Effect of the Starch Source on the Performance of Cationic Starches having Similar Degree of Substitution for Papermaking using Deinked Pulp

Jin Liu, Rendang Yang, and Fei Yang*

Cationic waxy corn starch was prepared from waxy corn starch with 2,3-epoxypropyl trimethyl ammonium chloride (ETMAC) as a cationic etherifying reagent. Its structure was identified by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and X-ray powder diffraction (XRD). The results showed that quaternary ammonium groups were introduced successfully into the waxy corn starch, and the cationic reaction occurred on the surface of the starch granules. Cationic waxy corn starch was then applied into deinked pulp as a paper reinforcer, and the result was compared with that of cationic tapioca starch and cationic maize starch. In general, the physical strengths of the paper were improved significantly with an increasing dosage of cationic starches. Cationic waxy corn starch was superior in terms of enhancing the physical properties of paper. In addition, with the use of cationic waxy corn starch, anionic trash in the slurry could be better removed .

Keywords: Waxy corn starch; Cationization; Deinked pulp

*Contact information: State Key Laboratory of Pulp and Paper Engineering. South China University of Technology, 510640, Guangzhou, P. R. China; *Corresponding author: yangfei@scut.edu.cn*

INTRODUCTION

With the development of online shopping and e-commerce, the demand for packaging paper and cardboard has increased. Meanwhile, due to a shortage of wood pulp, extensive research has focused on finding a suitable substitute for conventional forest-based materials used in papermaking manufacture (Fatehi *et al.* 2009). Among the possible alternatives, recycled paper is currently at the center of attention (Ghasemian *et al.* 2012). However, the strength of recycled paper is gradually reduced by repeated use, which is mainly caused by the decrease in the fiber bonding strength due to the hornification phenomenon (Hamzeh *et al.* 2012). Therefore, it is also not sufficient to meet the industry's demand, and its application is restricted. The use of paper reinforcing agents provides an effective solution to solve that problem (Laleg and Pikulik 1993; Kitaoka and Tanaka 2001; Yamauchi and Hatanaka 2002). Paper reinforcing agents promote bonding between pulp fibers and improve the strength properties of paper; these interactions are generally termed as van der Waals forces, hydrogen bonding, ionic attractions, and covalent bond formation (Hamzeh *et al.* 2012).

Cationic starch represents an important commercial modified starch that is widely used as an additive in paper, textile, oil field drilling, wastewater treatment, and the cosmetics industry because of its relatively low price, excellent performance, good biodegradability, and biocompatibility (Khalil and Aly 2001; Zhang 2001; Heinze *et al.* 2004). Cationic starch is preferred because the positive charge that has been introduced onto the starch molecule chain tends to form an electrostatic bond with the negatively charged sites on the cellulosic fibers (Hubbe 2007). Starch is a semicrystalline composite of biopolymers of glucose composed of linear α-(1,4)-linked residues with α-(1,6)-linked branch chains (Vamadevan *et al.* 2013). Generally, most starches, such as maize starch, tapioca starch, and potato starch contain amylose and amylopectin at proportions of 70% to 80% and 20% to 30%, respectively. However, waxy corn starch essentially consists of amylopectin alone and is often studied as a model of amylopectin (Kurakake *et al.* 2009). Amylopectin is a macromolecule with branching and α-(1, 6)-linkages and has a crystalline region formed by short linear side chains. The amorphous regions in starch granules, which mostly consist of internal chain segments of amylopectin, can be highly influential to the physicochemical properties of the starch (Donovan 1979; Slade and Levine 1988). With a strong and stable viscosity characteristic, waxy corn starch could be used in food, paper, textiles, and medicine, which reduce costs and improve quality. Currently, chemically modified waxy corn starch has been mostly used as a thickener, emulsifier, binder, and suspending agent for the food industry (Yeh and Yeh 1993; Permans 1997; Garzóan *et al.* 2003; Goff 2004). The use of cationic waxy corn starch as an enhancer for production of paper from recovered fibers has been rarely reported.

In this work, cationic waxy corn starch was prepared, characterized, and evaluated. Different dosages of cationic starches were individually added to deinked pulp and the hand-sheet properties in terms of tensile, tearing, and bursting properties were investigated. In addition, the changes charge demand after adding cationic starches were analyzed.

EXPERIMENTAL

Materials

Waxy corn starch was obtained from Tong di Co (Jining, China). The cationic etherifying reagent 2,3-epoxypropyl trimethyl ammonium chloride (ETMAC), was provided by Dow Chemical Company (USA). Cationic tapioca starch and cationic maize starch (tertiary amine starch) were acquired from Hua tai Co. (Dongying, China). All other chemicals were of analytical grade and used as received without further purification.

Methods

Preparation of cationic waxy corn starch

Waxy corn starch (50 g, on a dry weight basis) was suspended in 125 mL of sodium chloride solution (7.5 g, on a dry weight basis) and mixed with NaOH (10 wt.%) to adjust the pH between 11 to 12. Afterwards the cationic etherifying reagent, 2,3-epoxypropyl trimethyl ammonium chloride (ETMAC) (70 mL, 3 wt.%) was added to the suspension. The reaction was carried out at 80 °C with continuous stirring (200 rpm) for 2 h. After the etherification reaction, acetic acid (10 wt.%) was added to the starch suspension, which was neutralized to a pH of 6.5 to 7.0. The subsequent starch suspension was vacuum-filtered and washed with aqueous ethanol solution (60 wt.%) a total of five times. The obtained cationic waxy corn starch was placed in a vacuum oven dried at 40 °C overnight. The Kjeldahl method described by AACC (2000) was used to determine the nitrogen content of the cationic starches. The degree of substitution (DS) of each sample was calculated using Eq. (1) (Mourya and Inamdar 2008).

$$\mathrm{DS}=\frac{(162.15\times\%\mathrm{nitrogen})}{1401-(154.64\times\%nitrogen)} \tag{1}$$

Determinations of DS were run in triplicate for each sample.

Sheet formation and paper testing

Cationic starches were used in dosages of 0.2%, 0.4%, 0.6%, and 0.8%, respectively based on the oven dried weight of the pulp. After mixing the pulp suspension, handsheets with a target basis weight of 80 g/m^2 were made in a British handsheet former as per TAPPI Standard T205 sp-02 (2002). For determination of strength properties, the samples were conditioned at 50 ± 2% relative humidity and 23 ± 1 °C according to TAPPI T402 sp-98 (2004) for at least 4 h. The tensile, tearing, and bursting properties were tested according to ISO 1924-2 (2008) and ISO 1924-3 (2005). Four replications were tested for each treatment. The pH of the papermaking water was about 7.5. To simplify the experiments, no other substances were added to the slurry.

Characteristics of the cationic starches

The viscosity of cationic waxy corn starch was evaluated using a MDJ rotary viscometer (Shanghai, China). The pH of cationic waxy corn starch was determined with a Mettler SevenGo Pro (Shanghai, China). The solubility, ash content, and moisture content of cationic waxy corn starch were determined by the method of Vamadevan *et al.* (2013).

Scanning electron microscopy (SEM) analysis

Granular shapes and the surface structures of the native and cationic waxy corn starch were observed by using SEM (ZEISS EVO18, Germany). The sample was mounted on a circular aluminum stub with a double-sided tape, coated with gold using an ion sputter (Hitachi E101; Tokyo, Japan), and examined by SEM at an accelerating voltage of 10 kV.

Fourier transform infrared (FT-IR) analysis

The FTIR spectra of waxy corn starch, cationic waxy corn starch, and ETMAC were recorded on an IR-Prestige-21 spectrometer (Shimadzu Corp., Japan) using the KBr disc technique. For FTIR measurement, the samples were placed in a desiccator over time then mixed with anhydrous KBr and compressed into thin disk-shaped pellets.

X-Ray diffraction (XRD) analysis

X-ray powder diffraction measurements were conducted on a D8 FOCUS X-ray diffractometer (Bruker AXS Corporation, Germany) operating at 35 mA and 40 kV. The X-ray source was Cu-K α1 filtered radiation (k = 0.15418 nm). The scattering angle (2θ) was varied from 5^o to 40^o with a step width of 0.02^o.

Streaming current titration analysis

The pulp was prepared at a concentration of 0.5%, and then cationic maize starch, cationic waxy corn starch, or cationic tapioca starch were added in dosages of 0.5%, 1.0%, 1.5%, 2.0%, 2.5% or 3.0% based on the oven dried weight of the pulp under continuous stirring (300 rpm). Potassium polyvinylsulfate (PVSK) or polydiallyldimethylammonium chloride (P-DADMAC) was used to titrate each sample, and the titration endpoint was determined by a particle charge tester (BTG Mütek, Sweden). The cationic demand of each sample was calculated using Eq. 2,

$$q = Vc/w_t \tag{2}$$

where V is the volume of standard solution consumed by the sample (mL), c is the charge density of standard solution (mol/L), W_t is the weight of sample (g), and q is the charge amount (μmol /g). The charge determinations were run in triplicate for each sample.

RESULTS AND DISCUSSION

Characteristics of Cationic Starches

The cationic starches were dispersed in distilled water and heated to 95 °C in a water bath with periodic stirring, and the suspension was maintained at this temperature for 20 to 40 min. The solution was then diluted with distilled water and chilled before use. Some characteristics of the cationic starches are listed in Table 1.

Table 1. Characteristics of the Cationic Starches

Parameter	Cationic tapioca starch	Cationic maize starch	Cationic waxy corn starch
pH	7.00	7.00	7.00
Viscosity cP	47.0	45.0	50.0
Solubility %	99.9	99.9	100
Ash content %	0.280	0.310	0.270
Moisture content %	9.60	9.40	10.2
Degree of substitution	0.0370	0.0330	0.0350
Supplier	Tong di Co.	Tong di Co.	Self-regulating

FTIR Spectra of Starches and ETMAC

The FTIR spectra of waxy corn starch, cationic waxy corn starch, and ETMAC are depicted in Fig. 1.

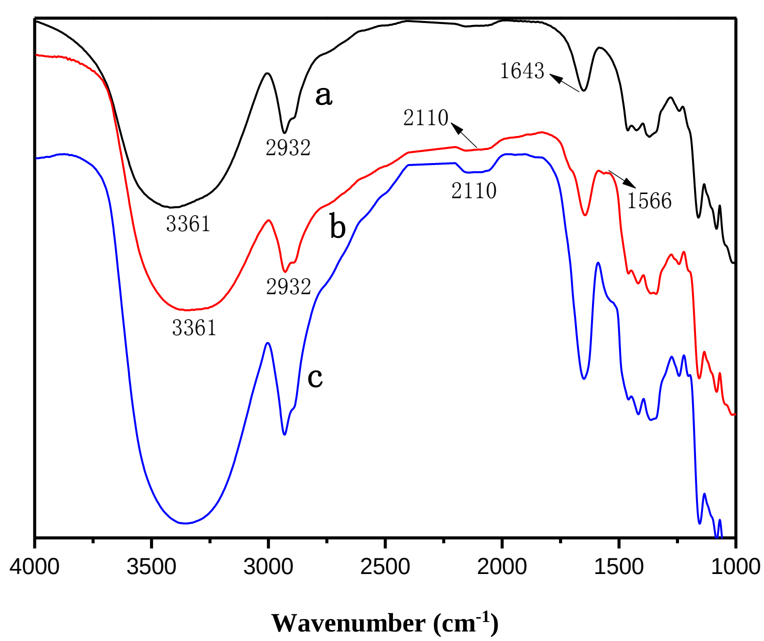

Fig. 1. FTIR spectra of (a) waxy corn starch, (b) cationic waxy corn starch, and (c) ETMAC

In the IR spectrum of waxy corn starch (Fig. 1a), the extremely broad band at 3361 cm^{-1} and the band at 2932 cm^{-1} were attributed to the O–H stretching and the C–H stretching vibrations, respectively. Meanwhile, the bands at 1165 and 1100 cm^{-1} were characteristic of the C–O stretching vibrations of AGU (Pal *et al.* 2005). Figure 1c shows the broad band at 3452 cm^{-1} in the FTIR spectrum of ETMAC was assigned to the O–H stretching vibration of water that remained in the specimen. A band at 2110 cm^{-1} recorded in the IR spectrum of ETMAC was associated with the NH^+ stretching vibration. Besides, the bands at 1481 and 1566 cm^{-1} originated from the C–H and the N–H vibrations, respectively.

In the case of cationic waxy corn starch (Fig. 1b), the IR profile was similar to that of native starch. In addition to the characteristic peaks of the starch backbone, some additional bands appeared at 1482, 2110, and 1566 cm^{-1} and they were assignable to the C–H, NH^+ stretching vibration, and N–H deformation vibration. These bands were not present in waxy corn starch, providing evidence for the incorporation of a cationic moiety onto the backbone of starch.

Morphology of Native and Cationic Waxy Corn Starch

Figure 2 shows the morphology of granules of native and cationic waxy corn starch. Waxy corn starch, Figs. 2a and 2b, were composed of granules having spherical, ellipsoid, or polygonal shapes and various sizes.

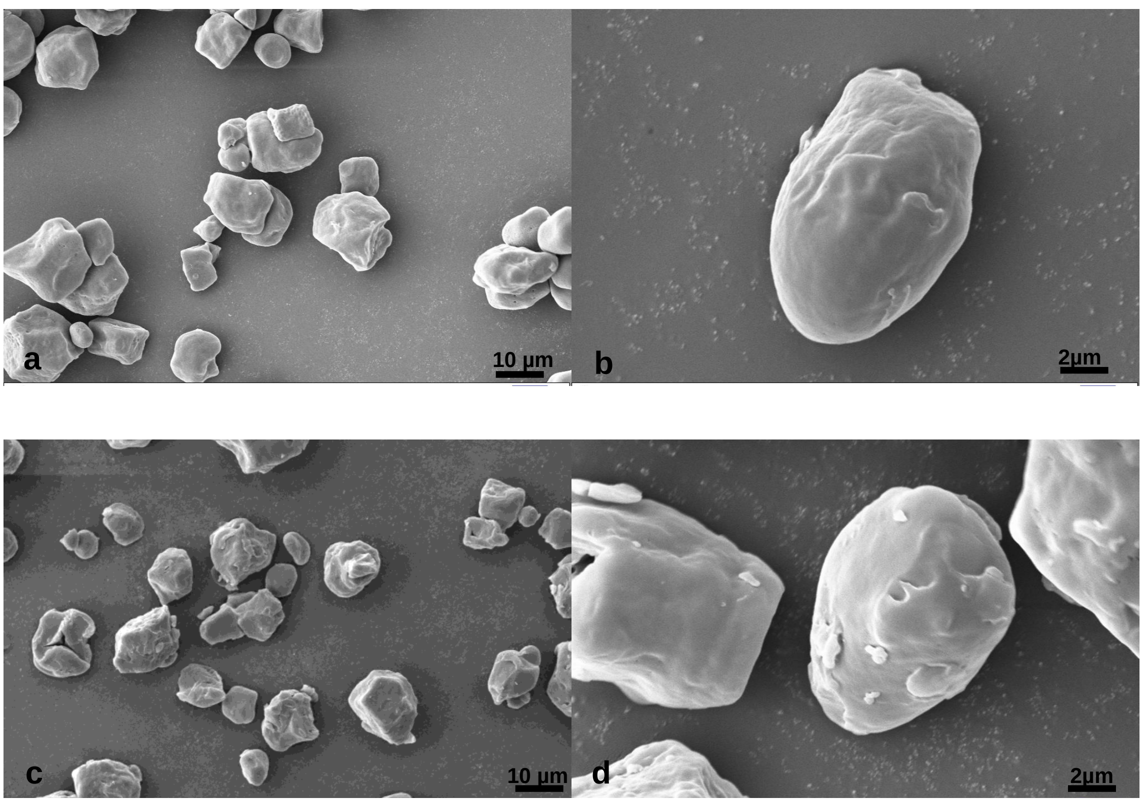

Fig. 2. Morphology of (a) waxy corn starch, (b) waxy corn starch at a higher magnification, (c) cationic waxy corn starch, and (d) cationic waxy corn starch at a higher magnification

After the cationic reaction, partial granules and small fragments apparently disintegrated as shown in Figs. 2c and 2d, and the surface morphology of cationic waxy corn starch was changed slightly. Its surface was scaly and presented with some small depressions. This is good evidence that the cationic reaction occurs on the surface of the starch granules with low DS. This result is consistent with a previous study (Kuo and Lai 2007).

X-Ray Diffraction Patterns of Starches

The X-ray powder diffraction patterns of starches are displayed in Fig. 3. From this figure, native waxy corn starch exhibited a characteristic A-type X-ray diffraction pattern. In the XRD pattern of native corn starch, strong reflections (2θ) were found at 15.16°, 17.22°, 17.88°, and 23.08°. X-ray diffraction patterns of cationic starches showed that the pattern of native starch amorphism increased after cationization of starch. This result was supported by previous research (Wang and Xie 2010).

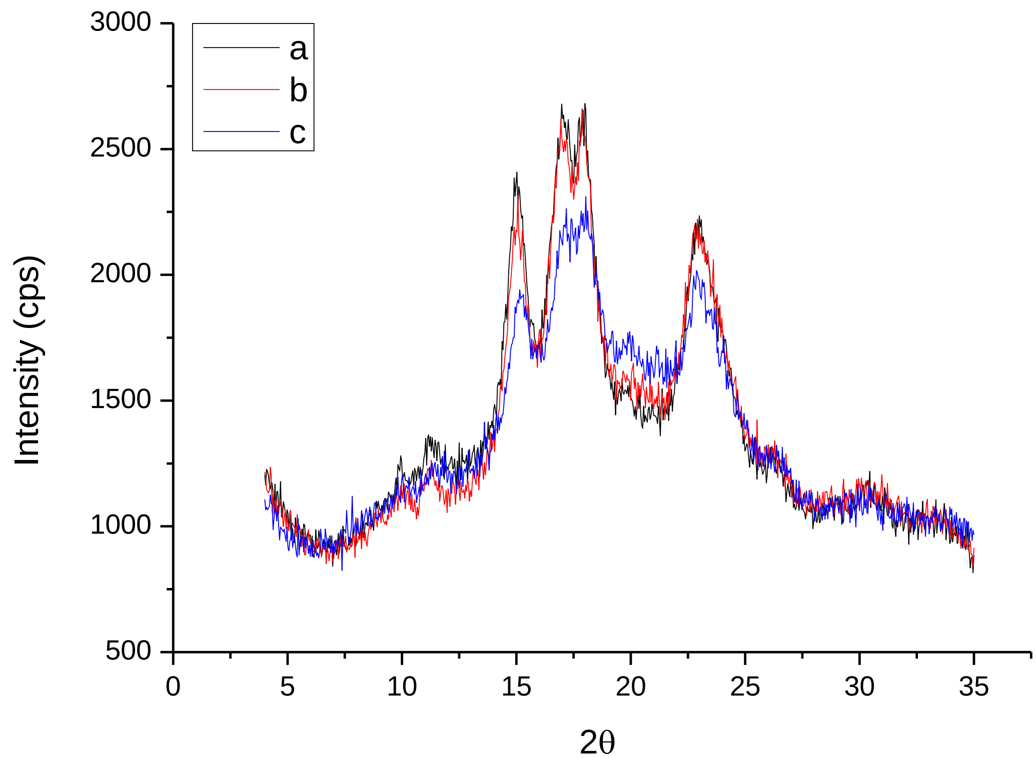

Fig. 3. X-ray diffraction patterns of (a) waxy corn starch, (b) cationic waxy corn starch with a DS of 0.035, and (c) cationic waxy corn starch with a DS of 0.07

Charge Titration

Determination of the charge is important to characterize the paper machine wet-end systems (Hubbe and Chen 2004). With a variety of measuring instruments, especially the charge analyzer, wet chemical control technology has been greatly developed (Patton and Lee 1993). By analyzing changes in the charge demand, the situation in cationic starch and fiber or pulp adsorption of anionic trash can be better characterized.

As shown in Table 2, a positive value indicates the slurry is negatively charged and a negative value demonstrates the slurry is positively charged, *i.e.*, the value represents the charge demand of the slurry. With the amount of cationic starch increasing, the charge demand of the slurry showed a downward trend due to the fact that the negatively charged substance in pulp was adsorbed. A dosage of 0.5% cationic waxy corn starch added to the slurry resulted in a balanced state of charge. The result showed that the cationic waxy corn starch had a more positive charge under the same DS and consumption, and the ability to bind fines and eliminate anionic trash became stronger.

Table 2. Changes in Charge Demand of Pulp

Dosage of cationic starches (%)	Charge demand (μmol/g)		
	Cationic tapioca starch	Cationic maize starch	Cationic waxy corn starch
0.00	2.580±02	2.580±02	2.580±02
0.50	2.160±02	0.240±02	0.000±01
1.00	0.330±03	0.290±03	-0.370±02
1.50	-1.800±02	0.280±01	-0.830±04
2.00	-2.130±05	0.320±01	-2.380±02
2.50	-3.070±02	0.400±04	-2.540±05
3.00	-2.030±03	0.290±01	-3.510±04

Effect of Cationic Starches on Paper Properties

Data on tensile, tearing, and bursting properties of sheets treated by three distinct cationic starches are presented in Fig. 4. The results showed that the tensile strength, tearing strength, and bursting strength were increased with the increase amount of cationic starch and showed an upward trend. The reason is that cationic starch with a positive charge is first to combine with small fibers with a negative charge, promoting binding between the fibers. This result is in good agreement with previous findings. For instance, at a 0.4% dosage of cationic maize starch (Fig. 3c), the increase of tearing strength was about 25% compared with that of the blank sample. However, the amount of cationic starch was beyond 0.4%, increasing the use of cationic from 0.4 to 0.8% resulted only in a 10 to 20% gain in strength. This suggests that the cationic starch should be used according to the process cost and effectiveness requirements and the final product quality.

The trend was observed that cationic waxy corn starch had a unique effect on the strength property compared with the other cationic starches. At a 0.4% dosage of cationic waxy corn starch (Fig. 4d), the increase in tearing strength was about 10% more than the control sample. This can be explained by the differences in the molecular weights, and that highly branched structures produce additional contacts between fibers in comparison to other cationic starches. Similar trends were found for the cationic treated samples shown in Figs. 4a, 4b, and 4c. The physical properties of paper depend on inter-fiber bonding (Haslach 2000; Whitten *et al.* 2005), presumably because waxy corn starch is a wholly branched structure with higher molecular weight and more reactive sites and thus could absorb more fines and exert its beneficial effects on paper.

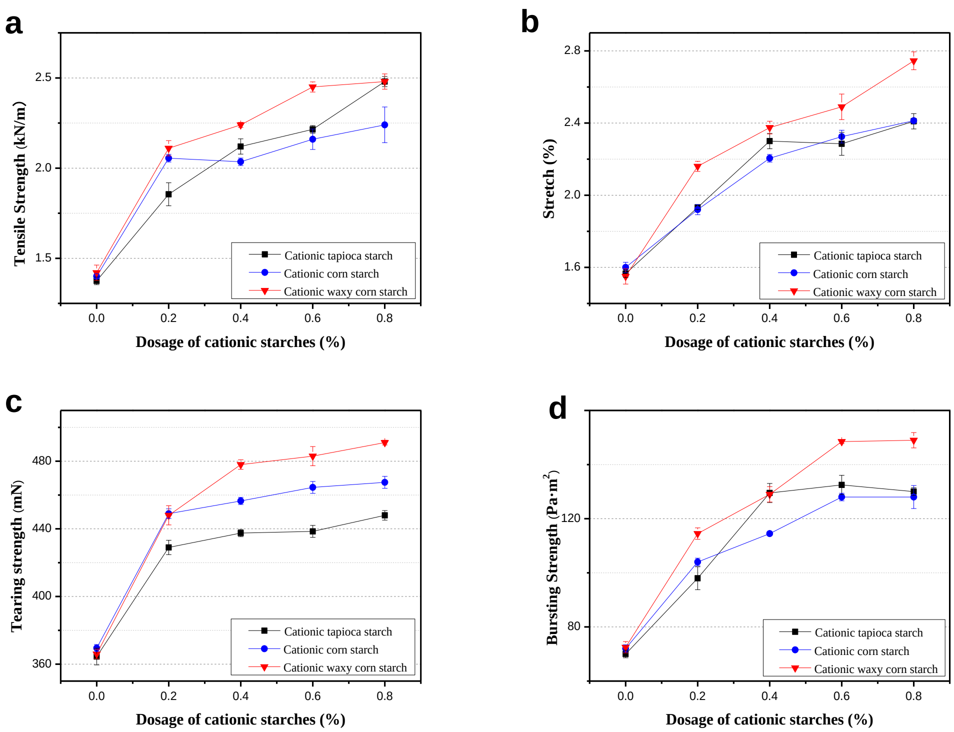

Fig. 4. Effect of cationic starches on (a and b) tensile, (c) tearing, and (d) bursting properties. Data reported as the mean ± standard deviation

CONCLUSIONS

1. Cationic waxy corn starch was prepared and characterized. The results indicated that the reaction occurred on the surface of the starch granules.
2. Cationic starches were applied and used in dosages of 0.2%, 0.4%, 0.6%, and 0.8%, and the results showed that the tensile strength, tearing strength, and bursting strength were increased with the amount of cationic starch. A dosage of 0.4% was superior in increasing the physical strength of the paper; further addition of cationic starches decreased the growth rate of physical strength.
3. Considering the charge demand analysis, it was found that a dosage of 0.5% cationic waxy corn starch added to the slurry resulted in a balanced state of charge. The result showed that cationic waxy corn starch is more cost-efficient in deinked pulp applications.

ACKNOWLEDGMENT

The authors would like to acknowledge the support of the National Key Technology R&D Program (2013BAC01B03).

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Article submitted: August 4, 2014; Peer review completed: September 21, 2014; Revised version received: December 3, 2014; Accepted: December 4, 2014; Published: December 15, 2014.