CH_{15%} addition did not affect burst strength even at high dosages (*i.e.*, 2%). Figures 4c and 4d illustrate that CH_{30%} and CH_{75%} addition improved burst strength at low dosage levels; burst indices increased by 30.4% and 26.6% *versus* the control when 2% CH_{30%} and CH_{75%}, respectively, were

added. Hence, CH_{30%} was observed to be the most effective additive examined to improve burst index of recycled pulp handsheets without fines.

As shown in Fig. 4e-4h, the burst index of the control handsheets with white water fines was 2.35 kPa·m²·g⁻¹, which was also higher than the control handsheets without fines (*i.e.*, 1.81 kPa·m²·g⁻¹). The addition of cationic hemicellulosic fractions improved the burst indices of the handsheets made with fines (Fig. 4e-4h). At a dosage of 0.5%, the burst indices increased to 2.57, 2.50, 2.47 and 2.45 kPa·m²·g⁻¹ when CH_{pH5.5}, CH_{15%}, CH_{30%} and CH_{75%}, respectively, were added. When the cationic hemicellulosic fraction dosage increased to 2%, the burst indices of handsheets with CH_{pH5.5}, CH_{15%}, CH_{30%} and CH_{75%} increased further to 2.72, 2.75, 2.68, and 2.53 kPa·m²·g⁻¹, which represented strength improvements of 15.8%, 17.3%, 14.0%, and 7.8%, respectively. Hence, it was observed that CH_{pH5.5}, CH_{15%}, and CH_{30%} were effective additives versus CH_{75%} to enhance the burst strength of handsheets containing fines.

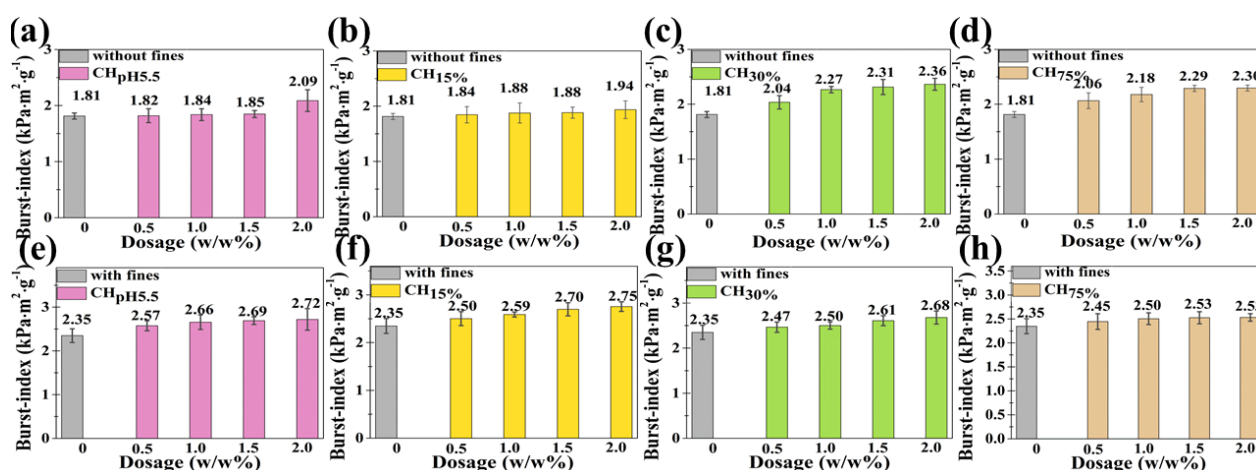


Fig. 4. Influence of various cationic hemicellulosic fractions, at different dosages, on the burst indices of handsheets in the absence and presence of fines and the error bars represent standard deviation

Figures 5a to 5d present tear index of control handsheets without fines (7.2 mN·m²·g⁻¹), as well as the handsheets containing the various cationic hemicellulosic fraction additions. For example, at a dosage of 2% derivatized hemicelluloses, the tear index only increased by 4.89%, 7.73%, 9.34%, and 5.78% for CH_{pH5.5}, CH_{15%}, CH_{30%}, and CH_{75%}, respectively. As shown in Fig. 5e-5h, the addition of cationic hemicellulosic fractions were not effective strength aids to improve tear for handsheets made from recycled pulp in the presence of fines. Even at a dosage of 2%, the tear indices of the handsheets made with CH_{pH5.5}, CH_{15%}, CH_{30%} and CH_{75%} just increased by 5.40%, 4.91%, 8.53% and 7.34%, respectively. It should be noted that among all the derivatized hemicellulosic fractions tested that CH_{30%} addition slightly enhanced the tear strength of the handsheets made in the absence and presence of fines.

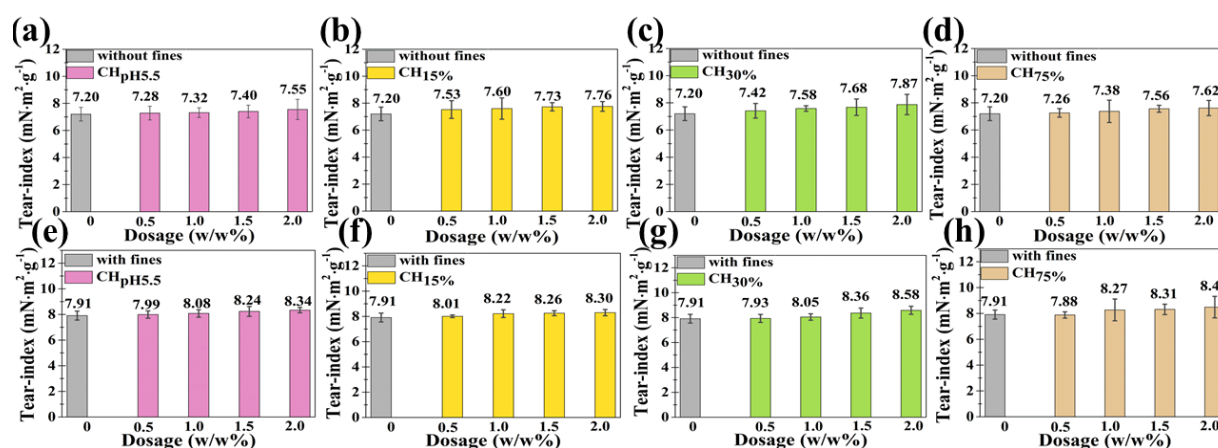


Fig. 5. Influence of various cationic hemicellulosic fractions, at different dosages, on the tear indices of handsheets in the absence and presence of fines and the error bars represent standard deviation

Obviously, the addition of small amounts of paper machine white water fines can improve the mechanical strength of handsheets, which might be attributed to fines enhancing the interaction among the pulp fibers (Bäckström *et al.* 2008; Joseleau *et al.* 2012; Chen *et al.* 2013). Although the addition of these cationic hemicellulosic fractions can improve some of the physical strength properties of the handsheets, the inclusion of fines had a negative influence on the amount of strength developed. The adsorption of cationic hemicellulosic fractions onto the surfaces of the fines was supposed to affect their interaction among the recycled pulp fibers. The best enhance effect caused by CH_{30%} should be due to the highest molecular weight and the highest substitution degree of the CHMAC group.

SEM Analysis

Figure 6 showed that the paper machine white water fines were composed of some fiber fibrils (fragments) and large amounts of fillers (Fig. 6a). As compared with handsheets without cationic hemicellulosic fraction and fines (Fig. 6b), the fibers in the handsheets with only 2% CH_{30%} were more compactly packed (Fig. 6c), which indicated a stronger interaction between the fibers caused by the CH_{30%} addition. As shown in Fig. 6d, the addition of fines also resulted in a compact fiber network. It was hypothesized that the fines not only filled the pores within the fibrous network, but also interacted with the fibers to improve the mechanical strength of the formed handsheets, which was observed from the various physical test results of this study. The differences in the fibrous network of the handsheets with and without CH_{30%} addition in the presence of fines were not noticeable, as shown in Fig. 6d and 6e.

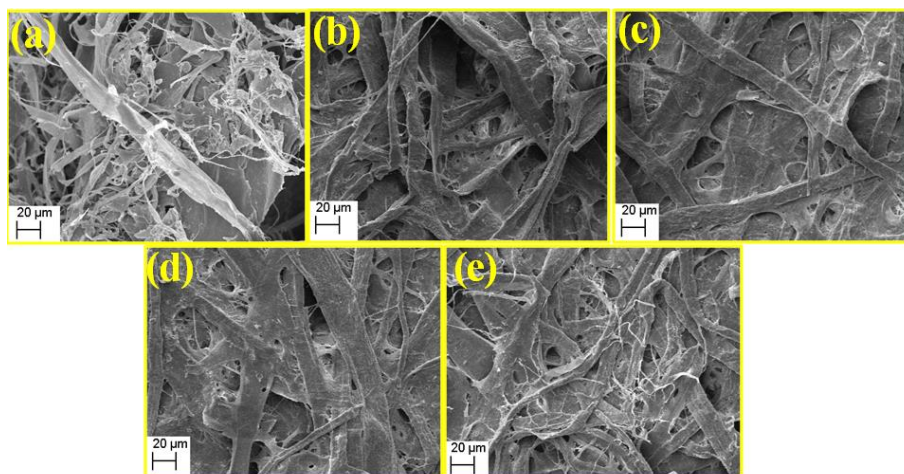


Fig. 6. SEM images of freeze-dried fines (a), handsheets without fines and cationic hemicellulosic fractions (b), with only 2% CH_{30%} (c), with only fines (5%) (d), and with fines (5%) and 2% CH_{30%} (e)

CONCLUSIONS

1. All hemicellulosic fractions prepared from corncob graded ethanol precipitation can be chemically modified to produce strengthening additives to increase appreciably the mechanical strength of recycled fiber handsheets.
2. Although the addition of paper machine white water fines to the pulp slurry can increase the mechanical strength of handsheets, the addition of cationic hemicellulosic fractions showed more remarkable paper strength gains with handsheets made in the absence of fines.
3. Among the hemicellulosic fractions isolated by ethanol precipitation and subsequently chemical modification, CH_{30%} was observed to be the best paper strength additive examined in this study. It was proposed that this observation was attributable to the high level of polysaccharide branching, molecular weight, and degree of substitution of CHMAC groups on the CH_{30%} heteropolymer.

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