

Synthesis of Cationic Xylan Derivatives and Application as Strengthening Agents in Papermaking

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Cationic xylan derivatives were prepared by etherification using 3-chloro-2-hydroxypropyltrimethylammonium chloride as the cationic reagent under an alkaline condition. These derivatives were utilized as strengthening agents to enhance the mechanical strength properties of paper. Cationic xylan derivatives with different degree of substitution (DS) values (0.11 to 0.35) that corresponded to different cationic charge densities (0.51 mmol/g to 0.85 mmol/g) were successfully synthesized, and the reaction parameters were optimized based on the DS and charge density. The cationic xylan derivatives were characterized by means of elemental analysis, Fourier transform infrared spectroscopy, and nuclear magnetic resonance spectrometry. The xylan derivatives had a good performance in strengthening the physical properties of the paper, such as the tensile, tear, and burst strengths. When the DS of the cationic xylan derivative was higher, the strengthening effectiveness was better. At a 2.4-wt.% (based on dried pulp) dosage with the xylan derivative that had a DS of 0.32, the tensile, tear, and burst indices of the pulp increased by 63%, 58%, and 42%, respectively. For the pulps with different beating degrees, the cationic xylan derivative was more beneficial to the pulps with a lower beating degree.

Keywords: Xylan; 3-chloro-2-hydroxypropyltrimethylammonium chloride; Cationic xylan derivative; Paper strengthening agent

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INTRODUCTION

Hemicellulose, which is the second most abundant polysaccharide in the plant kingdom after cellulose, comprises roughly one-fourth to one-third of most plant material, and its amount varies according to the particular plant material (Bai *et al.* 2015). For instance, there is 32% to 38% hemicellulose in wheat straw, and 36% to 38% in corn cobs. About 2 to 3 billion dry tons of crop stalks are produced annually throughout the world. The output of crop stalks is very rich in China, at 556 million tons a year. These crop stalks are rich in hemicellulose, which mainly consists of xylan. Xylan constitutes 25 to 35 wt.% of woody biomass and approximately 50 wt.% of non-woody plant (Li *et al.* 2011; Konduri and Fatehi 2016). However, most crop stalks are burned or used as a domestic fuel. This has resulted in a huge waste of resources and pollution of the environment. With the depletion of fossil resources and decrease in the global forest area, people have gradually placed an emphasis on the research and utilization of agricultural and forestry wastes.

Xylan is an abundant natural renewable resource and the most common type of hemicellulose. Its unique biological activity and physiological function have aroused interest in many fields, such as the chemical, food, biological, pharmaceutical, and cosmetics fields (Peng *et al.* 2012; Cheng *et al.* 2017). So far, the use of xylan in the paper-making industry has remained at a low level because of its limitations, such as its low solubility and low charge density. Modification is a useful tool to improve the functionality of substances (Wang *et al.* 2015). Through chemical modifications, such as sulfonation (Cai *et al.* 2015), carboxymethylation (Peng *et al.* 2011; Konduri and Fatehi 2016; Konduri and Fatehi 2017), acetylation (Ren *et al.* 2007), and cationization (Wang *et al.* 2015), xylan and its derivatives can be modified to produce value-added products for different applications (Daus and Heinze 2010; Gordobil *et al.* 2014; Wu *et al.* 2014). The etherification of xylan with cationic agents can enhance its solubility and yield cationic or ampholytic polymers. Ruihua *et al.* (2012) developed a novel method to obtain N-(2-hydroxy)-propyl-3-trimethylammonium chitosan chloride using glycidyl trimethylammonium chloride and chitosan in a homogeneous system. Fan *et al.* (2012) prepared cationic pectin derivatives by reacting pectin with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) in the presence of sodium hydroxide. Additionally, Konduri and Fatehi (2016) successfully produced carboxymethylated-beechwood xylan as a dispersant. Cationic xylan polymer can be used as a flocculant for removing dyes from wastewater in the textile industry (Wang *et al.* 2015). Cationic xylan–METAC copolymers (METAC, [2-(methacryloyloxy) ethyl] trimethylammonium chloride) have also been used as a flocculant for kaolin and bentonite clay suspensions (Wang *et al.* 2016a). However, research concerning the application of cationic xylan derivatives with different degree of substitution (DS) values as a chemimechanical pulp strengthening agent (wet-end additives) for papermaking (Bigand *et al.* 2013; Ren *et al.* 2009; Song and Hubbe 2014) is still scarce. Ren *et al.* (2009) and Bigan *et al.* (2013) applied cationic hemicellulose as strengthening agent for chemical pulp, sulfate kraft pulp, or hardwood bleached chemical pulp. The application of cationic xylan derivatives in strengthening chemimechanical pulp properties, such as APMP, need to be investigated.

The cationization of xylan was performed in an alkaline aqueous medium in this paper, and the prepared cationic xylan was applied as a strengthening agent in papermaking. The objectives of the current work were: i) prepare cationic xylan derivatives with different DS values in an aqueous solution using CHPTAC as an etherifying agent and NaOH as a catalyst; and ii) investigate the application performances of the prepared xylan derivatives as strengthening agents in papermaking. Xylan derivatives with different DS values were prepared and characterized by elemental analysis, Fourier transform infrared (FT-IR) spectroscopy, and carbon nuclear magnetic resonance (^{13}C -NMR) spectroscopy. Also, the influences of the cationic xylylans as wet-end additives on the physical properties of paper were studied.

EXPERIMENTAL

Materials

Beechwood xylan (Poly(β -D-xylopyranose[1 \rightarrow 4]), > 90%, charge density, -0.6 meq/g) was purchased from Sigma-Aldrich Trade Co. Ltd. (Shanghai, China). The CHPTAC was purchased from Guofeng Fine Chemical Co. Ltd. (Shandong, China) and

was used as an etherifying reagent without further purification. Polydiallyldimethylammonium chloride (PDADMAC, 100 to 200 kg/mol), 20 wt.% in water and sodium hydroxide (reagent grade) were obtained from Sigma-Aldrich company. Potassium polyvinyl sulfate (PVSU, 100 to 200 kg/mol, 97.7 wt.% esterified) was provided by Wako Pure Chem. Ltd., Osaka, Japan. All of the other reagents were of analytical grade and used without further purification. The poplar alkaline peroxide mechanical pulp (APMP) used in this experiment was obtained from Shandong Sun Paper Mill located in Shandong, China. The pulp was produced using one-stage pretreatment APMP process. The conditions for pretreatment at mill were 6.5% NaOH (based on oven-dry material, the same as below), 6.2% H₂O₂, 75 °C, 1.5 h, and 10% pulp consistency. The APMP pulp properties including chemical components were analyzed according to TAPPI standards (TAPPI 1996) and listed in Table 1.

Table 1. Chemical Component Analysis and Properties of Poplar APMP Pulp

Ash content (%)	Cellulose content /%	Pentosan content /%	Klason lignin content /%	Acid dissolved lignin /%	1%NaOH extractives content /%	Alcohol-benzene extractives content /%
0.43	50.47	15.12	17.22	3.52	11.23	1.26
Beating degree (°SR)	Brightness (%ISO)	Tensile index (N M g ⁻¹)	Tear index (mN m ² g ⁻¹)	Burst index (kPa m ² g ⁻¹)		
20	72.0	35.34	5.03	1.33		
30	71.8	38.32	5.23	1.45		
40	71.6	42.35	5.67	1.63		

Notes: Each content is based on the oven-dry material.

Synthesis of the Xylan Derivatives

The cationization procedure for xylan was identical to what was reported previously by Liu *et al.* (2011), Wang *et al.* (2012), and Kong *et al.* (2014) without the addition of a catalyst other than NaOH. The reactions were done in a 250-mL three-necked flask equipped with a magnetic stirrer. In a typical procedure, the xylan (0.01 mol) was dispersed in 30 mL of deionized water with stirring for 50 min at room temperature in a flask. A certain required amount of sodium hydroxide was then added to the flask, which was followed by another 20 min of stirring. Subsequently, the CHPTAC dissolved completely in water was added gradually into the flask. The total volume of the solution was 45 mL. The resulting suspension was stirred under the preset temperature for a certain time. After the reaction was finished, the solution was gradually added into 200 mL of 95% ethanol and stirred to precipitate the resulting product. The suspension was centrifuged, and the precipitate was washed thoroughly with 95% ethanol three times to remove the unreacted CHPTAC. Finally, the solid was dried in a vacuum desiccator containing P₂O₅ at 40 °C for 4 d to obtain the purified xylan derivatives.

Characterization of the Xylan Derivatives

The contents of carbon (C), hydrogen (H), and nitrogen (N) in the xylan and xylan derivatives were measured with an elemental analyzer (Vario EL III, Elementar Analysensysteme, Hanau, Germany). The samples were combusted at up to 900 °C to 1200 °C for analytical accuracy with a large dynamic range of elemental concentration, *e.g.* up to 30 mg of C or 10 mg of N absolute. The operation model of “CHN” with TCD detection

was used in this experiment.

The FT-IR spectra were obtained with a FT-IR spectrometer (IR Prestige-21, Shimadzu, Tokyo, Japan). The samples were prepared as KBr pellets. The FT-IR spectra were recorded over the wavenumber range of 400 cm⁻¹ to 4000 cm⁻¹ with a resolution of 0.5 cm⁻¹.

The ¹³C-NMR spectra for the xylan derivatives were recorded on a NMR spectrometer (Bruker AVANCE II 400 MHz, Karlsruhe, Germany) equipped with a Quad probe dedicated to ³¹P, ¹³C, ¹⁹F, ¹⁵N, and ¹H acquisition at 35 °C. The NMR apparatus used an inverse gated decoupling pulse sequence. The ¹³C-NMR analysis was done by dissolving approximately 150 mg of xylan derivative in 2.0 mL of D₂O, and the spectrum was recorded directly.

The DS and reaction efficiency (RE) were calculated using the following formulas (Prado *et al.* 2011), which were based on the nitrogen content determined from the elemental analysis,

$$DS_{cat} = \frac{132N_{cat}}{1400 - 152N_{cat}} \quad (1)$$

$$RE = \frac{DS_{cat}}{DS_{theor}} \times 100\% \quad (2)$$

$$\text{Where } DS_{theor} = \frac{M_{CHPTAC}}{M_{xylan}} \quad (3)$$

where N_{cat} is the percentage of nitrogen in the xylan derivative (%), DS_{theor} is the theoretical degree of substitution with the cationic groups, 132 is the mass of the primary unit of xylan (g/mol), 152 is the increased mass of CHPTAC attached to xylan (g/mol), M_{CHPTAC} , –, is amount of CHPTAC added in the course of the reaction (mol); and M_{xylan} , –, is amount of xylan taken for cationization (mol).

The Charge density analysis of unmodified xylan and xylan derivatives was carried out using a streaming current detector, Mütek PCD 04 Particle Charge Detector. Approximately, 0.05 g of samples was dissolved in 50 g of water, and the solution was immersed in a water bath shaker (Innova 3100, Brunswick Scientific, Edison, NJ, USA) and shaken (150 rpm) at 30 °C for 2 h. Then, 5 mL of this solution was used to titrate against 0.005 M PVSK or PDADMAC solution using the Mütek PCD04 to determine the endpoint. The charge density of xylan derivatives was determined according to Eq. 4.

$$\text{charge density (meq/g)} = \frac{V_{sample} \times 0.0050}{W_{sample}} \quad (4)$$

In Eq. 4, V_{sample} is the volume of 0.005 M PVSK or PDADMAC used for titrating xylan derivatives solution (mL); and W_{sample} is the weight of xylan derivative sample in 5 mL xylan derivative solution (g). The data presented here are the averages of three repetitions.

Performance Assessment of the Xylan Derivatives as Strengthening Agents in Papermaking

The refining of APMP pulp was carried out using a PFI mill (KRK, Japan) with 30 g of o.d. pulp at 10% consistency for 2,000 to 20,000 revolutions, following the TAPPI procedure T248 cm-85(1985) (TAPPI 1996).

As these xylan derivatives were positively charged, they could beneficially affect the inter-bonding of negatively charged cellulosic fibers during paper sheet formation (Kataja-aho *et al.* 2012). Therefore, the performances of the xylan derivatives used as

strengthening additives were evaluated using APMP, which is a chemi-mechanical pulp used for making most kinds of paper. In this experiment, the xylan derivatives were first dissolved in water by stirring for 1 h at 40 °C. Then, different amounts of a xylan derivative, *e.g.* 0.6 wt.% to 3.0 wt.% (based on the dried pulp weight), were added to the 1% pulp slurry. The pulp slurry containing a xylan derivative was stirred at 800 rpm for 5 min before the formation of the handsheets. The handsheets were made by pouring the pulp slurry into the deckle of the paper sheet former, which was followed by draining the slurry through a metallic wire mesh (R200). Each formed hand sheet was dried on a rapid dryer at 98 °C. The hand sheet grammages were 60 g/m² and 100 g/m². Paper sheets with a grammage of 60 g/m² were used to test the tensile and tear indices. As the burst of APMP pulp used is quite low and close to the low limitation of burst analyze instrument, to avoid the error and make the burst value is at the right scale of the instrument, handsheets with 100 g/m² grammage were used to evaluate the burst index. Before testing the physical strength properties, the handsheets were kept in an environment with a constant temperature (23 °C) and humidity (50%) for 24 h. The tests for the three physical strength properties (tensile index, burst index and tear index) were performed according to the TAPPI T494 om-87 (1988), T403 om-91 (1991), and T414om-82 (1988) standards, respectively (TAPPI 1996). All data presented in this paper are the average value of three repetitions.

RESULTS AND DISCUSSION

Synthesis of the Xylan Derivatives

Figure 1 illustrates the cationization of xylan using CHPTAC as the etherifying agent. In the reaction, 2, 3-epoxypropyltrimethylammonium chloride was first produced from the CHPTAC *in situ*. Subsequently, the xylan derivative was formed through a reaction between the xylan and 2, 3-epoxypropyltrimethylammonium chloride. In Table 2, the conditions used for the cationization synthesis and the element analysis results are presented. The molar ratio of CHPTAC/xylose unit, molar ratio of NaOH/CHPTAC, reaction temperature, and reaction time were varied from 0.5 to 2.0, 0.5 to 2.0, 40 °C to 70 °C, and 2 h to 8 h, respectively.

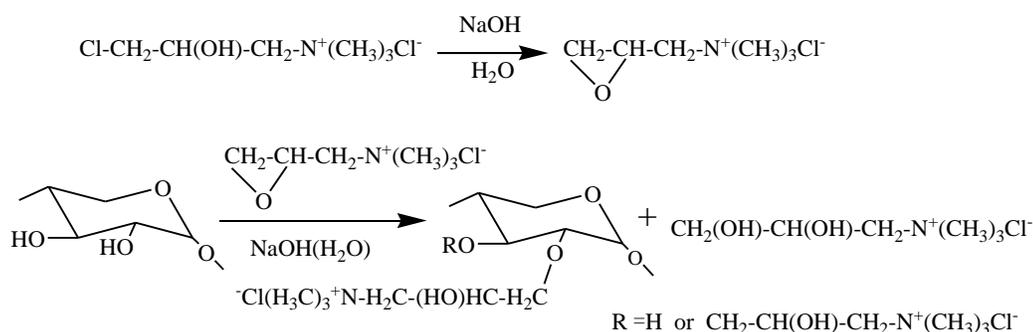


Fig. 1. Schematic representation of the synthesis of cationic xylan

Influence of the NaOH/CHPTAC molar ratio

The influence of the NaOH/CHPTAC molar ratio on the DS and charge density was first investigated in this experiment because a certain NaOH/CHPTAC molar ratio is necessary to activate the xylan (Kong *et al.* 2014). Additionally, the hydrolysis of the

reagent should be as low as possible. The molar ratio of NaOH/CHPTAC was varied from 0.5 to 2.0 by varying the NaOH concentration, while preserving a constant reaction volume. The results are presented in Fig. 2A. An increase in the molar ratio of NaOH/CHPTAC from 0.5 to 1.0 resulted in an increase in the DS from 0.25 to 0.32. It should be noted that the unmodified xylan has a 0.004 DS based on the nitrogen content, which is at an unnoticeable level compared with that of modified xylan, such as DS 0.25. However, the DS decreased by 0.12 when the molar ratio of NaOH/CHPTAC was increased from 1.0 to 2.0. At a low NaOH/CHPTAC ratio (between 0.5 and 1.0), the lower DS values were caused by an insufficiency of NaOH in the reaction medium, which reduced the epoxide formation. Meanwhile, at higher NaOH concentrations, side reactions, such as hydrolysis, with the CHPTAC occurred and subsequently the DS decreased. Furthermore, the changes in the charge density of the cationic xylan derivative followed a trend similar to that of the DS as a function of the NaOH/CHPTAC molar ratio, which confirmed that the changes in the DS of the cationic xylan derivative were because of the changes in the number of cationic groups on the backbone of the cationic xylan derivative. Similar results were also reported by Kong *et al.* (2014) for the preparation of cationic xylan with CHMAC as the cationization agent.

Influence of the reaction time

As a preliminary parameter, the effect of the reaction time on the DS and charge density was studied at 40 °C under a CHPTAC/xylose unit molar ratio of 1.0 and NaOH/CHPTAC molar ratio of 1.0. Figure 2B shows that the charge density marginally decreased from 0.83 mmol/g to 0.68 mmol/g with an increase in the reaction time from 2 h to 8 h. In contrast, the DS value gradually increased at first, and then reached a plateau at a reaction time of 4 h. Further increasing the reaction time resulted in a decrease in the DS. This was because when the reaction time was longer, more reactions were completed, which resulted in an increasing DS. However, the solution in the reaction system became increasingly viscous with longer reaction times, and thus mass transfer between the xylan and CHPTAC became difficult, which led to a reduction in the DS and charge density. Also, for the RE, its change trend was similar to that reported by Kuo and Lai (2009) and Kuo and Lai (2007), who studied the effects of the reaction time on the RE of cationic starch. Their results were basically identical to those recorded during this experiment.

Influence of the reaction temperature

Radosta *et al.* (2004) and Heinze *et al.* (2004) stressed that the reaction between CHPTAC and carbohydrates is usually performed at a relatively mild temperature. Therefore, reaction temperatures between the CHPTAC and xylan in the range of 40 °C to 70 °C were investigated. The effect of the reaction temperature on the DS and charge density is shown in Fig. 2C. By adjusting the temperature of the reaction from 40 °C to 70 °C, the DS and charge density decreased from 0.35 to 0.18 and from 0.85 mmol/g to 0.55 mmol/g, respectively. The maximum values for the DS (0.35) and charge density (0.85) were obtained with the etherified xylan at 40 °C. Increasing the temperature was not beneficial to the DS. It was possible that some diol was formed as a result of side reactions at high temperatures, and in this case, the main reaction of cationization of the xylan decreased. Partial degradation of the cationic starch derivatives has been reported by Heinze *et al.* (2004). Hence, the DS was reduced when the reaction temperature was above 40 °C.

Influence of the CHPTAC/xylose unit molar ratio

The CHPTAC/xylose unit molar ratio had a strong influence on the DS, charge density, and RE (Kong *et al.* 2014). Figure 2D shows that increasing the CHPTAC/xylose unit molar ratio from 0.5 to 1.5 noticeably increased the DS from 0.11 to 0.29 and the charge density from 0.51 mmol/g to 0.74 mmol/g. This could have resulted from CHPTAC continuously entering the xylan with an increase in the CHPTAC concentration and a greater availability of CHPTAC molecules in the proximity of the xylan molecules at higher concentrations of the etherifying agent. Thus, the reaction between the xylan and CHPTAC became complete, which led to an increase in the DS and charge density. However, with higher additions of CHPTAC to the xylan solution, the DS no longer increased and the charge density only marginally increased from 0.74 mmol/g to 0.75 mmol/g, which was probably because of the intermolecular polymerization of the CHPTAC. Furthermore, Fig. 1E showed the changes in the DS and RE of cationic xylan derivative as a function of molar ratio of CHPTAC/xylose unit. As the molar ratio of CHPTAC/xylose unit increased, the reaction efficiency decreased from 22% to 15%. A similar result was reported by Prado *et al.* (2011). The decrease of reaction efficiency is due to the higher CHPTAC dosage in the reaction. Although the CHPTAC reacted with xylan increased at higher CHPTAC dosage resulting a higher DS, the ratio of unreacted CHPTAC in total CHPTAC used in the reaction decreased.

Overall, the reaction process parameters including the NaOH/CHPTAC molar ratio, CHPTAC/xylose unit molar ratio, reaction time, and reaction temperature had remarkable effects on the charge density and DS of the resulting cationic xylan derivatives. The optimized conditions for the cationic modification of the xylan were a CHPTAC/xylose unit molar ratio of 1.0, NaOH/CHPTAC molar ratio of 1.0, reaction temperature of 40 °C, and reaction time of 4 h.

Table 2. Elemental Analysis of the Xylan Derivatives Prepared at Different Conditions

Sample no.	Molar Ratio ^a	Molar Ratio ^b	Time (h)	Temperature (°C)	C (%)	N (%)	H (%)
1	0	0	2	40	40.80	0.04	7.00
2	0.5	2.0	2	40	35.43	1.06	6.48
3	1.0	0.5	2	40	34.98	2.09	6.30
4	1.0	1.0	2	40	34.33	2.51	7.01
5	1.0	1.0	4	40	38.84	2.62	7.74
6	1.0	1.0	6	40	37.62	2.39	6.85
7	1.0	1.0	8	40	36.24	1.87	7.83
8	1.0	1.0	4	50	35.81	2.46	7.05
9	1.0	1.0	4	60	35.84	1.73	6.66
10	1.0	1.0	4	70	37.68	1.58	7.62
11	1.0	1.5	2	40	34.94	2.42	6.97
12	1.0	2.0	2	40	34.97	1.76	6.71
13	1.5	2.0	2	40	33.82	2.30	6.36
14	2.0	2.0	2	40	35.14	2.38	6.58

^a Molar ratio of CHPTAC/xylose unit (xylose unit $M = 132$)

^b Molar ratio of NaOH/CHPTAC

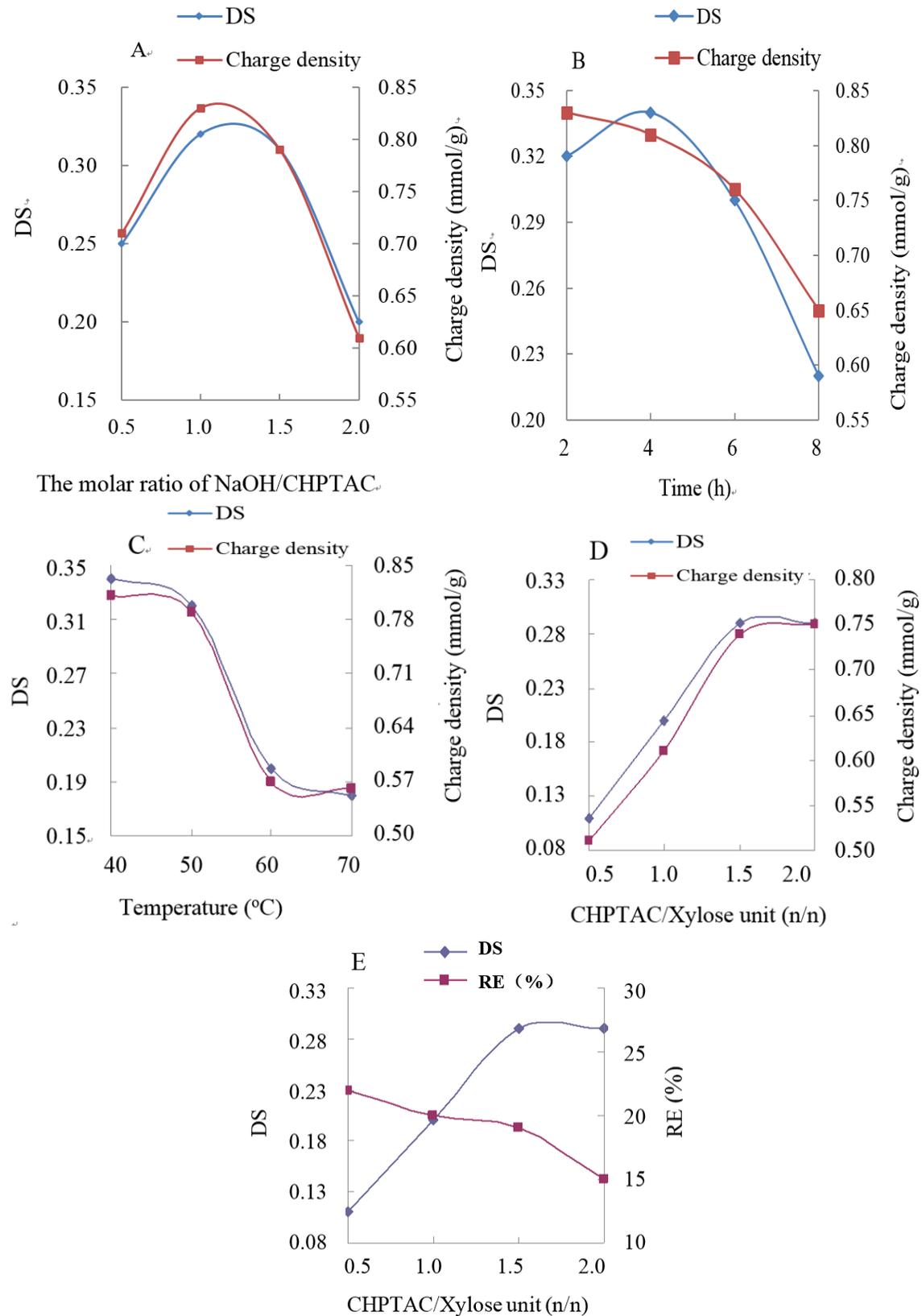


Fig. 2. Influence of the reaction parameters on the DS, charge density, and RE of the cationic xylan: (A) NaOH/CHPTAC molar ratio; (B) time; (C) temperature; and (D and E) CHPTAC/xylose unit molar ratio

Characterization of the Xylan Derivatives

The FT-IR spectra of the unmodified xylan and xylan derivative are shown in Fig. 3. The absorbance bands at 3419 cm^{-1} , 2914 cm^{-1} , 1614 cm^{-1} , 1411 cm^{-1} , 1043 cm^{-1} , and 900 cm^{-1} were observed in the spectrum of the unmodified xylan, which is shown as curve B in Fig. 3. The medium peak at 900 cm^{-1} was attributed to β -glycosidic linkages between the xylose units, which indicated that the xylose units that formed the xylan were linked by β -form bonds (Ren *et al.* 2009). The strong peak at 1043 cm^{-1} was assigned to C–O stretching in C–O–C linkages (Wang *et al.* 2017). The region between 1411 cm^{-1} and 1043 cm^{-1} was related to the C–H and C–O stretching frequencies. The intense band present at 1614 cm^{-1} originated from the glucuronic acid of xylan absorbed water in the isolated unmodified xylan (Peng *et al.* 2011; Ren *et al.* 2009) or the glucuronic acid of xylan (Gabrielii *et al.* 1998). The band at 2914 cm^{-1} was attributed to the symmetric C–H vibration (Wang *et al.* 2016b). The strong band assigned to O–H stretching absorption appeared at 3419 cm^{-1} (Konduri and Fatehi 2017). Compared with the spectrum of the unmodified xylan, the presence of a peak at 1471 cm^{-1} , which was assigned to the methyl group in ammonium, and peak at 967 cm^{-1} which is assigned to quaternary ammonium absorption band (Yudovin-Farber *et al.* 2010), in the spectrum of the xylan derivative (curve A in Fig. 3), provided evidence for successful etherification (Konduri *et al.* 2015; He *et al.* 2016; Jia *et al.* 2016). Moreover, an increase in the intensity of the symmetric C–H vibration band at 2914 cm^{-1} in Fig. 2A implied that CH_3 groups had been introduced to the xylan.

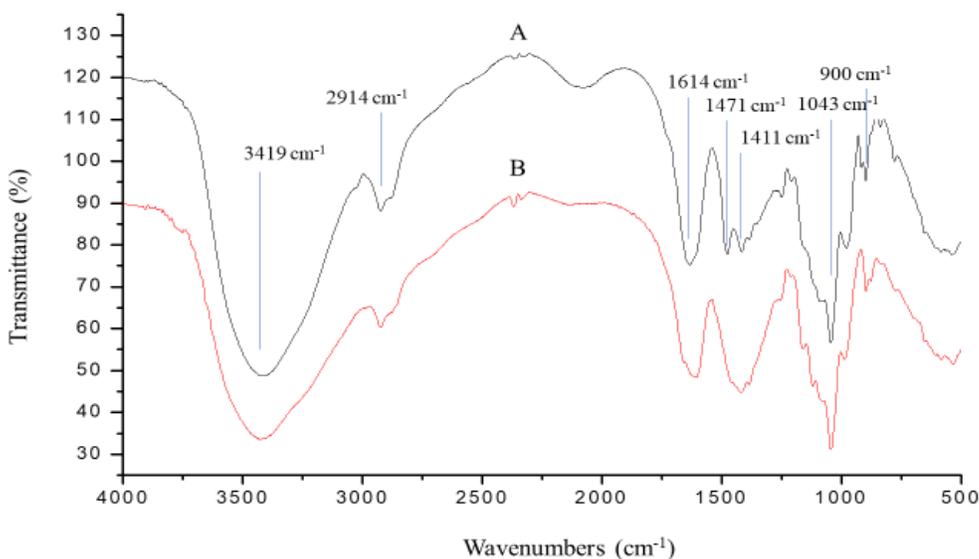


Fig. 3. FT-IR spectra of the xylan derivative (A) and unmodified xylan (B)

The ^{13}C -NMR spectra of the unmodified xylan and xylan derivative are shown in Figs. 4A and 4B, respectively. Compared with the spectrum of the unmodified xylan shown in Fig. 4A, new signals appeared in the xylan derivative spectrum at 73.558 ppm, 65.099 ppm, 66.279 ppm, and 54.847 ppm, which were assigned to C6 (CH_2), C7 (CHOH), C8 ($\text{CH}_2\text{-N}^+$), and C9 ($(\text{CH}_3)_3\text{N}^+$), respectively (Kataja-aho *et al.* 2012; Peng *et al.* 2012; Li *et al.* 2013). Additionally, the signals that appeared at about 101.4 ppm, 72.6 ppm, 73.5 ppm, 76.6 ppm, and 62.9 ppm were assigned to C–1, C–2, C–3, C–4, and C–5 of the xylose unit, respectively (Peng *et al.* 2012). Therefore, the results of the ^{13}C -NMR spectra further demonstrated the successful synthesis of the cationic xylan derivative.

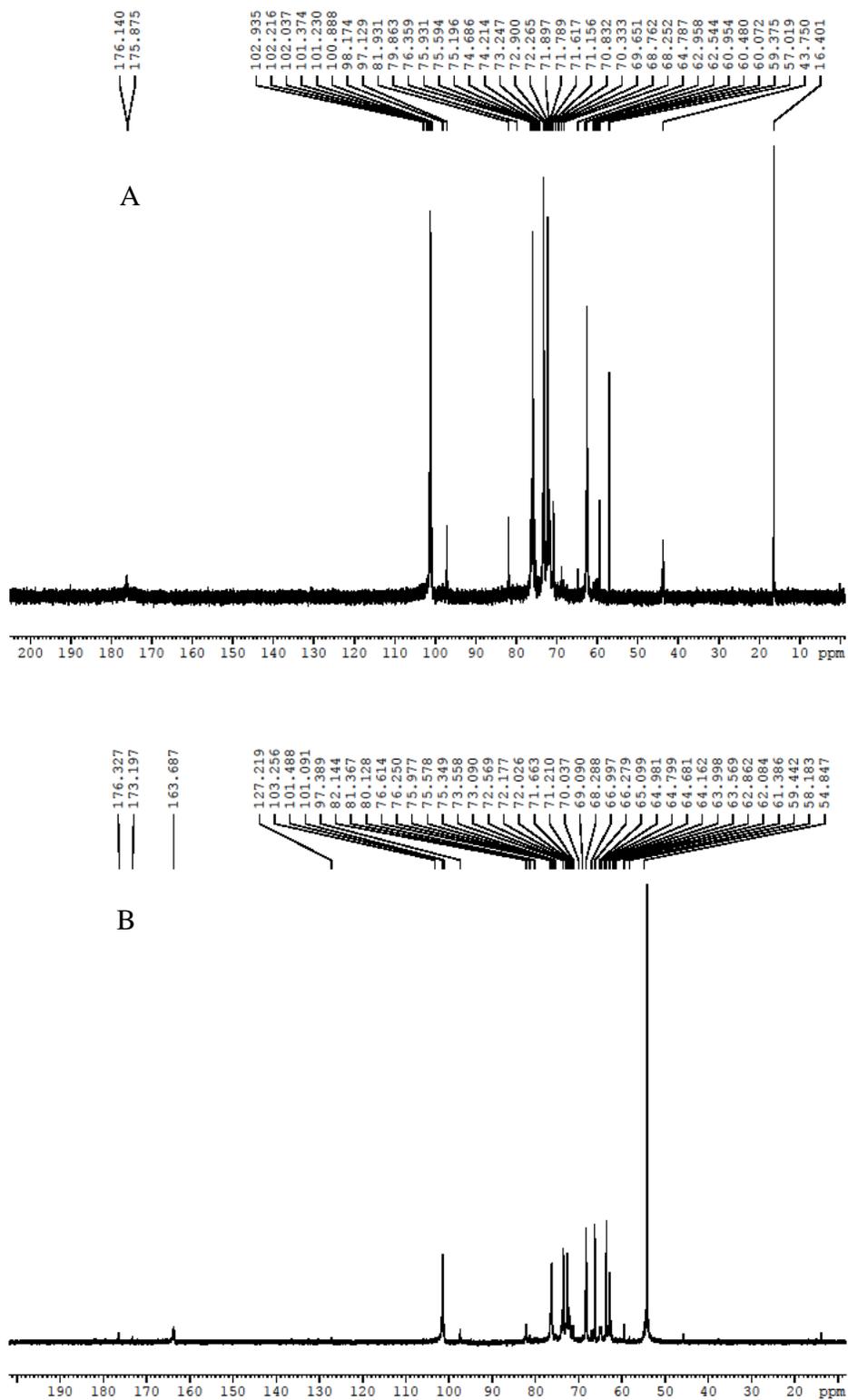


Fig. 4. ^{13}C -NMR spectra of the unmodified xylan (A) and xylan derivative (B)

Application of the Xylan Derivative as a Strengthening Agent in Papermaking

The xylan derivatives were evaluated as wet-end additives to improve the physical properties of paper. For the handsheet preparation, APMP, which is a pulp with a low physical strength and high optical properties, was used with different amounts of the xylan derivatives that corresponded to 0.6 wt.%, 1.2 wt.%, 1.8 wt.%, 2.4 wt.%, and 3.0 wt.% of the pulp on a dry basis in the aqueous solution. Additionally, the different beating degrees (20° SR, 30° SR, and 40° SR) of the pulp and different DS values (0.11, 0.18, 0.25, and 0.32) of the xylan derivatives were taken into consideration in this experiment. To evaluate the ability of the xylan derivative to improve the physical strength properties of the paper, measurements were taken of three physical strength properties of the paper sheets, which were the tensile, tear, and burst indices.

Influence of the xylan derivative additive dosage on the physical strength properties of the paper

The strength properties of the paper sheets made with different additive dosages of the xylan derivative were measured, and the data are shown in Fig. 5. Figure 5 shows the variations in the tensile, tear, and burst indices for the different dosages of additives with a pulp beating degree of 20° SR and xylan derivative DS of 0.32. It was found that the paper formation at the dosages investigated in this study is still good, and the tensile, tear, and burst indices all increased with an increase in the xylan derivative dosage. At the 2.4 wt.% dosage, the tensile, tear, and burst indices increased by 64%, 58%, and 42%, respectively. However, these three strength properties decreased slightly with a further increase in the dosage under the experimental conditions. This was attributed to the presence of an excessive amount of the xylan derivative, which resulted in a lower retention of the xylan derivative on the fibers. This occurred because the total amount of fibers was constant, and the capacity of fixation by positive-negative ions adsorption was limited by the specific surface of the fibers (Gao *et al.* 2016).

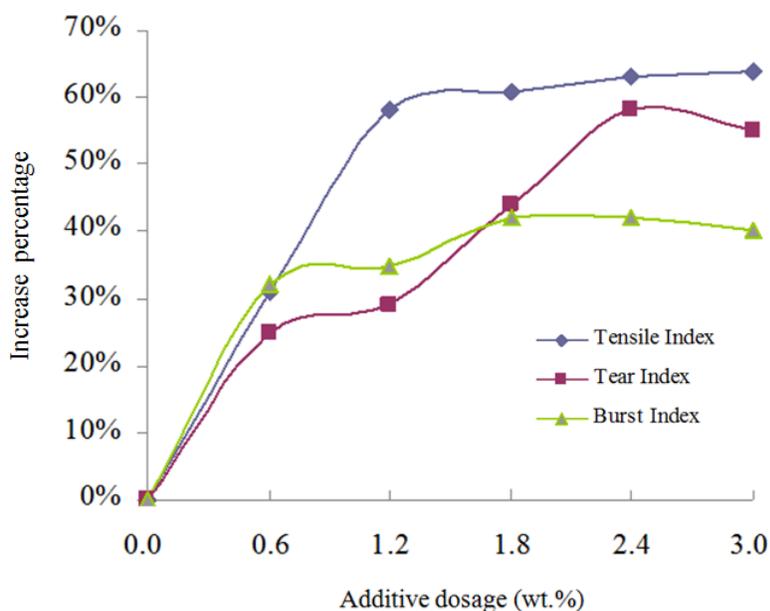


Fig. 5. Change in the paper strength as a function of the xylan derivative dosage (xylan derivative DS of 0.32, pulp beating degree 20° SR)

Influence of the xylan derivative DS on the physical strength properties of the paper

The strengthening performance of the xylan derivatives with DS values that ranged from 0.11 to 0.32 was evaluated at a 2.4-wt.% dosage and 20° SR beating degree, and the results are shown in Fig. 6. Figure 6 shows that all three physical strength properties increased with an increase in the DS of the xylan derivatives, which illustrated that a higher DS value in the xylan derivative can substantially improve the strength properties of the final paper sheets. It is found that with increasing DS of xylan derivative, the paper formation was still good. The tensile, tear, and burst indices were only increased by 22%, 28%, and 23%, respectively, for the xylan derivative with a DS of 0.11. However, these values increased by 63%, 58%, and 42%, respectively, for the xylan derivative with a DS of 0.32. Additionally, it was also found that the xylan derivatives with low DS values (0.11, 0.18, and 0.25) mainly increased the tear strength of the final paper sheets, and the xylan derivative with the highest DS (0.32) mainly affected the tensile strength. It was concluded from the above analysis that a cationic xylan derivative with a high DS is preferred to enhance the paper strength properties as a wet-end additive in the paper industry.

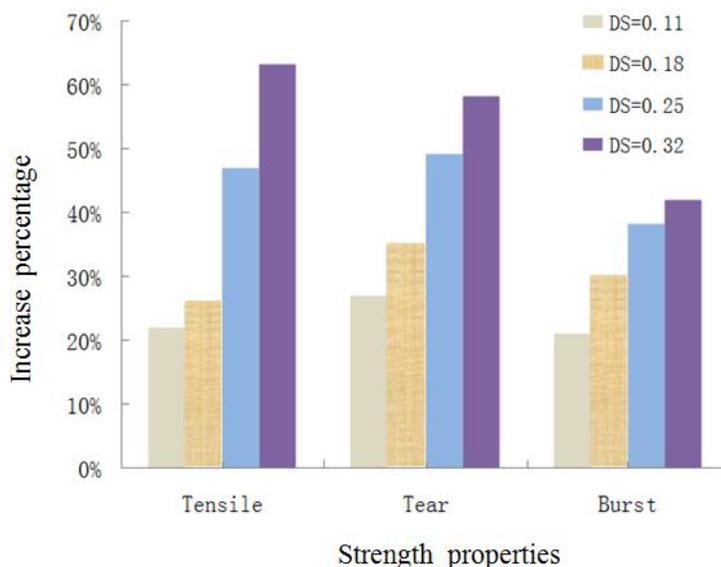


Fig. 6. Effect of the xylan derivative DS on the strength properties of the paper (2.4 wt.% dosage of xylan derivative, pulp beating degree 20° SR)

Influence of the pulp beating degree on the strengthening performance of the xylan derivatives

The effect of the pulp beating degree on the strengthening performance of the xylan derivative was investigated at a 2.4-wt.% dosage using the xylan derivative with a DS of 0.32. The data are shown in Fig. 7. Figure 7 shows that the xylan derivative noticeably increased the tensile index by 63%, tear index by 58%, and burst index by 42% when the pulp beating degree was 20° SR. However, this strengthening effect weakened when the beating degree was increased to 30° SR and 40° SR. The tensile, tear, and burst indices of the paper were increased by only 12%, 14%, and 27% at the 30° SR beating degree, respectively, and by 4%, 6%, and 12%, respectively, at the 40° SR beating degree.

As discussed above, the xylan derivative prepared in this paper can be used as the strengthening agent for papermaking industry without the negative influence on paper formation. As water soluble polymer and dry strengthening agent, it is suitable to be used

in food packaging paper, bleached paperboard, toilet paper, tissue paper, and for the surface layer of cardboard, *etc.* Similar to the application of polyacrylamide (PAM) or cationic starch as a strengthening agent in papermaking process, the solution containing xylan derivative, which could be the resultant solution after the reaction, is prepared at certain concentration initially and then the pH of the solution is adjusted to be neutral. After that, the solution could be pumped metrically into the pulp slurry at pulp pipe connected to fan pump, high flow box, or headbox in the papermaking process. In another way, this solution also could be sprayed onto the surface of a paper web at certain dosage to increase the dry strength as reported by Smith and Meier (2006).

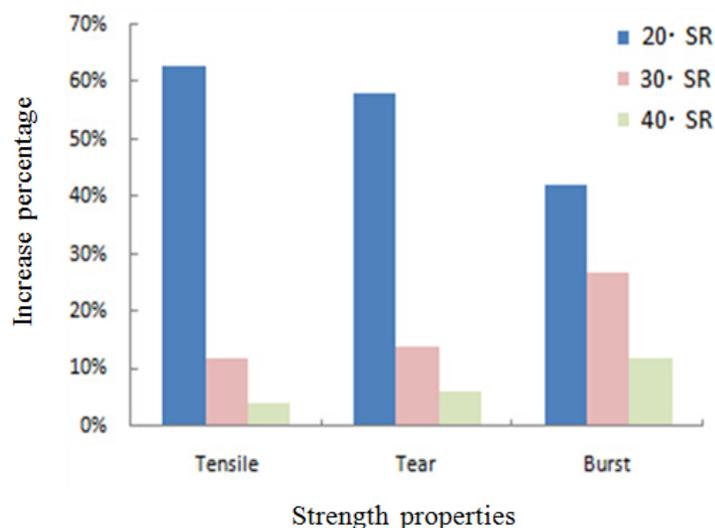


Fig. 7. Effect of the beating degree on the physical properties of the paper (2.4 wt.% dosage of xylan derivative, xylan derivative DS of 0.32)

CONCLUSIONS

1. The cationization of the xylan was carried out by reacting xylan with CHPTAC in an alkaline aqueous solution. The process parameters for the cationization reaction, including the molar ratio of NaOH/CHPTAC, molar ratio of CHPTAC/xylose unit, reaction time, and reaction temperature, had major effects on the charge density and degree of substitution (DS) of the resulting cationic xylan derivatives. The changes in the DS of the cationic xylan derivative followed a trend similar to that of the charge density. Xylan derivatives with different DS values were successfully synthesized. The optimum reaction conditions were determined to be a NaOH/CHPTAC molar ratio of 1.0, CHPTAC/xylose unit molar ratio of 1.0, reaction temperature of 40 °C, and reaction time of 4 h.
2. Elemental analysis, FTIR spectroscopy and NMR results confirmed that the cationization reaction was successful.
3. The cationic xylan derivatives were positively charged and tended to perform well in the inter-bonding of negatively charged cellulosic fibers during paper sheet formation. The use of the xylan derivatives as wet-end paper strengthening additives was studied. In this experiment, different additive dosages, xylan derivative DS values, and pulp

beating degrees were studied. Of all of the tested derivatives, it appeared that the paper had the best physical properties at a dosage of 2.4 wt.% of cationic xylan derivatives with DS values that ranged from 0.11 to 0.32. It was determined that the optimum DS value was 0.32. Furthermore, the effect of the xylan derivative remarkably increased the tensile index by 63%, tear index by 58%, and burst index by 42% for the paper with a beating degree of 20° SR. However, for the paper with beating degrees of 30° SR and 40° SR, the effect was limited. Therefore, further investigations should be conducted to increase the effect of the xylan derivatives on paper with higher beating degrees.

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