Enhancing the Alkaline Peroxide Mechanical Pulp Strength by Cationization with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride

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Alkaline peroxide mechanical pulp (APMP) is a newly emerging high yield pulp (HYP) with numerous advantages. However, the drawback of the alkaline peroxide mechanical pulp from untreated plant biomass is its poor network strength. In this work, 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) modification was proposed to enhance pulp network strength by fiber surface modification that could enhance fiber bonding. Three factors were analyzed by response surface methodology (RSM) to optimize treatment conditions based on factorial designs. The results showed that the optimal conditions were CHPTAC dosage of 0.8% (oven-dry pulp), NaOH dosage of 0.1% (oven-dry pulp), and pulp concentration of 8%. The modified pulp fibers were characterized by elemental analysis, charge density analysis, Fourier transform infrared spectroscopy (FTIR), thermal gravity analysis (TGA), and internal bond strength analysis, as well as zero span tensile analysis. The physical strength of the modified APMP pulp was increased in terms of tensile index, tear index, and burst index. After modification, the tensile index, tear index, and burst index increased by 35.3%, 29.2%, and 16.7% respectively. The internal bonding strength increased by 144.4%; however, the increase of zero span tensile index of modified pulp fibers was insignificant.

Keywords: CHPTAC; Tensile index; APMP; Fiber modification

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INTRODUCTION

Faced with shortages of raw materials in the pulp and paper industry, high yield pulping (HYP), a primary method using mechanical procedures including refining and grinding, provides an alternative technology (Ni 2005). Traditionally, the production yield of HYP is 60% to 80%, which is much higher than that of chemical pulp (30% to 40%) (Chen *et al.* 2013; Li *et al.* 2015). Presently, alkaline peroxide mechanical pulp (APMP) is the most popular HYP production process, particularly in China (Li *et al.* 2014). This is largely due to its effective use of hardwood resources and its low-environmental impact (Liu *et al.*2016). The addition of alkaline and peroxide in the pretreatment stage of APMP process shortens the production line and lowers the refining energy consumption (Wei and Zhang 2011). Compared with chemical pulps, APMP has some advantages, such as high yield, high bulk, and good printability (Tian *et al.* 2014). Thus, this pulp has been successfully applied in producing some high grade papers and multi-ply coated packaging

board. However, during the refining stage of APMP pulping process, hydrophobic materials, such as lignin, are precipitated onto the surface of APMP fibers (Hu *et al.* 2015), which negatively affect the bonding strength between fibers as stated in previous studies (Koljones *et al.* 2003). The inter-fiber bonding depends mainly on the intermolecular hydrogen bonding and van der Waals forces between adjacent fibers surfaces (Mader *et al.* 2016). Consequently, fiber modifications including chemical, biological, and mechanical modification have been taken to minimize these problems.

Chemical modification is an effective way to improve pulp strength and to tailor properties for specific end uses through attachment of new functional groups on fiber surfaces. Native lignocellulosic fibers, such as pulp fibers, mainly consists of cellulose, hemicellulose, and lignin (Hill *et al.* 1988). The anionic groups existed in these components, such as carboxyl groups, afford the pulp fibers with negative charge on the fiber surface which hinders the inter-fiber bonding formation, resulting low pulp strength (Liu *et al.* 2011b). To improve the pulp strength through chemical modification, various treatments have been reported including acetylation, alkylation, and cationization (Hashem *et al.* 2005; Enomoto-Rogers *et al.* 2013; Thankur *et al.* 2014). Modification of considerable natural fibers, such as ramie fiber, cotton fiber, jute fiber, eucalyptus pulp fiber, *etc.*, were also employed in the past studies (Kaewkuk *et al.* 2013; Acharya *et al.* 2014; Saenghirunwattana *et al.* 2014; Mendes *et al.* 2015).

A cationic hydroxylethyl cellulose-based flocculant for clay suspension was prepared by copolymerizing cellulose with N,N-dimethylacrylamide and acrylamide (Kaewkuk *et al.* 2013). Quaternized celluloses were homogeneously synthesized by reacting cellulose with 3-chloro-2-hydroxypropyltrimethylammonium chloride in NaOH/urea aqueous solutions (Song *et al.* 2008). Fibers of aspen chemi-thermomechanical pulp (CTMP), spruce CTMP, bleached kraft pulp (BKP), and kraft pulp were reported to be treated by low-temperature plasma (air) aiming at the detection of the relationship between chemical components on the surface and the properties of paper sheets. It was found that plasma treatment did not remove lignin on fiber surface in large amounts but improved the final strength properties of paper sheets (Xiao *et al.* 2015). However, chemical modification of APMP pulp fibers has not yet been investigated.

To increase the affinity between fibers of APMP, a cationic modified agent is required. 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (CHPTAC) was reported to be a good cationic agent (Fang *et al.* 2013). In this work, CHPTAC was chosen as a cationic agent to modify APMP fibers and enhance the APMP pulp physical strength. The effects of modification parameters including CHPTAC dosage, NaOH dosage, and pulp concentration on pulp strength properties were investigated using response surface methodology (RSM). At the same time, elementary analysis, charge density analysis, Fourier transform infrared spectroscopy (FTIR), thermal gravity analysis (TGA), and internal bond strength, as well as zero span tensile analysis were employed to characterize the properties of the modified APMP fibers.

EXPERIMENTAL

Materials

The poplar APMP pulp was kindly supplied by a pulping plant located in Shandong, China. The pulp was produced using one-stage pretreatment APMP process. The conditions for pretreatment at the mill were 6.0% NaOH (based on oven-dry material, the

same as below), 6.0% H_2O_2, 75 °C, 1.5 h, 10% pulp consistency. Chemicals including CHPTAC (69%) were purchased from the Shanxi Dasheng Chemical Tech Co. Ltd., Xian, China. Polydiallyldimethyl-ammonium chloride (PDADMAC, 100-200 kg/mol), 20 wt.% in water and sodium hydroxide (reagent grade) were obtained from Sigma-Aldrich company. Potassium polyvinyl sulfate (PVSK, 100-200 kg/mol, 97.7 wt.% esterified) was provided by Wako Pure Chem. Ltd., Osaka, Japan. All chemicals were applied without further purification. 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 /%
0.45	51.57	15.69	16.29	3.42	10.69	1.37
Yield (%)	Brightness (%ISO)	Tensile index (N M g^{-1})	Tear index (mN m^2 g^{-1})	Burst index (kPa m^2 g^{-1})		
87.6	72.3	8.23	1.03	1.13		

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

Methods

Experiment and response surface methodology (RSM)

The pulp modification was performed in a plastic bag (10 cm × 10 cm) at 50 °C (Wang and Song 2013) with 1 g of oven-dry pulp. A certain amount of NaOH (0.8%, 1.0% and 1.2%, based on oven-dry pulp) and CHPTAC (0.6%, 0.8% and 1.0%, based on oven-dry pulp) which contains quaternary ammonium group were added to the pulp slurry, and mixed well. After that, the bag was moved into a water bath for 60 min (Liu *et al.* 2007). Finally, the pulp was washed thoroughly with deionized water and filtered to make paper sheets.

Response surface methodology (RSM)

These experiments were carried out based on a 33 full factorial design using RSM and conducted using Design Expert 7.1 software (Stat-Ease, Minneapolis, MN, USA), which was adopted and reported in previous study (Liu *et al.* 2011a). The three factors were CHPTAC dosage (X_1, %, oven-dry pulp), NaOH dosage (X_2, %, oven-dry pulp), and pulp concentration (X_3, %). The levels and codes of the response surface methodology are listed in Table 2.

Table 2. Level and Code of Experimental Factors

Factor	Code	Level		
		-1	0	1
CHPTAC(%, oven-dry pulp)	X_1	0.6	0.8	1.0
NaOH(%, oven-dry pulp)	X_2	0.8	1.0	1.2
Pulp concentration (%)	X_3	6	8	10

In this set of experiments, handsheets (60 g/m^2) were prepared using a TAPPI standard handsheet machine (PTI, Germany) with unmodified and modified APMP pulp. Prior to the sheet preparation, the 1.0% pulp slurry was prepared and stirred for 5 min at 500 rpm. Afterwards, the 1.0% pulp slurry was placed in the handsheet former in order to

prepare handsheets according to the TAPPI T205 om-88 (1995) (TAPPI 1996). After drying, the tensile, burst, and tear strengths (Lorentzen & Wettre, Sweden), brightness, as well as the internal bonding strength (IBS, Scott type, TMI, 80-01, N.Y., USA) of the handsheets, were measured according to the TAPPI T494 om-87 (1988), T403 om-91 (1991), T414om-82 (1988), T452om-92 (1992), and T569 om-14 standards, respectively (Tappi, 1996). The dry zero span tensile index (DZSTI) and wet zero span tensile index (WZSTI) were estimated using a Pulmac tester (FQT-E2, USA) according to TAPPI T494 and T456, respectively.

Characterization method

The elemental analysis of unmodified pulp and modified pulp were determined using an elemental analyzer (Vario EL III, Elementar Analyze System, Germany) *via* the combustion method (Jahan *et al.* 2011). In preparation, the samples were first dried in an oven at 105 °C overnight to remove any moisture. Then, approximately 2.0 mg of each sample was analyzed for carbon, hydrogen, and nitrogen content. The grafting ratio of modified APMP was calculated based on Eq. 1. The charge density of each sample was measured using a Mutek PCD-03 particle charge detector (Arzbergerstraße, Herrsching, Germany) based on a back titration method (Liu *et al.* 2010; Zhang *et al*. 2007). A certain amount of oven-dry pulp fibers were added to 20 mL of 0.050 mol/L PVSK solution. The suspensions were then immersed in the water bath shaker (Innova 3100, Brunswick Scientific, Edison, NJ, USA) and shaken at 150 rpm at 30 °C for 2 h. The suspensions were filtered and 1 ml of the filtrate was titrated against PDADMAC solution (0.0050 mol/L) in order to calculate the charge density of sample according to Eq. 2. A separate 20 mL of 0.050 mol/L PVSK solution without adding pulp sample was used as control and titrated against PDADMAC solution (0.0050 mol/L) in order to determine the charge density of pulp according to Eq. 2. Thermogravimetric (TGA) analyses were conducted on a TGA Q50 (TA Instruments, New Castle, DE, USA) at a heating rate of 20 °C/ min and under a nitrogen atmosphere (Yang *et al*. 2013). The infrared spectra were recorded in the wavenumber range of 400 to 4000 cm^{-1} on a Fourier transform infrared (FTIR) spectrophotometer (IRPrestige-21, Shimadzu Co., Tokyo, Japan) using a potassium bromide (KBr) pellet containing about 1.0% sample (Wang *et al*. 2014).

$$Grafting\ ratio, \% = \frac{188\ N}{1400 - 188 \times N} \times 100 \qquad (1)$$

In Eq. 1, N is nitrogen content as determined by the elemental analysis (wt.%), and 188 is the molecular weight of CHPTAC.

$$surface\ charge\ density\ (meq/g) = \frac{(V_0 - V_{sample}) \times 0.0050}{W_{sample}} \qquad (2)$$

In Eq. 2, V_0 is the volume of PDADMAC used for titrating the control of 0.050 mol/L PVSK solution (mL); V_{sample} is the volume of PDADMAC used for titrating the filtrate of PVSK solution after treating with pulp (mL); and W_{sample} is the weight of pulp sample added into 20 mL of 0.050 mol/L PVSK solution (g). The data presented here are the averages of three repetitions.

RESULTS AND DISCUSSION

Mechanism of APMP Modification via CHTPAC

The APMP modification using CHTPAC followed the general procedure that has been used for the preparation of other cationic polysaccharides (Ebringerova *et al.* 1994; Liu *et al.* 2011; Ren *et al*. 2006). The reaction scheme of the poplar APMP fibers with CHTPAC is shown in Fig. 1. Sodium hydroxide was used here to 1) make APMP fibers swell in order to increase the accessibility of reaction sites as well as the reaction efficiency, as reported in the cationization of celulose, hemicellulose, kraft lignin, and starch with glycidyl-trimethylammonium chloride (GTMAC) in the literatures (Ebringerova *et al.* 1994; Kong *et al.* 2015; Liu *et al.* 2011; Wei *et al.* 2008), 2) function as a catalyst in this reaction to produce 2,3-epoxypropyltrimethylammonium chloride *in situ* from CHPTAC (Fig.1a), and 3) generate nucleophilic intermediate from hydroxyl groups of cellulose, hemicellulose, and lignin in APMP fibers. This nucleophilic intermediate attacks the highly reactive epoxy group on 2,3-epoxypropyltrimethylammonium chloride through an oxirane ring-opening reaction to produce CHTPAC-grafted APMP fibers (Fig.1b). Under alkaline conditions, the CHTPAC can also hydrolyze into a diol structure (Cho *et al.* 2006), which is an undesirable side reaction, limiting the overall reaction efficiency (Fig.1c). In addition, the hydrolysis of CHTPAC-grafted APMP fibers produced in the process may happen in this system under alkaline conditions (Fig.1d), as observed and reported in the cationization of hemicellulose using GTMAC by Liu *et al.* (2011) and the cationization of lignin using GTMAC by Kong *et al.* (2015). The grafting of CHTPAC onto APMP fiber surface renders the pulp cationic charge from the quaternary ammonium group of CHTPAC, which would increase the pulp strength properties. In order to maximize the reaction efficiency and minimize these side reactions, the reaction conditions were optimized based on the tensile index of the resultant pulp using RSM method.

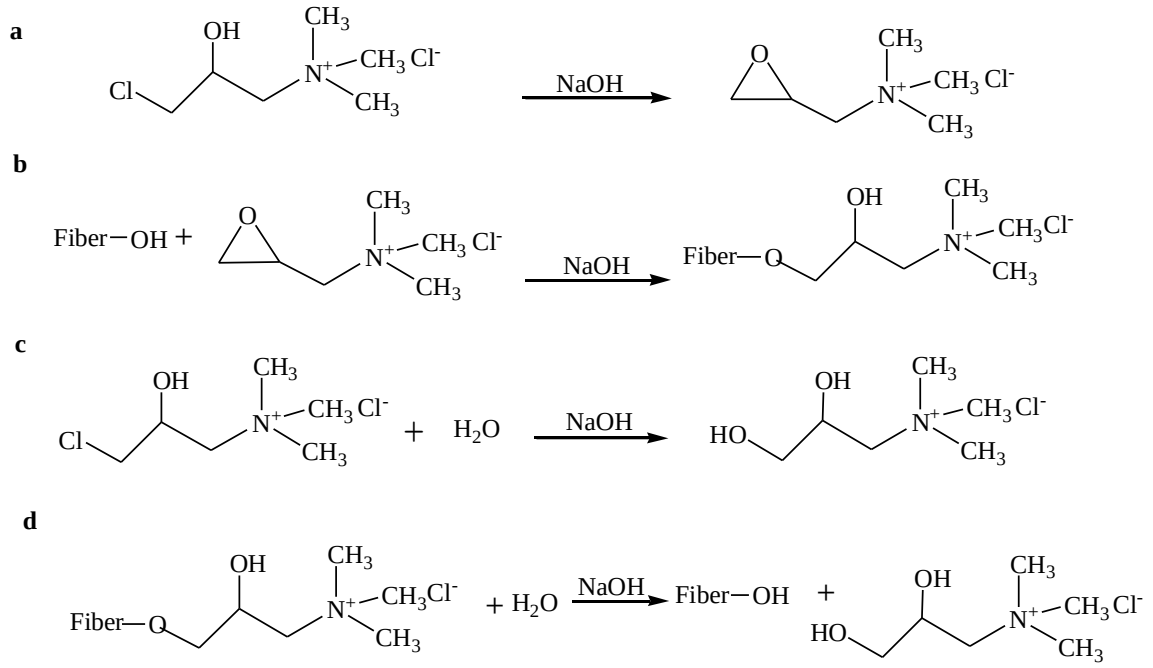

Fig. 1. Reaction schemes of a) production of 2, 3-epoxypropyltrimethylammonium chloride; b) grafting of APMP fibers; c) hydrolysis of CHTPAC, and d) hydrolysis of cationic fibers under alkaline condition

Optimization of APMP Modification Conditions using RSM Method

The experimental matrix and RSM results for each sample are shown in Table 3. The central points were triplicates at a CHPTAC dosage of 0.8%, NaOH dosage of 1.0%, and pulp concentration of 8%.

Table 3. Experimental Design and Results of RSM

Sample	CHPTAC (%)	NaOH (%)	Pulp Concentration (%)	Tensile Index (N·m/g)
1	0.6	0.8	8	9.27
2	1.0	0.8	8	11.27
3	0.6	1.2	8	9.45
4	1.0	1.2	8	11.43
5	0.6	1.0	6	9.83
6	1.0	1.0	6	11.83
7	0.6	1.0	10	9.82
8	1.0	1.0	10	11.81
9	0.8	0.8	6	10.23
10	0.8	1.2	6	10.43
11	0.8	0.8	10	10.22
12	0.8	1.0	10	10.41
13	0.8	1.0	8	10.68
14	0.8	1.0	8	10.68
15	0.8	1.0	8	10.68
16	0.8	1.0	8	10.68
17	0.8	1.0	8	10.68

RSM was used to determine the optimal response conditions to obtain the highest tensile index (Fig. 2). As shown in Figs. 2a and 2b, the dosage of CHPTAC had a major effect on the paper sheets tensile strength. With increasing CHPTAC dosage from 0.6% to 1.0%, the tensile index of the resultant paper sheets was improved significantly at NaOH dosages of 0.8% to 1.2%. This is because of a higher grafting ratio at higher CHPTAC dosage, grafting ratio of 24.6% and 14.6% respectively for CHPTAC dosage of 0.8% and 1.2% at 0.8% NaOH dosage. The quaternary ammonium group in CHPTAC-grafted APMP fibers increased the fiber bonding strength through electrostatic attraction, *i.e.*, between the cationic groups of CHPTAC-grafted fibers and the negative charge on the neighboring fiber surface (Gärdlund *et al*. 2003), which will be demonstrated in the following section. Another work reported a loss of pulp strength at an excessive dosage of a cationic emulsion copolymer (Yuan and Hauser 2014), which was not observed in the present study.

The results in Fig.2 also indicated that the NaOH was able to be used to control the reaction efficiency, treatment effectiveness. As shown in Fig. 2a and 2c, increasing the dosage of NaOH at range of 0.8% to 1.0% promoted the effectiveness of the modification. The pulp tensile index was increased significantly, which is due to the higher fiber swelling extent (Pönni *et al* 2013) and higher grafting ratio at higher NaOH dosage (grafting ratio of 26.6% and 14.6% respectively for NaOH dosage of 1.0% and 0.8% at 1.0% CHPTAC dosage). At a further increase of NaOH dosage to 1.2%, the tensile index of paper sheets decreased. This was caused by the decomposition of both CHPTAC and CHPTAC-grafted APMP fibers in this process at high NaOH dosage (Chen *et al.* 2015), as shown in Fig.1(scheme c and d), resulting a lower grafting ratio. Compared with the grafting ratio, 26.6%, at 1.0% NaOH dosage, the grafting ratio at 1.2% NaOH dosage with 1.0% CHPTAC dosage was only 19.6%, meaning that it was decreased by 5%. This phenomenon

were also reported in the preparation of cationic polysaccharides (Ebringerova *et al.* 1994; Liu *et al.* 2011; Ren *et al*. 2006).

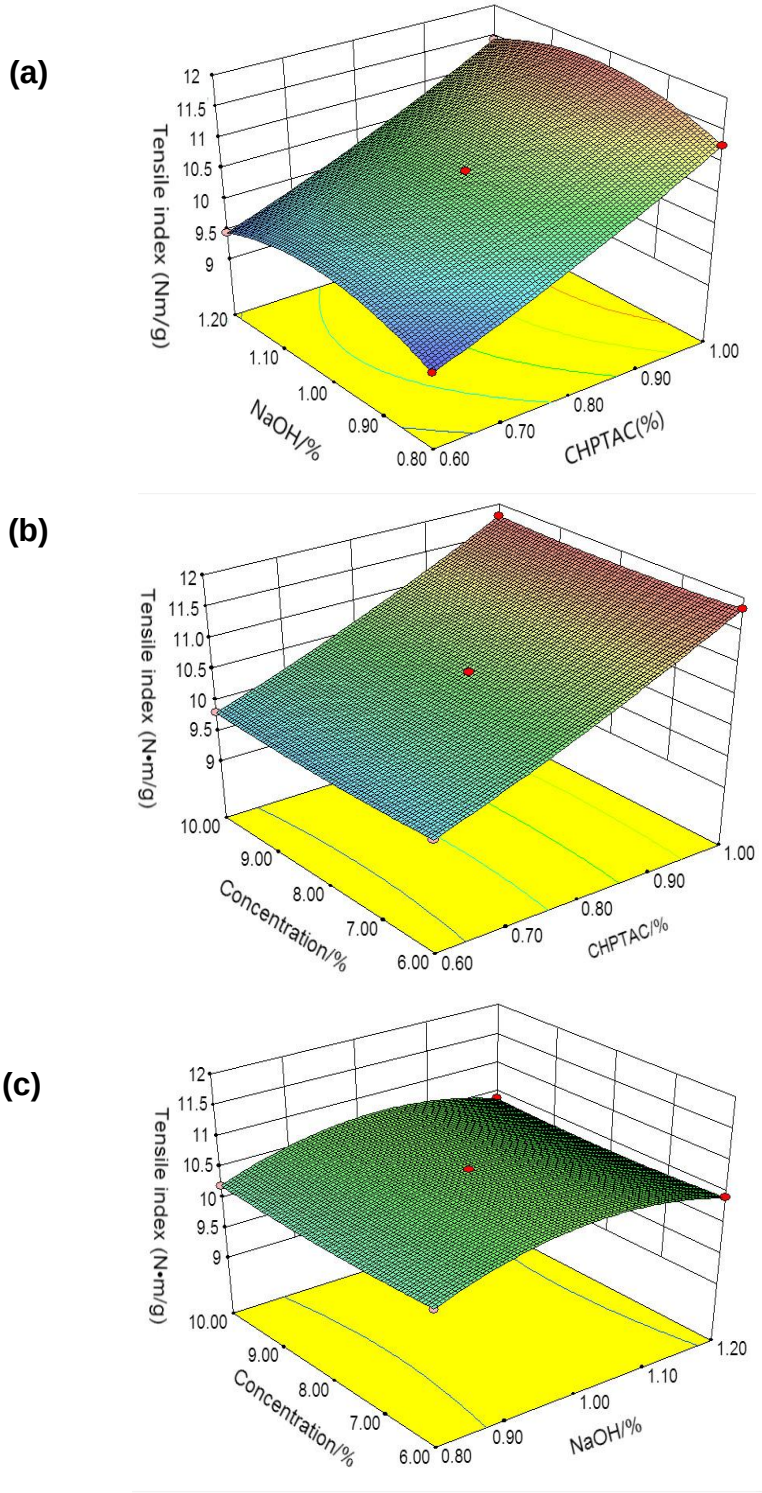

Fig. 2. Tensile index plots. (a) Tensile index versus NaOH and CHPTAC dosage; (b) tensile index versus pulp concentration and CHPTAC dosage; (c) tensile index versus pulp concentration and NaOH dosage

Pulp concentration was also an important parameter. As shown in Figs. 1b and 1c, with an increasing pulp concentration, the tensile strength of paper sheets increased and then decreased gradually. It should be pointed out that the high pulp concentration hindered the accessibility of reaction chemicals with reaction sites in pulp fibers, which decreased the reaction efficiency of grafting CHPTAC onto APMP fibers. The similar phenomena was reported by Fatehi *et al.* (2008) in investigating the influence of cationic poly(vinyl alcohol) on paper properties.

To further understand the impact of process parameters on the efficiency of reaction and to be able to predict the modification efficiency of APMP with CHPTAC, the outcomes of the modeling analysis in Fig. 2 (*i.e.* sum of squares, degrees of freedom, mean square, F-value, and P-values) were estimated and presented in Table 3. The F-value of 4144.14 and the P-value of <0.0001 implied the model was significant and functional (Yan *et al.* 2009). The "Lack of Fit" of 1.68 for F-value implied that it is insignificant relative to the pure error (Bezerra *et al.* 2008; Jeong *et al.* 2016). In the case of P-value, A, B, C, AB, AC, BC, A^2, B^2, C^2 were less than 0.05, implying that the correlation factors were significant. P-values higher than 0.1 indicated the model terms were not significant. In this case, F-value of C (pulp concentration) is the smallest of the three factors indicating the negligible effect of pulp concentration on tensile strength compared to other factors (CHPTAC dosage and NaOH dosage) in increasing the tensile index of paper sheet. The predicted R^2 of 0.9989 is in agreement with the adjusted R^2 of 0.9996. Furthermore, "Adeq Precision" determines the signal to noise ratio in modeling analysis. A ratio greater than 4 is desirable. The Adequate precision of 338.182 was observed in this work, which is much greater than 4, indicating effective and accuracy of the model. Based on this analysis, the tensile index (*Y*) of paper sheet made of modified fibers was made as a function of process parameters in Eq. 3,

$$Y = 10.68+1.00* X_1 +0.091* X_2 -7.500*E\text{-}003* X_3 -5.00*E\text{-}003* X_1 * X_2 -2.500*E\text{-}003 * X_1 * X_2 -2.500*E\text{-}003* X_2 * X_3 +0.087 * X_{12} -0.41* X_{22} +0.055 * X_{32} \quad (3)$$

where *Y* predicts the highest tensile index, X_1 is the CHPTAC dosage (%), X_2 is the NaoH dosage (%), and X_3 is the pulp concentration (%).

These results along with Eq. 2 can be used to predict the tensile index of modified APMP, which are crucial for determining the modification effectiveness and design of process used for APMP modification at large scales. Considering Eq. 3, the optimal conditions were determined at CHPTAC dosage of 0.8%, NaOH dosage of 1.0%, and pulp concentration of 8%. At these conditions, the highest tensile index of paper sheets made of modified fibers would be 10.69 N.m/g. To verify these conditions, test were carried out to see what happen to the tear index, burst index as well as the brightness of modified pulp. The properties of paper sheets made of modified pulp fibers at optimal conditions are listed in Table 4. As shown, the brightness of modified pulp decreased by 2.35%, from original 72.3 %ISO to 70.6 %ISO. The strength properties of modified pulp including tensile, tear and burst index increased at different extent. The tensile index, tear index and burst index of pulp were increased by 35.3%, 29.2%, and 16.7%, respectively. One can conclude from these results that the CHTPAC modification can significantly increase the APMP strength properties with a minimal loss of pulp brightness.

Table 3. Outcomes of the Response Surface Models for Optimization of APMP Modification

Source	Sum of squares	Degrees of freedom	Mean square	F-value	P-value
Model	1.17	9	0.13	4144.14	＜0.0001
A-CHTPAC dosage(X_1)	0.35	1	0.35	9079.26	＜0.0001
B-NaOH dosage(X_2)	0.64	1	0.64	20256.14	＜0.0001
C-Pulp concentration(X_3)	0.14	1	0.14	4291.87	＜0.0001
AB	0.039	1	0.039	1299.32	＜0.0001
AC	0.0032	1	0.0032	106.65	＜0.0001
BC	0.0045	1	0.0045	149.95	＜0.0001
A^2	0.0041	1	0.0041	136.60	＜0.0001
B^2	0.043	1	0.043	1432.58	＜0.0001
C^2	0.023	1	0.023	766.26	＜0.0001
Lack of Fit	0.000123	3	0.00004	1.68	0.2431
Pure error	0.00008	4	0.00002		

Table 4. Brightness and Physical Strength Properties of APMP and Modified APMP

	Brightness (%ISO)	Tensile index (N m $^{g-1}$)	Tear index (mN m^2 g^{-1})	Burste index (kPa m^2 g^{-1})
APMP	72.3	8.23	1.03	1.13
Modified APMP	70.6	11.14	1.33	1.32
Increased or decreased by (%)	2.35 ↓	35.3 ↑	29.2 ↑	16.7 ↑

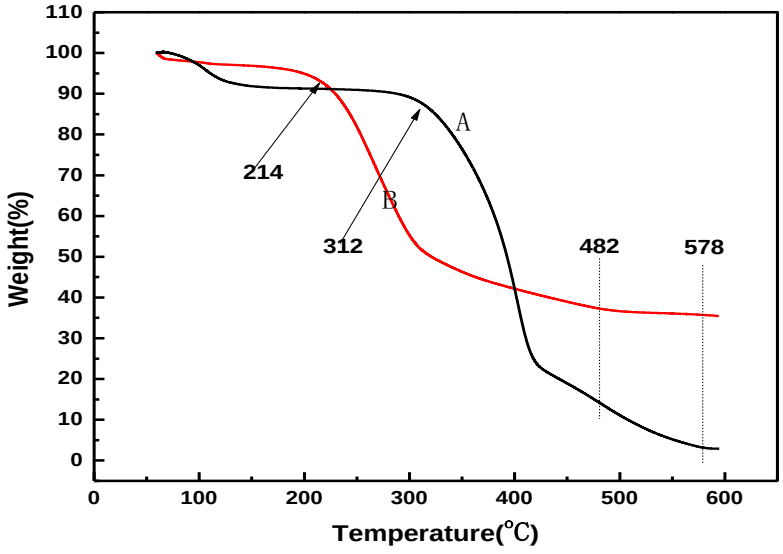

Fig. 3. Thermograms of the unmodified APMP (A) and the modified APMP (B)

Thermal Stability

The TGA analyses of the two different APMP samples are shown in Fig. 3. In the case of the unmodified APMP, after initial loss of moisture at about 100 to 312 °C, major decomposition proceeded from 312 °C to 578 °C. For the modified APMP, the starting decomposition temperature significantly decreased to 214 °C, and the main decomposition proceeded from 214 °C to 482 °C, about 100 °C lower than that of unmodified pulp, which is due to the easy degradation nature of the CHPTAC cationic segment in modified fibers. Furthermore, in comparison with the unmodified APMP, the modified APMP produced a higher amount of residual material after decomposition at 578 °C, which can be reasonably ascribed to the introduction of chloride (Liu *et al.* 2007). Other studies also reported a reduction in decomposition temperature for CHPTAC-modified hemicelluloses from sugarcane bagasse (Ren *et al.* 2007) and CHPTAC modified cellulose (Song *et al.* 2008). Despite the decomposition temperature of these cationized products decreased, their most potential applications were not influenced (Ren *et al.* 2007; Song *et al.* 2008). The TGA analysis demonstrated that the cationic CHPTAC agent was successfully grafted onto the surface of APMP fibers.

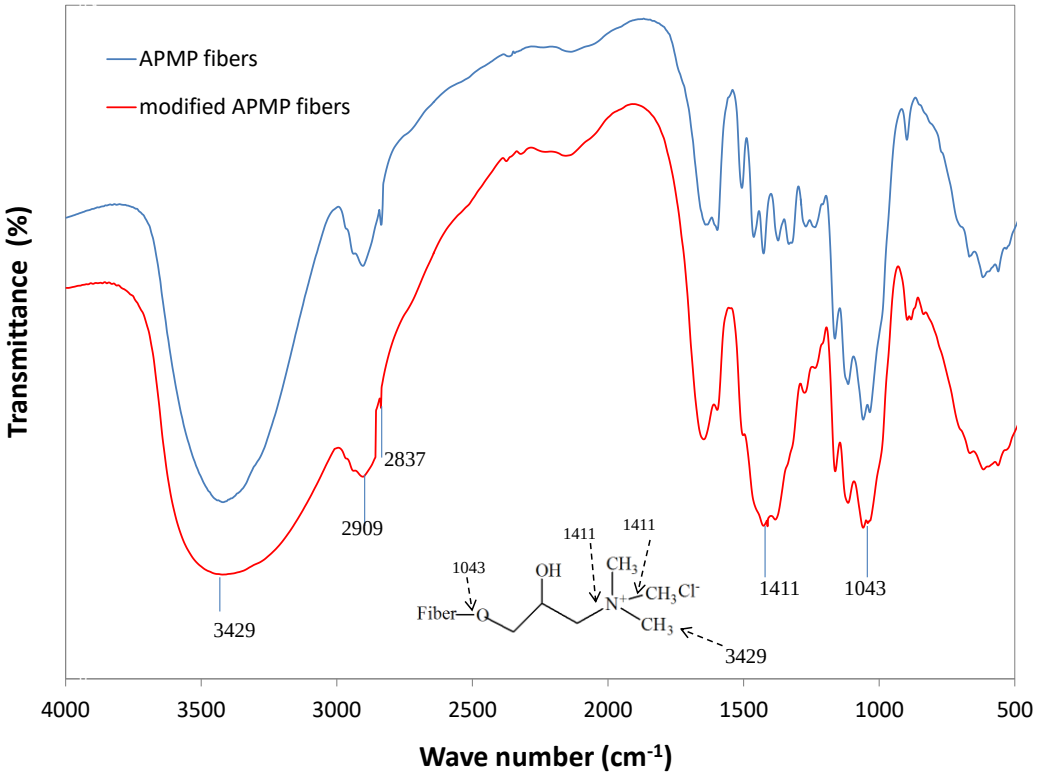

Fig. 4. FTIR spectra of fiber samples: (A) APMP fibers, and (B) modified APMP fibers

Fourier Transform Infrared Spectroscopy

Figure 4 shows the FTIR spectra of the APMP fibers and the modified APMP fibers. As the modification in this study is a cationization of APMP fibers with CHTPAC, which is grafted onto pulp fibers through etherification reaction between –OH group on fibers and epoxy group on 2,3-epoxypropyltrimethylammonium chloride, it should be pointed out here that the OH group on fibers includes OH group of cellulose, hemicellulose, and lignin of pulp fibers, as the cationization of these components using CHTPAC agent has been reported to be feasible at similar conditions in previous studies (Kong *et al.* 2015;

Peng *et al.* 2012; Yan *et al.* 2009). As illustrated in Fig. 4, the IR spectra of the APMP fibers and the modified fibers show a broad O-H stretching band at 3429 cm^{-1} due to hydrogen-bonded hydroxyls. The bands at 2909 cm^{-1} are assigned to the symmetric C-H vibration band of CH_3 group, and the bands at 2837 cm^{-1} are assigned to the stretching vibration of $–CH_2–$ groups. Compared with the spectrum of unmodified APMP fibers, the spectrum of modified APMP fibers provides the evidence of modification. Clearly, the modification reactions were monitored by being observed an enhancement in the intensity of the ether bond absorbance at 1043 cm^{-1}. A change appeared in an increase in intensity of the band at 1411cm^{-1} assigned to the C-N stretching vibration (Pal *et al.* 2005; Peng *et al.* 2012). These changes represented a clear proof of incorporation of cationic agent onto the APMP fibers. In addition, a decrease in the absorption band for hydroxyl groups (OH) at 3429 cm^{-1} in modified APMP fibers as compared to the spectrum of unmodified APMP indicated a partial etherification. These findings are consistent with those reported for the reactions of cellulose (Yan *et al.* 2009; Hebeish *et al.* 2010), carboxymethyl cellulose (Kolya *et al.* 2013), hemicellulose (Peng *et al.* 2012) and kraft lignin (Kong *et al.* 2015) with the similar cationic agent.

Charge Density Analysis

The modified APMP obtained at conditions of 0.8% cationic agent concentration, 1% alkali concentration, 50°C, 1 h reaction time, and 8% pulp concentration was used to analyze the charge density. The results showed that the charge density of modified APMP fibers had positive charge density, 1.53 mmol/g, which is due to the cationic group (ammonium group) of the CHPTAC grafted onto fibers. This high positive charge density would strengthen the bridges among neighboring fibers to increase the pulp strength properties (Fatehi *et al.* 2008).

Strength Properties, Internal Bond Strength and Zero Span Tensile Analysis

The strength properties, internal bond strength and zero span tensile of modified APMP obtained at different modification conditions were listed in Table 5. As shown in Table 5, both CHPTAC treatment (Table 5, run 3) and NaOH treatment (Table 5, run 2) significantly increased the pulp physical strength properties including tensile, tear and burst index, and internal bond strength. The treatment with NaOH alone was much more effective than the treatment with just CHPTAC. The combination of NaOH and CHPTAC treatment (Table 5, run 4) increased the strength properties as well as internal bond strength more pronouncedly. The internal bond strength was increased by 144.4%, and the tensile index, tear index, and burst index were increased by 35.3%, 29.2% and 16.7% respectively. A similar phenomenon was obtained by Liu *et al.* (2012) when studying the pulp properties and fiber characteristics of xylanase-treated aspen APMP. However, the zero span tensile index, no matter dry or wet, did not change too much, indicating that the influence of this modification (treatment) of APMP on fiber wall strength is insignificant. One can conclude that the pulp strength improvement of this modification for APMP is partially attributable to fiber swelling under alkaline conditions and partially from the cationic groups grafted onto the fiber surfaces that strengthens the bridges among neighboring fibers. In addition, the cationic pulp fibers would be expected to increase the efficiency of retention of polymeric and colloidal materials, including cellulosic fines and hemicellulose, which would contribute to inter-fiber bonding of paper sheets (Hubbe and Rojas 2008).

Table 5. Results for Strength Properties, Internal Bond Strength, and Zero Span Tensile Index

Sample No.	1	2	3	4
Modifier Dosage (%, oven-dry pulp)	0	0	0.8	0.8
NaOH Dosage (%, oven-dry pulp)	0	1	0	1
Internal bond strength (J/m^2)	145.7	237.9	178.4	356.1
Tensile index ($N\ m\ ^{g-1}$)	8.23	9.88	8.56	11.14
Tear index ($mN\ m^2\ g^{-1}$)	1.03	1.21	1.13	1.33
Burst index ($kPa\ m^2\ g^{-1}$)	1.13	1.24	1.12	1.32
DZSTI ($N\ m\ ^{g-1}$)	123	130	121	125
WZSTI ($N\ m\ ^{g-1}$)	103	102	105	110

Note: other modification conditions were: 50 °C, 1 h reaction time and 8% pulp concentration.

CONCLUSIONS

1. Based on the RSM-designed experiment, the optimal modification conditions of APMP were a CHPTAC dosage of 0.8% (oven-dry pulp), NaOH dosage of 1.0% (oven-dry pulp), and pulp concentration of 8% (oven-dry pulp). Through this modification, the CHPTAC containing cationic group was successfully grafted onto APMP fibers through etherification reaction.
2. The strength of the modified pulp was increased in terms of tensile index, tear index and burst index. After modification, the tensile index, tear index and burst index increased by 35.3%, 29.2% and 16.7% respectively. The internal bond strength was increased by 144.4%, and this modification gave an insignificant influence on zero span tensile index of APMP fibers.
3. The pulp strength increased after cationic modification of APMP for two reasons. First, the fibers became swollen at alkali condition, and second, the positive charges of CHPTAC grafted onto APMP fibers were favorable for electrostatic attraction with negative charges of the neighboring fibers.

ACKNOWLEDGMENTS

The authors are grateful for the National Natural Science Foundation of China (Grant Nos. 31570566, 31500489, and 31170547), the Key Laboratory of Pulp & Paper Engineering of Jiangsu Province, China (No. 201030), the Taishan Scholars Project Special Funds, and the Natural Science Foundation of Shandong (ZR2011CM011 and ZR2013CQ020) for their financial support of this project.

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Article submitted: July 19, 2016; Peer review completed: August 28, 2016; Revised version received: July 31, 2017; Accepted: August 1, 2017; Published: August 3, 2017.
DOI: 10.15376/biores.12.4.6956-6970