

Research Article

Preparation and Application of Cationic Modified Cellulose Fibrils as a Papermaking Additive

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Received 21 February 2016; Revised 11 May 2016; Accepted 26 May 2016

Academic Editor: Haisong Qi

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This paper deals with cationic modified cellulose fibrils obtained by reacting the cellulose fibrils with 2,3-epoxypropyltrimethylammonium chloride (EPTMAC). The physical and chemical properties of unmodified cellulose fibrils (UMCF) and cationic modified cellulose fibrils (CMCF) were characterized by SEM, FTIR, degree of substitution, colloid titration, zeta potential, and thermogravimetric analysis. The experimental results showed that, after cationization, surface charge density and zeta potential reversed, thermal stability decreased, and new functional groups appeared, while the surface morphology did not show much difference from the UMCF. With the addition of three kinds of additives (UMCF, CMCF, and cationic starch (CS)) to BCTMP, the addition of UMCF and CMCF had little effect on zeta potential, while the addition of CS changed zeta potential obviously. With the increasing of additive amount, the bulk of paper sheets added CMCF did not change obviously, while the bulk of paper sheets added UMCF and CS decreased rapidly. With regard to physical strength, all the three kinds of additives could improve the tensile index and tear index; the tensile index of paper sheets added CS was higher than that of added UMCF and CMCF, while the tear index of paper sheets added CMCF was the highest among the three additives.

1. Introduction

Cellulose is the most abundant polysaccharide in nature; its renewability, sustainability, and biodegradability have brought cellulose more and more attentions all over the world [1, 2]. The chemical modification of cellulose is introduction of new functional groups on the cellulose chain by reacting hydroxyl groups with modification reagent, which can enrich its functionality and thus expand application range. Cellulose derivatives are products of esterification and etherification of hydroxyl groups with chemical reagent on cellulose; according to the structural features, cellulose derivatives can be divided into cellulose ether, cellulose ester, and cellulose ether ester [3].

As an important cellulose derivative, cationic cellulose is widely applied in various fields, such as papermaking process, cosmetic, adsorbents, and antibacterial agents [4–7]. There are three kinds of methods to prepare cationic modified fibers. The first method is direct cationize fibers to

get the cellulose fiber amine derivatives. The second method is cationic prepolymer of short chain coupled to the fiber surface to obtain high surface charge density fiber. The third method is graft copolymerization of cationic polymers to the fiber; cationic monomer and neutral monomers are connected to the fiber surface by free radical copolymerization. All these three methods can make the fiber cationic, but the connection types of cationic and fibers are different, and finally the fiber morphology and performance are also different [8]. There are few ways of introduction of cationic groups in cellulose by chemical reaction, for instance, attaching quaternary ammonium groups by using of 2,3-epoxypropyl trimethylammonium chloride (EPTMAC) [9–11]. One end of the cationic reagent is quaternary ammonium salt, showing cationic character, and the other end of the structure is an epoxy group. The covalent addition of a quaternary amine to polysaccharide is used extensively in cationic starch production [12].

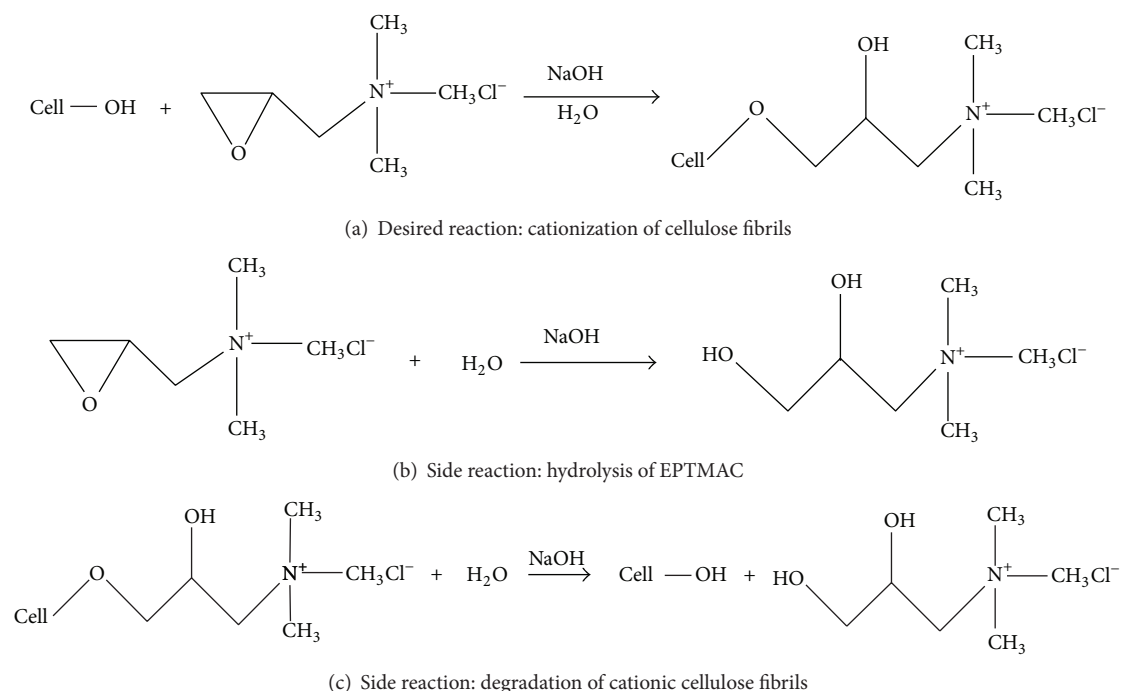


FIGURE 1: Competitive reactions during the cationic modification of cellulose fibrils using EPTMAC/H₂O/NaOH System.

The cationic modification of cellulose fibrils consists of an etherification reaction between the alkali activated hydroxyl group of cellulose fibrils and epoxy group of EPTMAC (Figure 1(a) reaction). However, it has been reported in many studies that the main etherification reaction is also accompanied by the alkaline hydrolysis [13–15]; that is, during cationization process, EPTMAC is consumed in two ways: cationization of fibrils (Figure 1(a)), which is desirable, and the EPTMAC hydrolysis reaction (Figure 1(b)), which is undesirable [16]. When the reaction system has higher water content, more hydrolysis of EPTMAC will occur (Figure 1(b)). Thus, less EPTMAC will be available for the cationization reaction. Moreover, at high water content, the hydrolysis of cationically modified fibrils will occur (Figure 1(c)), which results in a decrease of cationization efficiency [13]. Thus, the water content is very important for the cationic reaction.

In the field of pulp and paper making, the concept of cationic fiber was introduced to serve as a substitute for the traditional cationic polymer used in papermaking industry [17–20]. The cationic modification makes the fiber surface positive charged; therefore, the addition of cationic fiber results in high filler retention, well drainage property, and strong ability of absorbing anion distracters [8]. In recent ten years, this method has been paid more and more attention in papermaking industry, Xie and coworkers investigated the cationic modified fibers, which can improve the retention rate of Precipitated Calcium Carbonate (PCC), with an added proportion of 0.9%, and the retention rate increased from 57.73% to 72.21%, with the turbidity of white water decreased at the same time [21]. Cationized cellulose fibers improved strength and adsorption of anionic fines and fillers by increasing positive charges on fiber surface [20]. Cationized

cellulose fibers were applied to improve paper sheets strength and retention of anionic fines and fillers [22].

The requirements for paper bulk and cost control have made papermaking enterprises pour more and more interests into high yield pulp (HYP), especially BCTMP (bleached chemithermomechanical pulp); due to their particular characteristics [23–26], paper and board products having high bulk require a smaller amount of fibers, which is desirable for economical and environmental reasons. However, the physical strengths such as tensile and tear of BCTMP are lower than those of chemical pulps. Professor Korpinen and Fardim [27] investigated the reinforcement potential of sawdust kraft pulp in different mechanical pulp; the addition of unrefined and refined sawdust kraft pulp has different influence on physical properties of pulp. Zhang et al. [28] used bleached wheat straw pulp to improve the tensile strength of HYP without affecting the bulk. Lin et al. [29] used premixed fines and fillers to improve retention, paper sheets strength, and optical properties.

Many investigations have aimed at the improvement and utilization of BCTMP, while cationic modified cellulose fibrils has hardly been considered. Therefore, the aim of this study is to investigate the effects on the physical properties of BCTMP paper sheets by adding three kinds of additives (CMCF, UMCF, and CS); differences may be detected on the strength properties of BCTMP paper sheets between the addition of CMCF and the other two additives.

2. Materials and Methods

2.1. Preparation of Cellulose Fibrils. Cellulose fibrils were produced from HBKP (hardwood bleach kraft pulp) by mechanical treatment in PFI mill (FRANK-PTI P40110.E000), with

a beating gap of 0 mm in accordance with the TAPPI standard method (T 248 sp-00), refining at 10 wt.% total solids at 20,000 total revolutions; the shearing and compression forces produced by the impacts of the rotor bars cause intrafiber bond breaking, external fibrillation, and fiber cutting [30–32]; after PFI refining, the obtained cellulose fibrils were collected into a sealed plastic bag for further study.

2.2. Chemical Reagent Involved in This Paper. EPTMAC was used as a cationization agent and obtained from Aoerte Chemical Ltd. in Zibo, Shandong province, with a purity of 60 wt.%. Polydiallyl dimethyl ammonium chloride (PDADMAC) and polyethene sodium sulfonate (PES-Na) were provided by BTG Instruments GmbH, Germany, applied without further purification. Sodium hydroxide, acetic acid, and ethanol were all analytical grade chemicals from Sinopharm Chemical Reagent Beijing Co., Ltd. Cationic starch (Cato. 304, DS 0.033–0.035) was received from National Starch Inc.

2.3. Cationic Modification of Cellulose Fibrils. In previous studies, the 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHMAC) and 2,3-(epoxy propyl)-trimethylammonium chloride (EPTMAC) were widely applied in the etherification field; the latter was found to be more active for cationization efficiency and easy to produce cationic fiber under similar conditions [33]. In this study, EPTMAC was selected as the cationization agent to cationize cellulose fibrils.

The cationization of cellulose fibrils has been carried out in a laboratory kneading machine (TYPE: SH-O); during the process, the staff of the cellulose fibrils was firstly diluted to 10 wt.%; then a certain amount of sodium hydroxide was added to the staff and kneaded for half an hour in the kneading machine; then the cationization reagent was slowly added to the mixing systems kneading for 150 minutes; and the temperature was kept at 30°C; when reached the reaction time, the mixture was neutralized with a certain amount of acetic acid and then washed with a large amount of deionized water to remove the excess chemical reagents; also, for a blank test, none of the chemicals was added, which was called unmodified cellulose fibrils (UMCF). Cationic modified cellulose fibrils (CMCF) were prepared under the conditions of EPTMAC to cellulose molar ratio of 0.4, NaOH dosage of 30 wt.% of cellulose fibrils, and water content of 90 wt.%.

2.4. Fiber Quality Analysis (FQA). The fiber quality analysis of cellulose fibrils before and after cationic modification was detected by L&W fiber tester; the test items included fiber length, fiber width, and kink index.

2.5. Scanning Electron Microscopy (SEM). The surface morphology of cellulose fibrils was observed by SEM (SU1510, HITACHI, Japan) at the acceleration voltages of 10.0 kV after being freeze-dried and sputtered with gold-palladium.

2.6. Fourier Transform Infrared Spectroscopy (FTIR) Analysis. FTIR analysis of the UMCF and CMCF was performed using a Fourier Infrared Spectrometer (TENSOR 22, BRUKER, GmbH) in transmission mode. For transmission mode,

a sample of KBr powder (IR grade, Aldrich) was used as the background; the sample was first dried through a vacuum freeze dryer (FD-1D-50) provided by Beijing Boyikang Experimental Instrument Co., Ltd.; the dried sample was then grinded with a mortar and pestle in KBr, with a 2 wt.% of KBr. The spectrum was obtained at a nominal resolution of 2 cm⁻¹, and the spectrum region was recorded between 600 cm⁻¹ and 4,000 cm⁻¹.

2.7. Determination of Degree of Substitution. The degree of substitution of quaternary ammonium groups on the CMCF was calculated through the nitrogen content, according to formula (1). The cellulose fibrils nitrogen content before and after modification was determined by using a CHNS Elemental Analyzer (Vario EL cube) provided by Elementar, Germany. One has

$$DS = \frac{162 \text{ g/mol} \times N\%}{14 \text{ g/mol} \times 100 - 151.63 \text{ g/mol} \times N\%}, \quad (1)$$

where N% is the nitrogen content of cationically modified cellulose fibrils; 162 g/mol is the molecular mass of anhydroglucose unit; 14 g/mol is the molecular mass of N; and 151.63 g/mol is the molecular mass of EPTMAC.

2.8. Surface Charge Density Measurement. Surface charge density of UMCF and CMCF was measured using a colloidal titration method with a Mutek™ PCD-04 (Travel) provided by BTG Instruments GmbH, Germany. During the colloidal titration, the samples were diluted to 1 g/L and then titrated with standard cationic polyelectrolyte [poly(diallyldimethylammonium chloride) (poly-DADMAC)] and standard anionic polyelectrolyte [polyethene sodium sulfonate (PES-Na)] with the concentration of 0.1 mN, which are widely used as the cationic and anionic reactants in colloidal titration. Three parallel tests were completed to obtain an average value for each sample.

2.9. Zeta Potential Measurement. The zeta potential of UMCF and CMCF without electrolyte was measured at 25°C using a zeta potential analysis (Mutek SZP 06). The samples were diluted to 5 g/L with deionized water and dispersed by homogenizer, IKA T18 basic (ULTRA TURRAX), the PH value of the samples was kept at 7, and the set pressure was given to be 200 mbar.

2.10. Thermogravimetric Analysis (TGA). The TGA of all samples was operated using Thermogravimetric Analyzer (TGA/DSC1) provided by Mettler Toledo; the TG and DTG curves were obtained under the nitrogen gas with flowing rate of 35 mL·min⁻¹ and heating rate of 10°C·min⁻¹ from 25°C to 450°C; the added sample mass was about 6.0 mg in a ceramic pan.

2.11. Preparation of Paper Sheets. The bleached chemithermo-mechanical pulp (BCTMP) with a beating degree of about 40°SR was obtained through a Valley beater; then the BCTMP was screened with a 0.35 mm sieve according to TAPPI standard methods T275 sp-02; after screening, the obtained

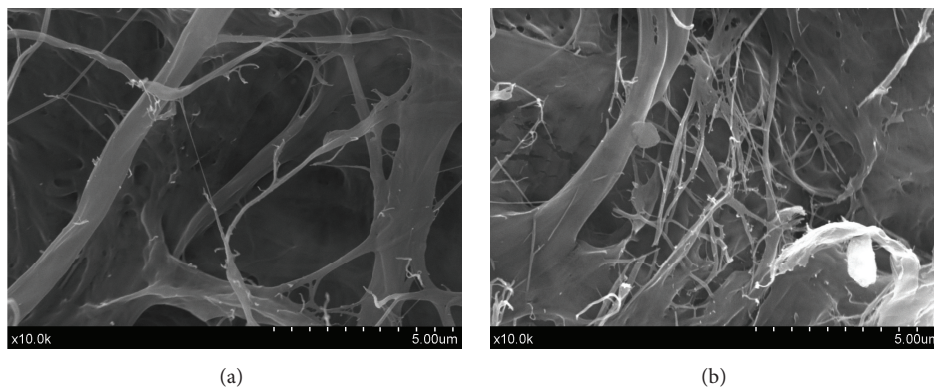


FIGURE 2: SEM micrographs of cellulose fibrils. (a) UMCF and (b) CMCF.

TABLE 1: The fiber quality analysis of UMCF and CMCF.

Sample	Mean length [mm]	Mean width [μm]	Kink index
UMCF	0.656	17.5	1.309
CMCF	0.672	18.0	2.564

BCTMP was collected and the beating degree was measured to be 41°SR. This pulp was used to make paper sheets (grammage 60 g/m²) containing various proportions of additives (UMCF, CMCF, and CS); according to TAPPI standard methods T205 sp-02, ten paper sheets were made of each additive amount, while five paper sheets were picked out for mechanical testing; the rest of pulp suspensions were retained for zeta potential analysis according to Section 2.9.

2.12. Mechanical Testing of Paper Sheets. Physical properties of the paper sheets were measured in an atmosphere of 50% relative humidity at 23°C for 24 h in accordance with TAPPI standard method (T402-sp-03); the main physical properties (grammage, thickness, bulk, tensile strength, and tear strength) were measured according to TAPPI standard T220 sp-01 (physical testing of pulp handsheets).

3. Results and Discussion

3.1. Fiber Quality Analysis of Cellulose Fibrils. Table 1 shows the fiber quality analysis of UMCF and CMCF; the mean length and mean width have no difference between UMCF and CMCF; nevertheless, the kink index of CMCF is much higher than that of UMCF. The conclusion was cationic modification had almost no impact on fiber length and width but could increase kink index.

3.2. Morphological Analysis of Cellulose Fibrils. Surface morphology of UMCF (Figure 2(a)) and CMCF (Figure 2(b)) are similar in Figure 4. As can be seen from the micrographs, both the two micrographs have some fibrils with diameters of several hundred nanometers and lengths of tens of microns. Compared with PFI refining process, the cationic modification process had no obvious influence on cellulose fibrils' surface morphology.

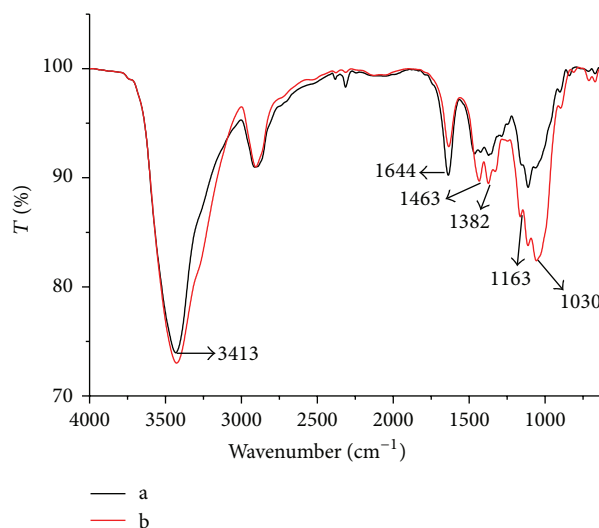


FIGURE 3: FTIR spectrum of UMCF (Spectrum a) and CMCF (Spectrum b).

3.3. Fourier Transform Infrared Spectroscopy. The FTIR spectra of the UMCF and CMCF are shown in Figure 3. A strong band due to hydroxyl (-OH) stretching appears at 3413 cm⁻¹ [34–37]. An intense band at 1644 cm⁻¹ originates from the absorbed moisture of the cellulose [38]. The absorbance between 1030 cm⁻¹ and 1163 cm⁻¹ is attributed to the C-O stretching in major ether bands [36, 39].

Compared to Spectrum a, Spectrum b of the CMCF gives clear evidence of quaternization in cellulose fibrils. An increase in intensity of the major ether bonds in the spectrum region between 1030 cm⁻¹ and 1163 cm⁻¹ provides evidence of grafting of EPTMAC onto the fibril surface [38]. In addition, a prominent band at 1463 cm⁻¹ is observed, which can be deduced to CH₂ bending mode and methyl groups of the cationic substituent [38, 40]. The band at 1382 cm⁻¹ is C-H bending vibration peak of -CH₃.

3.4. Degree of Substitution. Generally speaking, there are no molecular containing nitrogen in cellulose chains; experimental data showed that the UMCF had no nitrogen, while

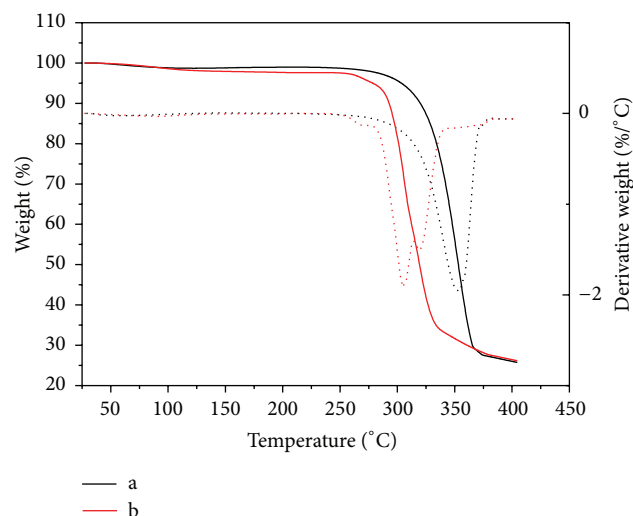


FIGURE 4: The TG and DTG curves of UMCF (a) and CMCF (b).

the obtained nitrogen content of CMCF was 1.16%; according to formula (1), the degree of substitution (DS) was calculated to be 0.154. The DS could represent the extent of the etherification reaction.

3.5. Surface Charge Density and Zeta Potential. The cationic modification of cellulose fibrils consists of nucleophilic reaction between the alkali activated hydroxyl group of cellulose fiber and epoxy group of EPTMAC (Figure 1(a) reaction), with the combination of quaternary ammonium to fiber surface by etherification reaction; the surface charge density will be transformed [20, 36]. As shown in Table 2, cationic modification could dramatically reverse the surface charge density (i.e., from $-14.29 \mu\text{eq/g}$ for the UMCF to $+18.68 \mu\text{eq/g}$ for CMCF), while the surface charge density of CS was measured to be $+505 \mu\text{eq/g}$, 27 times higher than that of the CMCF. The zeta potential results also confirmed the charge reversal of cellulose fibrils after cationic modification, from $-23.7 \pm 0.5 \text{ mV}$ for UMCF to $+15.7 \pm 0.5 \text{ mV}$ for CMCF.

3.6. Thermal Decomposition of Cellulose Fibrils. The TG and DTG curves of UMCF and CMCF under the same conditions are shown in Figure 4. The results indicate that the thermal stability of cellulose fibrils after cationic modification is decreased, the thermal degradation temperature of UMCF is 328.06°C , and after cationic modification, the thermal degradation temperature of CMCF decreases to 314.24°C . The weight loss peak of UMCF is at 360°C , while the CMCF has two weight loss peaks, 305°C and 325°C . This results showed that the cationic modification reduced the thermal stability of cellulose fibrils to some extent; the possible reason was that the introduction of quaternary ammonium enhanced the mechanism of random chain scission due to its nucleophilic character [41–43].

3.7. Zeta Potential of Pulp Suspension. Figure 5 shows the zeta potentials of pulp suspensions added three kinds of additives at various additive amounts. The pulp fibers were sufficiently

TABLE 2: The analysis of surface charge density and zeta potential.

Sample	Surface charge density [$\mu\text{eq/g}$]	Zeta potential [mV]
UMCF	-14.29 ± 0.3	-23.7 ± 0.5
CMCF	$+18.68 \pm 0.5$	$+15.7 \pm 0.5$
CS	$+505 \pm 5$	ND

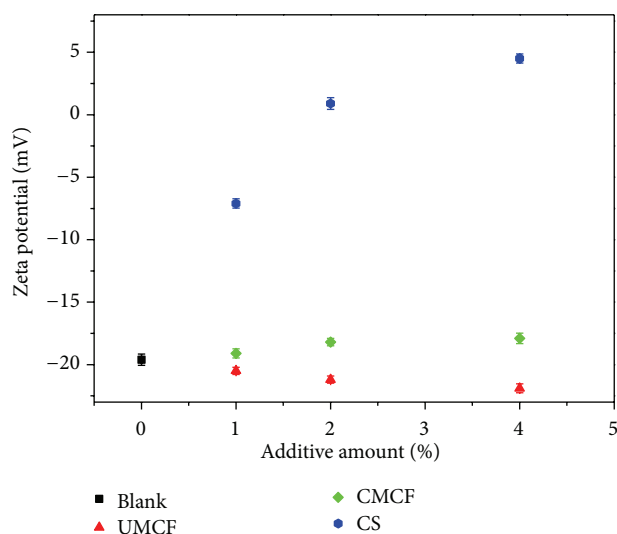


FIGURE 5: Zeta potentials of pulp suspensions with various additive amounts of three kinds of additives (UMCF, CMCF, and CS).

stable with no significant change of zeta potentials during the measurements, with a solid concentration of 2.4 g/L , the same with paper sheets making process. The zeta potential of pulp suspensions added UMCF slightly decreases with the increase of additive amount; it is because the UMCF contains large amount of anionic which can decrease the total zeta potential of the pulp suspensions. The addition of both CMCF and CS increases the zeta potential due to the existence of positive charge; the increase of zeta potential added CMCF is much less than that of added CS due to its far lower cationic charge density than that of CS. The zeta potential of pulp suspensions added CS is negative at 1%, but its sign is changed at 2% and 4%; the point of zero zeta potential (isoelectric point) is located between 1% and 2%.

3.8. Physical Properties of Paper Sheets. As mentioned, bulk is one of the most important features for BCTMP and should be paid more attention. Figure 6 shows the bulk of paper sheets added three kinds of additives, when added UMCF; the bulk decreases as the additive amount increases; this is due to the high density of hydroxyl which can form a large number of hydrogen bonds; thus the bonding strength is enhanced and the bulk decreases; the bulk of paper sheets added CS has the same tendency. While added CMCF, the bulk shows steady increase with the increase of additive amount. The bulk of paper sheets added fibrils (UMCF or CMCF) is higher than that of added CS; this is because fibrils can act as binders between the fibers and fines, playing the role of physical

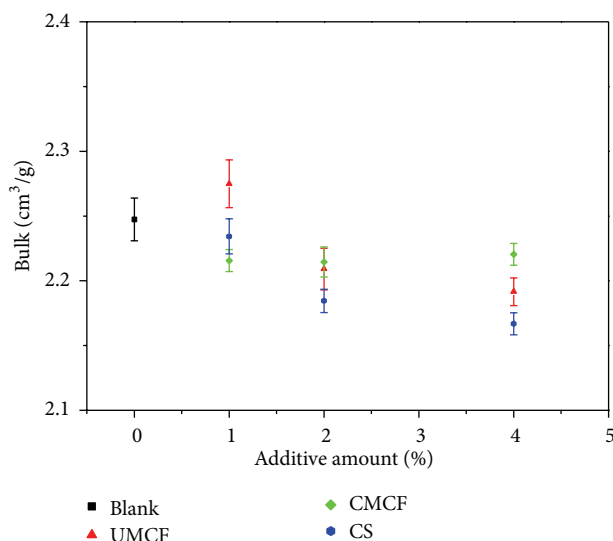


FIGURE 6: Bulk of paper sheets with various additive amounts of three additives (UMCF, CMCF, and CS).

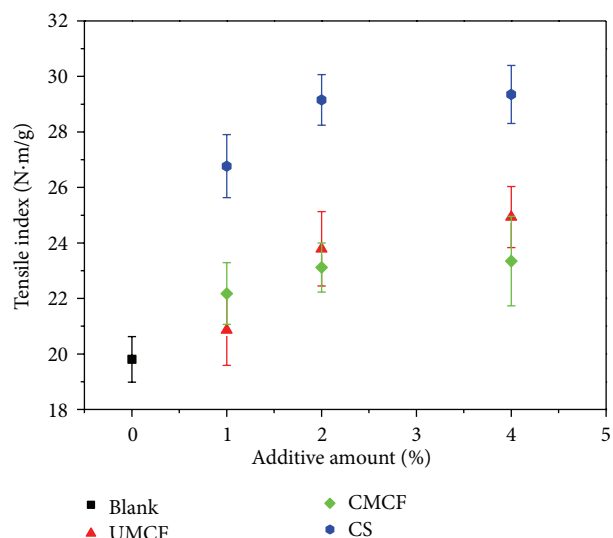


FIGURE 7: The tensile index of paper sheets with various additive amounts of three additives (UMCF, CMCF, and CS).

fillers, while the CS strengthens fiber-fiber and fiber-fines bonding capacity; thus the bulk decreases. The bulk of paper sheets added CMCF is higher than that of UMCF at additive amount of 2% and 4%; this may due to the repulsion force between the already absorbed cationic fibrils on the fiber surface and the fibrils approaching to the fiber, which leads to a weak binding network [44], while the addition of UMCF generates large number of hydrogen bonds, which lead to a tight network.

Results in Figure 7 indicate that all the three kinds of additives can act as strength additives to improve the tensile index of paper sheets; it can be found that the tensile index of paper sheets added CS is the highest among the three additives at the same additive amount, while the tensile index of paper sheets added CMCF is slightly lower than that

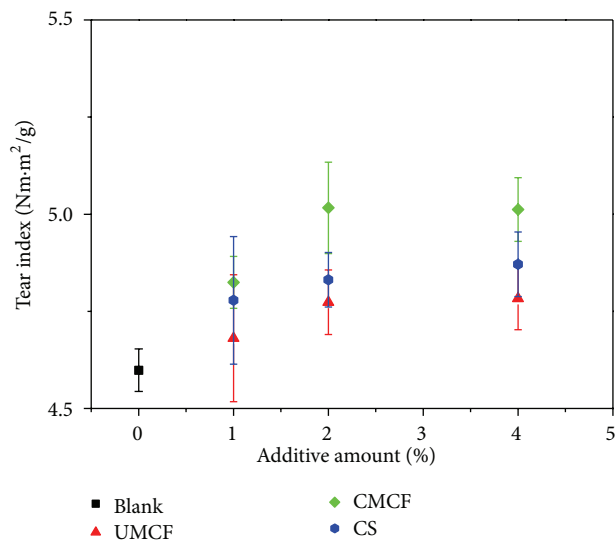


FIGURE 8: Tear index of paper sheets with various additive amounts of three additives (UMCF, CMCF, and CS).

of added UMCF. From 0% to 2%, the addition of CS into BCTMP can dramatically increase the tensile index, due to the high positive charge density which can bind the negative charged fines and fibers, when the additive amount is 4%; the tensile index will not be improved, as the isoelectric point is located between 1% and 2%, and the extra CS may have little effect on paper sheets strength. For the paper sheets added UMCF, with the increasing of additive amount, the tensile index steadily increases; this can be contributed to the increase of hydrogen bonds. For the paper sheets added CMCF, with the additive amount from 1% to 4%, the increase of tensile index is considered to be relatively small; that is because the amount of total fibers is constant, and the capacity of fixation by positive-negative ions adsorption is limited by the specific surface of fibers which is readily saturated by the CMCF due to its large size.

The results of tear index from the paper sheets added three kinds of additives are shown in Figure 8. Tear strength of paper or cardboard is an important physical performance indicator in practice, since most of paper or cardboard is often bearing tear. It can be seen that the addition of all three kinds of additives can improve the tear index; the tear index increases with the increase of additive amount. The tear index of the paper sheets added CMCF is the highest among the three kinds of additives. The tear index of paper sheets added CMCF is higher than that added UMCF; as cationic modification increased the kink index of cellulose fibrils, a number of studies have shown that kinked fibrils could improve the tear index, as more energy was needed in straightening and breaking bonds between the fibers [45–47]. In addition, the change of surface charge density would influence the fiber bonding capacity, and the tear index would be influenced [48]. The tear index of paper sheets added CMCF is higher than that added CS at all additive amount, since the larger size of the fibrils can increase the number of fiber junctions, which is positively correlated with tear index.

4. Conclusions

In this study, CMCF was prepared by cationization of cellulose fibrils with EPTMAC, with the cellulose fibrils produced from mechanical treatment in a PFI mill at a high revolution. Due to the quaternary ammonium connecting to the fibril surface, the chemical properties of the cellulose fibrils were thus extremely changed after cationic modification, the inversion of electrical property, reduction of thermal stability, and appearance of new functional groups. While the surface morphology of cellulose fibrils before and after cationization showed no obvious difference. The addition of UMCF and CMCF had little effect on zeta potential compared with CS. The tensile index and tear index could be improved with the addition of CMCF, UMCF, and CS; at the same time, CMCF could preserve the BCTMP's high bulk property to some extent.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

Acknowledgments

The authors thank China National Pulp & Paper Research Institute and Tianjin Key Laboratory of Pulp & Paper for the technical support.

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