Preparing Cationic Cellulose Derivative in NaOH/Urea Aqueous Solution and its Performance as Filler Modifier

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Cellulose etherification with 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTAC) was carried out in NaOH/urea aqueous solution, under homogeneous conditions. The substitution degree of the prepared quaternized cellulose, cellulose-CHPTAC, increased with increasing molar ratio of CHPTAC/anhydroglucose unit (AGU), reaction temperature, and reaction time. The structure of the cellulose-CHPTAC was characterized using Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (^{1}H- and ^{13}C-NMR), and thermal gravimetric analysis (TGA). Moreover, a cellulose-CHPTAC sample (DS=0.52) was used to modify ground calcium carbonate (GCC) fillers by the surface wrapping method. The results showed that the filler retention was improved by surface modification of GCC fillers using cellulose-CHPTAC, and the negative impact of filler addition on paper strength was reduced. The quaternized cellulose prepared in NaOH/urea aqueous solution could be considered a new, promising filler modifier.

Keywords: Cellulose; NaOH/urea; Homogeneous etherification; Modification of filler

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INTRODUCTION

Filler addition, which can reduce cost and improve paper properties such as brightness, opacity, smoothness, and printing quality, is a vital process for manufacturing some paper grades (Dong *et al.* 2008; Shen *et al.* 2009; Song *et al.* 2009; Huang *et al.* 2014). However, because of the natural differences between the fillers and various fibers, much of the added filler may fail to stay on the fibers during the traditional filling process, which is a serious waste of fillers and pollution of the environment. To compensate for this shortcoming, retention aids such as cationic poly(acrylamide), a water-soluble, high-molecular weight polymer, poly(dimethyl-diallylammonium chloride), a low-molecular weight, high-cationic charge density polymer (Masumi *et al.* 2014), or poly(ethylene oxide) (Hubbe *et al.* 2009) must be used.

Unfortunately, although these chemical additives can increase filler content in the paper to a certain extent, poor filler retention rate is still a practical problem in papermaking because of the poor combination between the fillers and fibers. Moreover, the use of fillers in papermaking can have negative effects on paper strength and sizing properties (Yoon and Deng 2006; Shen *et al.* 2009; Song *et al.* 2009). Therefore, filler modification is a recommended procedure to improve the content of fillers in papers and thereby promote the comprehensive quality of paper in desirable applications (Yoon and Deng 2006; Shen *et al.* 2009; Song *et al.* 2009; Huang *et al.* 2013, 2014).

Methods for modifying fillers include nanoengineering, chemical modification, surface encapsulation, and mechanical modification (Yoon and Deng 2006; Shen *et al.* 2011). Surface modification and encapsulation are the most common methods adapted to enhance interactions between the filler surface and the fibers (Jaakkola and Mannu 2001; Nelson and Deng 2008; Song *et al.* 2009; Huang *et al.* 2013). Many properties of fillers, such as bonding ability, acid tolerance, magnetism, and thermal buffering, can be improved or acquired by surface encapsulation modification. Because modifiers that are coated or anchored on the surface of fillers ensure a good affinity with the fibers, the bonding force between fibers and fillers is enhanced (Myllymäki *et al.* 2006; Yoon and Deng 2006), leading to high filler retention and enhanced physical properties of cellulosic paper.

In recent years, surface modification of fillers using natural polymers and their derivatives, such as starch, chitosan, guar gum, and cellulose, to improve filler-fiber bonding has attracted considerable interest (Yan *et al.* 2005; Zhao *et al.* 2005; Shen *et al.* 2009; Song *et al.* 2009; Deng *et al.* 2010; Yang *et al.* 2013; Gendy *et al.* 2014). Starch, sodium oleate, and calcium chloride have been used by Huang *et al.* (2014) to surface encapsulate calcium carbonate fillers so that the negative impact of filler addition on paper strength can be reduced. Cao *et al.* (2011) modified kaolin clay particles using a starch-fatty acid complex to improve the bonding between the clay filler and lignocellulosic fiber. The results showed that addition of starch-modified filler could improve the paper strength by approximately 15% because of better bonding and contact between fillers and fibers. According to Yoon and Deng (2007), significant improvements in paper strength can be attributed to the formation of a fiber-starch-filler sandwich structure, which avoids direct contact between filler and fibers.

As the most abundant natural polymer of the world, cellulose has attracted increasing attention because of its unique functionality, low cost, biodegradability, renewability, and environmental friendliness (Nelson and Deng 2008). Nelson and Deng (2008) modified precipitated calcium carbonate (PCC) filler with regenerated cellulose to enhance the bonding ability between inorganic particles and polysaccharide substrate. Other studies also showed that cellulose has great potential for surface modification of fillers to improve the bonding strength between the filler and fibers (Nelson and Deng 2008; Shen *et al.* 2009). However, pure cellulose has not previously been used as a discrete coating material because of its poor processability in water and in most common organic solvents (Nelson and Deng 2008). Moreover, introducing effective functional groups that can form chemical, physical, or hydrogen bonds between filler and fibers into inorganic filler particles is very important for improving the bonding ability of filler particles to wood fibers and maintaining paper strength at a high filler addition level (Song *et al.* 2009). Cellulose derivatives obtained by functionalization of the three hydroxyl groups have been shown to be good filler modifiers because of their great compatibility with the fibers (Shen *et al.* 2009). Modification of PCC with cellulose acetate and cellulose acetate butyrate was used because of their additional potential to establish hydrogen bonds with cellulosic fibers through the carbonyl groups of the ester bonds (Gamelas *et al.* 2014). Using carboxymethyl cellulose (CMC) to modify the PCC filler, Shen *et al.* (2010) found that modified filler particles more effectively adhered and bonded to the pulp fibers. Gendy *et al.* (2014) also found that modification of kaolin with hemicellulose and CMC/alum could significantly enhance the physical properties of handsheets as well as the amount of the retained kaolin. However, filler modification with CMC alone results in a decrease in filler retention, which can be explained by the role of negatively charged cellulose in dispersing the filler particles (Yang *et al.* 2013). Therefore, cationic cellulosic derivatives are expected to be more suitable for filler modification.

Etherification has been proven to be a useful and effective solution for synthesis or preparation of cationic cellulose derivatives (Fox *et al.* 2011). The major obstruction is the difficult synthesis of homogeneous cationic cellulose derivatives because cellulose has a large number of hydrogen bonds in inter- and intra-molecular linkages, causing a very low solubility in water and in most common organic solvents (Song *et al.* 2008). New cellulose-dissolving solvents that are suitable for chemical transformations at low temperature, including NaOH/urea, NaOH/thiourea, and LiOH/urea aqueous solutions, have been developed (Lu *et al.* 2011). Moreover, these solvent systems are suitable for the preparation of cellulose ethers through the etherification reaction, which is generally completed under alkaline conditions. Much research concerning the preparation of cellulose derivatives with the etherification reaction has been carried out in NaOH/urea aqueous solutions (Song *et al.* 2008; Yan *et al.* 2009). Although cationic cellulose derivatives have been used as gene carriers (Song *et al.* 2010), flocculants (Yan *et al.* 2009), and coating materials (Zhao *et al.* 2012), little effort toward the application of its derivatives in filler modification has been made. In this work, cationic groups were introduced into the cellulose backbone by a reaction between cellulose and 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTAC) in a NaOH/urea aqueous solution. The performance of the products as ground calcium carbonate (GCC) filler modifier was evaluated, and the effect of the modified fillers on paper properties was also investigated.

EXPERIMENTAL

Materials

Cotton dissolving pulp (DP = 430, cellulose content ≥ 93%) was kindly donated by Shandong Silver Hawk Chemical Fibre Co., Ltd., (China). It was dried at 45 °C in a vacuum drying oven for 24 h. 3-Chloro-2-hydroxypropyl-trimethylammonium chloride (*ca.* 65% in water, Tokyo Chemical Industry Co., Ltd., Japan) was used without further purification. Urea, sodium hydroxide (NaOH), and hydrochloric acid (HCl) were all of analytical grade. Aspen APMP was provided by Huatai Group Corp. Ltd (China), and was refined in a PFI beater to a beating degree of 45 °SR. The GCC with a dimension of 230 nm was provided by Huatai Group Corp. Ltd (China).

Etherification of Cellulose with CHPTAC in NaOH/Urea

Sodium hydroxide (7 g) and urea (14 g) were added to a 100-mL beaker containing 79 g of deionized water, and the mixture was stirred with a glass rod until the NaOH and urea had dissolved completely. After the NaOH/urea aqueous solution was prepared (7 wt% NaOH/14 wt% urea, pH=13.66), it was cooled down to room temperature and kept in a refrigerator to be pre-cooled to -14 °C for 50 min. Then, a weighed amount of cellulose was added to 10 g of the NaOH/urea aqueous solution with vigorous stirring for 5 min, and a transparent and viscous solution of cellulose (3 wt%) was acquired.

The cellulose solution thus prepared was transferred into a 50-mL three-necked flask and was then pre-cooled down to 0 °C using an ice bath. A weighed amount of CHPTAC (0.27, 0.81, 1.62, 2.43, or 3.24 g) was added dropwise from a constant pressure drop funnel to the cooled cellulose solution. When the first drop of CHPTAC was added, the cellulose precipitated (Yan *et al.* 2009). However, the precipitated cellulose dissolved after stirring for a period of short time, and then the rest of CHPTAC was added continuously within 1.5 h. After all of the CHPTAC was added, the neck of the flask was sealed by sealing film. The etherification reaction was carried out for a scheduled time (4, 6, 8, 10, 12, 14, or 18 h) and temperature (25, 40, 50, 60, 70, 80, or 90 °C) in an oil bath under a predetermined stir speed. After the reaction, the solution was neutralized with 0.5 M HCl and the product was dialyzed for seven days in deionized water. The obtained product, cellulose-CHPTAC, was dried by vacuum freeze drying for approximately 72 h.

Characterization of Cellulose-CHPTAC

FT-IR spectra of native cellulose, regenerated cellulose, and cellulose-CHPTAC were acquired with an FT-IR spectrophotometer (IRPrestige-21, Shimadzu, Japan) from finely ground samples in KBr pellets at a resolution of 2 cm^{-1}, in the range of 500 to 4000 cm^{-1}. ^{1}H- and ^{13}C-NMR spectra of the cellulose-CHPTAC in D_2O were recorded on an AVANCE II 400 spectrometer (Bruker, Switzerland) at room temperature. The ^{1}H NMR spectrum was recorded on the spectrometer with a minimum of 8 scans, a sample concentration of 30 $mg \cdot mL^{-1}$, a sweep width of 80 kHz, and a delay time of 3 s. The ^{13}C NMR spectrum was recorded on the spectrometer with a minimum of 20000 scans, a sample concentration of 30 $mg \cdot mL^{-1}$, a sweep width of 80 kHz, and a delay time of 1.5 s.

Elemental analysis was carried out on a Vario EL III analyzer (Elemental Analysis System Co. Ltd., Germany) to measure the nitrogen content (N%) of the cellulose-CHPTAC. The substitution degree (DS) value of the cellulose-CHPTAC was calculated from the nitrogen content according to the method of Song *et al.* (2008).

Thermal gravimetric analysis (TGA) of native cellulose, regenerated cellulose, and cellulose-CHPTAC was carried out on a thermal gravimetric analyzer (TGA Q50, TA instruments, USA) to determine the decomposition temperature (T_d). The samples were measured under nitrogen atmosphere with a temperature increase of 10 °C/min from ambient temperature to 600 °C.

Filler Modification

First, 0.3 g of cellulose-CHPTAC and 10 mL of deionized water were added to a 50-mL three-necked flask with a magnetic stirrer for about 30 min. After the cellulose-CHPTAC dissolved completely in the deionized water, 6 g of GCC was added and the mixture was stirred with a magnetic stirrer for 1 h. Then, the modified GCC was dried at 60 °C in a vacuum drying oven for 24 h.

Preparation of Handsheets and Determination of Paper Properties

Handsheets with target basis weight of 60 g/m^2 were prepared using a Blattbildner-Sheet former (RK-3A, Austria) (Huang *et al.* 2013; Yang *et al.* 2013). The slurry used for making the handsheets consisted of APMP and filler (modified/unmodified GCC, 20% based on the target dry weight of the handsheets). The aqueous slurry was sufficiently mixed by stirring with a magnetic stirrer for 10 min at 200 rpm and then was formed into handsheets. The handsheets were then conditioned at 25.0 °C and 50.0% relative humidity overnight. The tensile index, burst index, and tear index of the handsheets were analyzed using a tensile strength tester (ZL-100A, China), bursting strength tester (BSM-1600B, China), and tearing tester (SLY-1000, China) according to GB/T 12914-2008 (2008), GB/T

454-2002 (2002), and GB/T 455-2002 (2002), respectively. The filler content was determined by incinerating the handsheets in a muffle oven according to TAPPI T211 om-02 (2002). The filler retention was calculated according to method of Shen *et al.* (2010).

SEM Observation of GCC and Handsheets

Scanning electron microscopy (SEM) observations of the modified and unmodified GCC, as well as the handsheets, were performed using a scanning electron microscope (QUANTA 200, FEI, USA) for morphology and surface analyses. All samples for SEM analysis were coated with a thin film of gold.

RESULTS AND DISCUSSION

Effects of Reaction Conditions on DS of Cellulose-CHPTAC

Cotton dissolving pulp was reacted homogeneously with CHPTAC in a NaOH/urea aqueous solution to obtain quaternized cellulose (cellulose-CHPTAC). Figure 1 illustrates the synthesis route of the cellulose-CHPTAC. The DS values of the products were determined by elemental analysis, and the effects of reaction conditions such as the molar ratio of CHPTAC to AGU, reaction time, and reaction temperature on the DS are shown in Table 1.

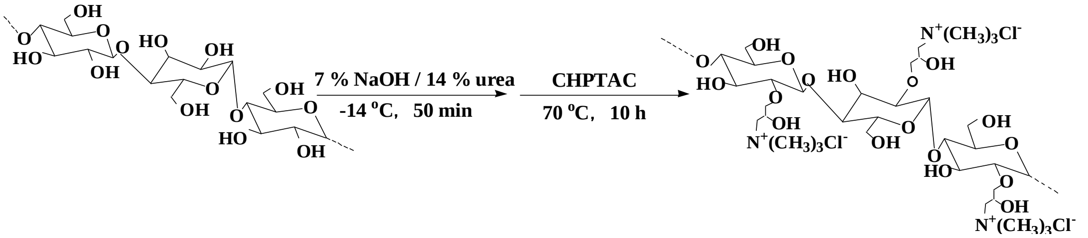


Fig. 1. Reaction scheme for the synthesis of cellulose-CHPTAC in NaOH/urea aqueous solution

As can be seen from Table 1, the DS values of the cellulose-CHPTAC increased with the molar ratio of CHPTAC to AGU, when the reaction was carried out at 90 °C for a reaction time of 6 h. When the molar ratio of CHPTAC/AGU was increased to 9:1, a high DS of 0.398 was obtained. This can be attributed to the fact that the collision probability between CHPTAC and –OH groups in cellulose increased with increasing molar ratio of CHPTAC/AGU, resulting in a higher DS of cationic cellulose derivative. However, when the molar ratio reached 12:1, the DS of the cellulose-CHPTAC declined to 0.169, much lower than that of 9:1. This occurred because the excessive presence of the etherification agent promoted the partial re-precipitation of cellulose from the solution, reducing the reaction efficiency.

Table 1 shows that improving the reaction temperature properly (from 25 to 70 °C) can accelerate the molecular motion of reactants and speed up the etherification reaction rate, consequently increasing the DS value of cellulose-CHPTAC. However, when the reaction temperature was increased to 80 °C, the DS of cellulose-CHPTAC declined. Further increases in temperature could result in the gelation of the cellulose solution (Song *et al*. 2008), and the reaction was carried out in a heterogeneous environment, resulting in a low DS value.

The results in Table 1 also illustrate that the DS of cellulose-CHPTAC increased apparently *vs.* reaction time, suggesting that the etherification extent of cellulose increased. When the reaction was carried out for 10 h, a higher DS of 0.44 for cellulose-CHPTAC was obtained, implying that the etherification reaction reached equilibrium. However, further prolonging the reaction time, the DS of cellulose-CHPTAC slightly decreased. This may have occurred because the side reaction, the hydrolysis of cellulose-CHPTAC, took place, leading to a low DS. On the other hand, some of the CHPTAC also might hydrolyze because of the high concentration of sodium hydroxide in the NaOH/urea aqueous solution, causing a low reaction activity of the etherification agent (Yan *et al*. 2009).

Table 1. Conditions and Results of Homogeneous Reaction of Cellulose with CHPTAC in NaOH/Urea Aqueous Solution

Sample [a]	Molar ratio [b]	Temperature (°C)	Reaction time (h)	DS [c]
1	6:1	25	6	0.19
2	6:1	40	6	0.28
3	6:1	50	6	0.35
4	6:1	60	6	0.40
5	6:1	70	6	0.41
6	6:1	80	6	0.36
7	6:1	90	6	0.37
8	1:1	90	6	0.13
9	3:1	90	6	0.21
10	9:1	90	6	0.43
11	12:1	90	6	0.39
12	6:1	70	4	0.34
13	6:1	70	8	0.39
14	6:1	70	10	0.44
15	6:1	70	12	0.36
16	6:1	70	14	0.38
17	6:1	70	18	0.43
18	9:1	70	10	0.52

[a] The concentration of cellulose was 3%
[b] mol CHPTAC per mol AGU
[c] Degree of substitution determined by elemental analysis

Characterization of the Cellulose-CHPTAC

Figure 2 gives the FT-IR spectra of the native cellulose, regenerated cellulose, and cellulose-CHPTAC with a DS of 0.40. The absorption peaks of the native cellulose (a) and regenerated cellulose (b) were rather similar, implying that the chemical structure of cellulose had not been changed. Moreover, no evidence indicated a side reaction was found during the dissolving process in NaOH/urea. However, as can be seen from the spectra of regenerated cellulose (b), the band at 893 cm^{-1}, which belongs to the amorphous regions of cellulose, became more intense and sharper than that of the native cellulose. Also, the intensity of the band at 1431 cm^{-1}, which belongs to the crystalline region of cellulose, seemed to be weaker than that of native cellulose, suggesting that the crystalline region was destroyed during the dissolving process.

As can be seen from Fig. 2, there was a strong absorption band at 1479 cm^{-1} in the spectra of cellulose-CHPTAC corresponding to the stretching vibration of methyl groups of quaternary ammonium, which is similar to the report of Song *et al.* (2008). The band at 1415 cm^{-1} belongs to the C-N stretching vibration. Furthermore, a strong absorption band appeared at 1060 cm^{-1}, which may be the stretching vibration of the newly formed ether bond. All of these gave evidence of the introduction of a quaternary ammonium salt group on the cellulose backbone (Song *et al.* 2008; Yan *et al.* 2009).

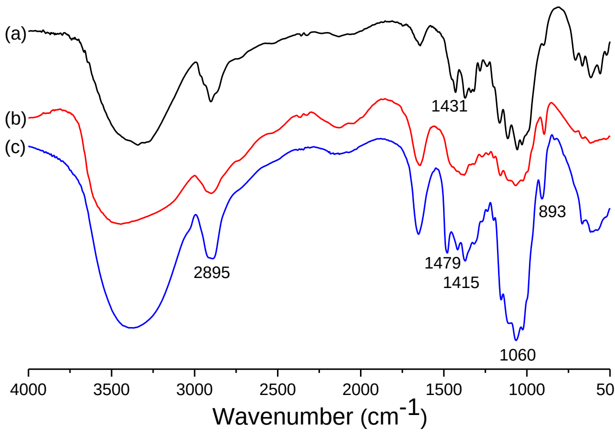


Fig. 2. FT-IR spectra of (a) native cellulose, (b) regenerated cellulose, and (c) cellulose-CHPTAC

Figure 3 gives the typical ^{1}H NMR and ^{13}C NMR spectra of the cellulose-CHPTAC in D_2O. As shown in Fig. 3 (a), the chemical shift from δ 3.0 to 5.0 ppm (b, except D_2O) can be assigned to the protons of the cellulose backbone, and the strong peak at δ 3.2 ppm is attributed to the methyl protons of the quaternary-ammonium moieties (Yan *et al*. 2009).

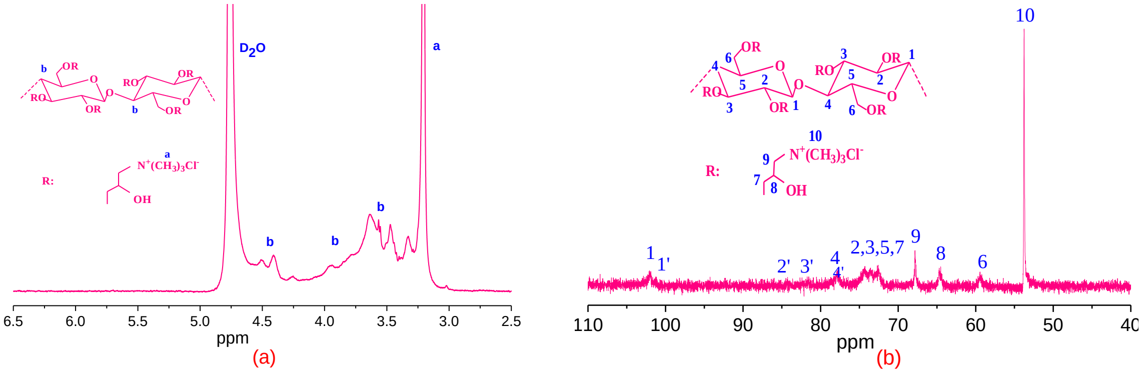
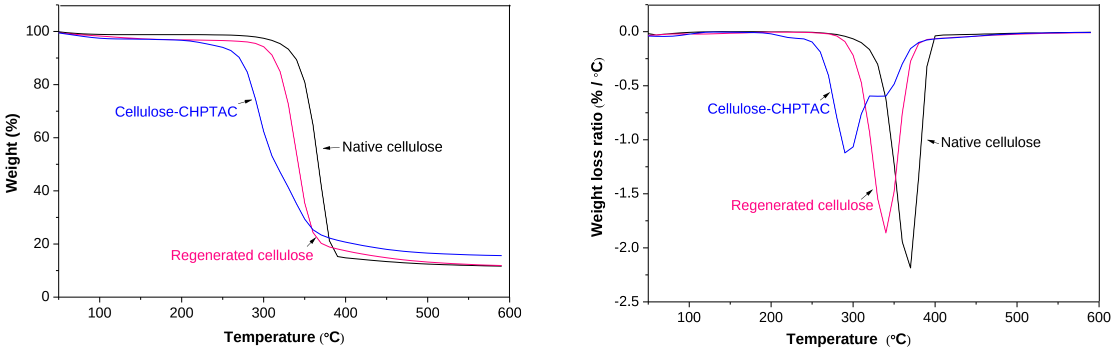


Fig. 3. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of cellulose-CHPTAC in D_2O

In Fig. 3 (b), the vibrational peaks at δ 102.04, 101.34, and 59.59 ppm can be assigned to C1, C1', and C6 carbons, respectively. The emergence of C1' occurred because the hydroxyl groups in C2 were substituted by cationic groups, which would lead to a change in the chemical shift of C1. The resonance peaks in the range of δ 72.31 to 74.64 ppm can be attributed to the carbon atoms of C2, C3, C5, and C7, respectively (Yan *et al*. 2009). Noticeably, there was a strong vibrational peak at δ 53.87 ppm, which can be attributed to the signal of $N^{+}(CH_3)_3$ (C10) (Song *et al.* 2008; Yan *et al*. 2009). Furthermore, signals appearing at δ 64.4, 67.6, and 78.2 ppm can be assigned to C8, C9, and C4 carbons, respectively. The NMR results further demonstrate that the quaternary ammonium salt group was successfully introduced onto the cellulose chain during the process of etherification (Song *et al.* 2008).

The thermal behavior of the native cellulose, regenerated cellulose, and cellulose-CHPTAC is shown in Fig. 4 and Table 2. The initial decomposition temperature (T_{di}) of native cellulose is 270 °C, and it can reach a maximum decomposition rate at 370 °C. The T_{di}, T_{dm}, and T_{df} of the regenerated cellulose are 256, 340, and 400 °C, respectively, implying that the regenerated cellulose has a poor thermal stability compared with the native cellulose (Zhao *et al*. 2013). This may occur because the crystalline region of cellulose is destroyed and the cellulose macromolecular structure is partially degraded during the dissolution process in the NaOH/urea aqueous solution.



(a) (b)

Fig. 4. (a) Thermogravimetry curves and (b) derivative thermogravimetry curves of native cellulose, regenerated cellulose, and cellulose-CHPTAC

Table 2. Thermal Stability Data for Native Cellulose, Regenerated Cellulose, and Cellulose-CHPTAC

Sample	T_{di} (°C)	T_{dm} (°C)	T_{df} (°C)	Residual mass (wt%)
Native cellulose	270	370	423	11.19
Regenerated cellulose	256	340	400	11.57
Cellulose-CHPTAC	178	290, 340	388	15.70

$T_{di,}$ the initial decomposition temperature of the samples
$T_{dm,}$ the maximum decomposition rate temperature of the samples
$T_{df,}$ the final decomposition temperature of the samples

Although the unmodified cellulose exhibited monomodal weight loss curves, the cellulose-CHPTAC had two weight loss stages (Zhao *et al*. 2013). The first stage took place at 178 °C; this was due to the thermal decomposition of the introduced CHPTAC groups. The second stage started at 320 °C and was primarily due to the decomposition of the cellulose backbone. Furthermore, the cellulose-CHPTAC has much poorer thermal stability. Its T_{di}, T_{dm}, and T_{df} were lower than that of the unmodified cellulose.

In addition, the residual mass above 600 °C was 11.19 wt% for native cellulose, 11.57 wt% for regenerated cellulose, and 15.70 wt% for cellulose-CHPTAC. The higher pyrolysis residue of the regenerated cellulose than that of the native cellulose occurred because more inorganic salts remained as residues after dissolution and regeneration in NaOH/urea. The cellulose-CHPTAC produced a higher amount of residue after decomposition at 600 °C than the native cellulose and regenerated cellulose, which may be attributed to the introduction of chloride in the chain of cellulose-CHPTAC (Yan *et al*. 2009).

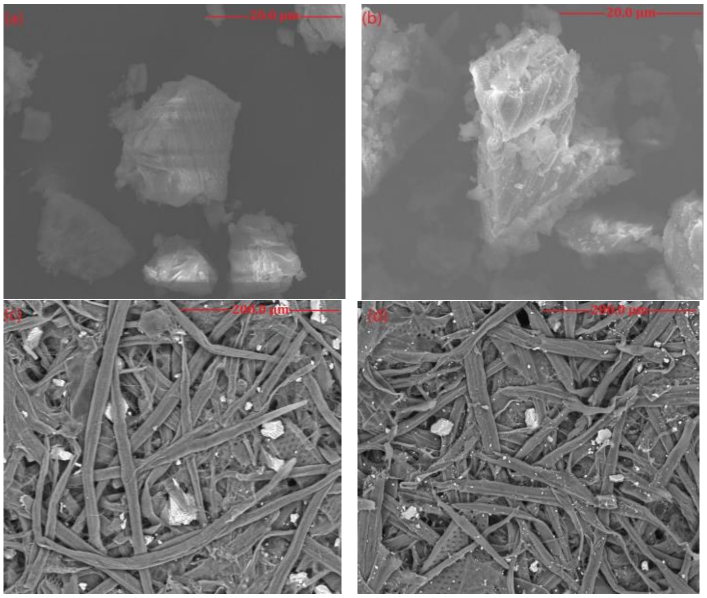


Fig. 5. SEM images of fillers and paper-sheets: (a) unmodified GCC filler; (b) cellulose-CHPTAC modified GCC filler; (c) handsheet filled with unmodified GCC filler; (d) handsheet filled with modified GCC filler

Preparing Cellulose-CHPTAC Modified GCC

Mixing of GCC fillers with cellulose-CHPTAC was performed to obtain a new kind of modified filler for papermaking with improved or preserved strength properties of filled papers. A simple preparation method based on precipitation of cellulose-CHPTAC onto the surface of GCC fillers was employed, and sample 18 (DS = 0.52) was selected. Figure 5 illustrates the morphology of the unmodified GCC particles and cellulose-CHPTAC modified GCC particles. The surface of the unmodified GCC particles was smooth, while the surface of the modified GCC particles was rough and covered with some other material, indicating that the GCC filler particles were readily precipitated by the cationic cellulose-CHPTAC. Moreover, the SEM pictures clearly show that after modification with the cationic cellulose, the particles of GCC appeared as clusters rather than individual particles. This means that the use of cationic polymers (*e.g.*, cellulose-CHPTAC) in filler modification can result in pre-flocculation/aggregation of filler particles (Yang *et al.* 2013).

The influence of modification time on the retention behavior of cellulose-CHPTAC modified GCC fillers is shown in Fig. 6. The retention rate of the modified GCC fillers in the handsheets increased with modification time. When the mixture of cellulose-CHPTAC and GCC fillers was mixed for 2 h, the retention rate of the resulting modified GCC fillers reached a maximum value. A further increase in the mixing time did not improve the retention behavior of the cellulose-CHPTAC modified GCC fillers, meaning that the precipitation of the cellulose-CHPTAC on the surface of filler particles reached a balance.

SEM images of the handsheets filled with unmodified GCC fillers and modified GCC fillers are shown in Fig. 5. More GCC filler, particularly small filler particles, stayed in the handsheet filled with modified GCC fillers. In contrast, the sheet filled with unmodified GCC fillers had no small filler particles, indicating that only large particles can stay in the sheet through the interception by fibers. The SEM images clearly showed that modification of GCC fillers with cellulose-CHPTAC improved the attachment of GCC filler to fibers.

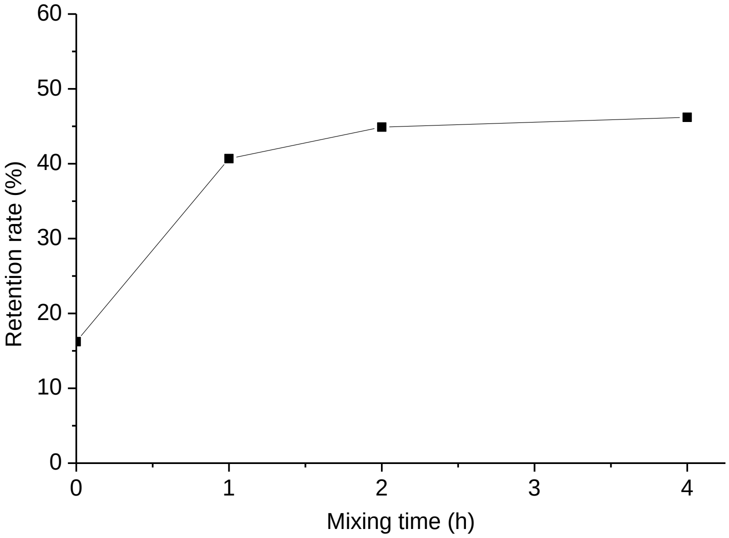


Fig. 6. Influence of modification time on retention behavior of cellulose-CHPTAC modified GCC fillers

Effects of Filler Modification on Paper Properties

Modification of fillers is expected to lead to a reduced negative impact of filler addition on paper strength. The effects of the addition of modified GCC filler on the paper properties are shown in Table 3. The results showed that the tensile index, burst index, and tear index of the handsheets filled with unmodified GCC fillers decreased by 33.6%, 26.9%, and 18.8%, respectively, compared with the unfilled handsheets. The retention rate of the unmodified GCC fillers in the handsheet was only 16.1%. The poor strength properties of papers and low filler retention rate can be attributed to the interference of non-bondable filler particles with inter-fiber bonding (Yang *et al*. 2013) and the poor combination between the unmodified GCC fillers and fibers. However, the strength properties of the handsheets filled with modified GCC were much better than that filled with unmodified GCC. The tensile index, burst index, and tear index of the modified-GCC-filled handsheets were improved by 41.8%, 25.0%, and 20.4%, respectively. Meanwhile, the filler retention rate of the modified GCC fillers increased to 48.4%. Therefore, it can be concluded that the filler retention can be improved and the negative impact of filler addition on paper strength can be reduced by surface modification of GCC with cellulose-CHPTAC because of the improved bonding ability between the filler and fibers.

Table 3. Strength Properties of Paper Sheets and Retention Rate of GCC Filler

Handsheet	Tensile index (N m^2/g)	Burst index (kPa m^2/g)	Tear index (mN m^2/g)	Filler retention efficiency (%)
Unfilled	23.8	0.93	2.60	-
Unmodified GCC-filled	15.8	0.68	2.11	16.1
Modified GCC filled	22.4	0.85	2.54	48.4

CONCLUSIONS

1. A cationic cellulose derivative, cellulose-CHPTAC, can be produced by homogeneous etherification of cellulose with CHPTAC in a NaOH/urea aqueous solution. The DS values of the quaternized cellulose derivatives could be obtained by changing the molar ratio of CHPTAC/AGU, the reaction time, and the reaction temperature. It appears from this study that the optimum reaction conditions for synthesis of the cellulose-CHPTAC with a high DS are: reaction time of 10 h, reaction temperature of 70 °C, and CHPTAC/AGU molar ratio of 9:1.
2. Etherification weakened the thermal stability of cellulose, and the cellulose-CHPTAC exhibited two weight loss stages.
3. The cellulose-CHPTAC had a positive charge and could be used to modify fillers by the surface wrapping method. The retention rate of the modified fillers was improved, and the negative impact of filler addition on paper strength properties such as tensile strength, burst strength, and tearing strength was reduced.

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