Modification of APMP fibers using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC) and its influence on pulp properties

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Abstract. Alkaline peroxide mechanical pulp (APMP) is a kind of high yield pulp that comes with the comprehensive utilization of plant material, such as poplar. APMP has lots of benefits, such as easy preparation, good bulkness, good stiffness, excellent optical performance and good printability. However, it also has disadvantages of lower pulp physical strength. In this paper, 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC) was used to modify the APMP pulp fibers for improving its strength properties. The effects of modification conditions on APMP properties, and the related modification mechanism were investigated. The results showed that the optimal conditions were CHTAC dosage 0.8 % (based on oven dried pulp), NaOH dosage 1 % (oven dried pulp), temperature 50 ˚C and pulp consistency 8 %. The improvement of treated pulp strength was evaluated in terms of tensile index, tear index and burst index. Internal bonding strength and FTIR analysis were used to discuss the positive effect of CHTAC treatment on APMP pulp. This paper also provides a promising technology to improve the APMP pulp properties and broaden its application fields.

Introduction

The shortage of raw material and energy, environment pollution problems in pulp and paper industry are being more pronounced in recent years. More and more research emphases are putting on appropriate pulping technology to improve the utilization rate of plant fiber, save energy and improve product quality. As a kind of high yield pulp, APMP has been paid more attention [1]. With the development of mechanical pulp in pulping technology, there seems to be more and more obvious advantages, such as high yield, good bulkness, and fine printability and so on. But there are also some disadvantages that limited the application of APMP, such as poor pulp strength [2]. In recent years, fiber modification was paid much more attention for improving mechanical pulp characteristics.

The significant improvement of pulp properties was observed by Zhang et al when studying the effect of cationic modification of softwood kraft pulp [3]. In addition, the beating sensitivity of cationic cellulose pulp was significantly increased for papermaking system [4]. And also, the preparation of cationic Kraft pulp by grafting copolymerization was investigated by Mao et al [5]. For our case, using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride to produce cationic APMP pulp was studied based on grafting technology. The challenge is the high lignin content in

APMP, which might hamper the grafting reaction. Up to now, there are few of detail report on this.

In this paper, the CHTAC was used to modify pulp fibers of APMP. The modification conditions were optimized based on resulted pulp properties and the successful grafting of CHTAC to fibers was testified by FIIR and internal bonding strength. The improvement mechanism of strengthening pulp properties was also discussed.

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Material and methods

Materials. APMP pulp was kindly supplied by a pulping plant located in Shandong, China. Chemicals including 3-Cl-2-HTAC (68 % solution) and NaOH (99.0 %, solid powder) were purchased commercially from Sigma-Aldrich company. All the chemicals were used as it was supplied without further purification.

Refining of APMP. Before modification, the pulp was refined according to the QB/T 1463-1992 method; Robust refining of APMP pulp was carried out in a PFI mill (Austria), 10,000–12,000 rpm, with pulp consistency of 10 %. The refining degree of pulp was estimated by Schopper-Riegler beating degree tester at different retention times following the GB/T3332—1982 method.[6] The refined pulp was used to react with CHTAC. The beating degree of the refined pulp used in this paper was 37 °SR.

Modification of APMP. Certain amount of NaOH, cationic modification agent, CHTAC, and deionized water required to achieve required pulp consistency were added to plastic bags containing APMP pulp. Then, the pulp and chemicals were mixed well through kneading. After that, the plastic bags were put into a water bath for certain time. After reaction, the pulp was thoroughly washed using deionized water until the pH of filtrate reached neutral.

Handsheets preparation. Handsheets were prepared following the ISO5269-2 method in an RTI Rapid-Kothen handsheetforming machine (Austria).[6] The base weight of handsheets was controlled at 80 g/m^2.

Measurement of handsheets properties. The tensile index, tear index and burst index of handsheets were measured according to the methods of GB/ 453-1989, GB/T 455.1-1989 and GB/T 451.2-1989 respectively.[6]

FTIR. FT-IR spectra were obtained on a Fourier transform infrared (FT-IR) spectrophotometer (Bruker Vector 22) using a KBr disc containing 1 % (w/w) of solid product. All the spectra were obtained by accumulation of 16 scans, with a resolution of 4 cm^{-1}, at 400–4000cm^{-1}.[7]

Internal bonding strength analysis(Scott type). The internal bonding strength of sample was measured according to GB/T 26203-2010[8]. The specimen of 25.4 mm in width and 140 mm in length was prepared accurately from each handsheet samples, which should be kept free from abnormalities, creases, or wrinkles.

Results and discussion

Modification of APMP using CHTAC

Effect of CHTAC dosage on pulp properites. Figure 1 showed that the tensile index, tear index and burst index of the pulp increased at a certain degree with the increase of CHTAC dosage from 0.2 % to 0.8 %. At 0.8 % of CHTAC, the pulp properties reached the highest level. When the dosage of CHTAC was higher than 0.8 %, the tensile, tear and burst index of pulp decreased slightly. This phenomena were attributed to the increase of positive charge on pulp fiber surface after modification, and this positive charge, which comes from the ammonium group of CHTAC, can attract the negative charge on another fiber surface and benefit the bonding capability between the fibers.[9] Further increase the dosage of CHTAC to 0.9 %, the paper properties was decreased at a certain extent, which may cause by the excessive dosage of cationic agent. Similarly, Zhang et al. also observed the pulp strength loss when studying the effect of cationic emulsion copolymer on pulp strength at excessive dosage.[10] The optimum CHTAC dosage was 0.8%.

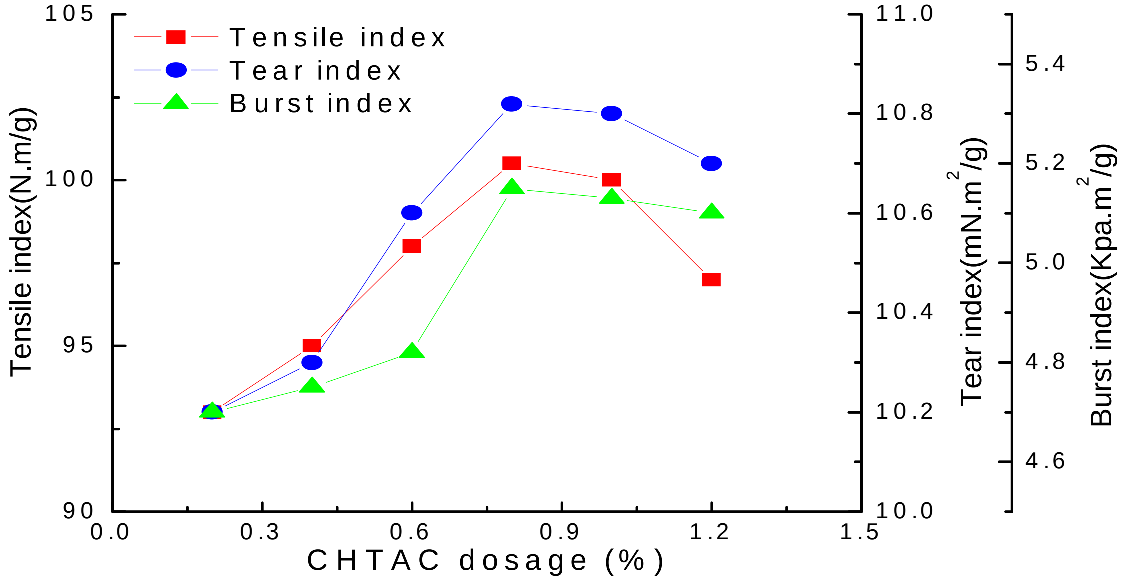

Figure 1 effect of CHTAC dosage on pulp properties. (50˚C, 0.5 % NaOH, 60min and 10% pulp consistency)

Effect of NaOH dosage. Figure 2 showed that the tensile index, tear index and burst index of the handsheets increased at a certain degree with the increase of NaOH dosage, which is due to that the APMP fibers can swell more at higher concentration of NaOH to benefit the bonding capability between fibers.[7] However, further increase NaOH dosage to 1.2%, the increase of pulp strength properties was marginal. In the literature, this phenomenon was also reported by Wang et al[10]. Considering the application of this technology in the industry, the optimum NaOH dosage is chosen as 1.0 %.

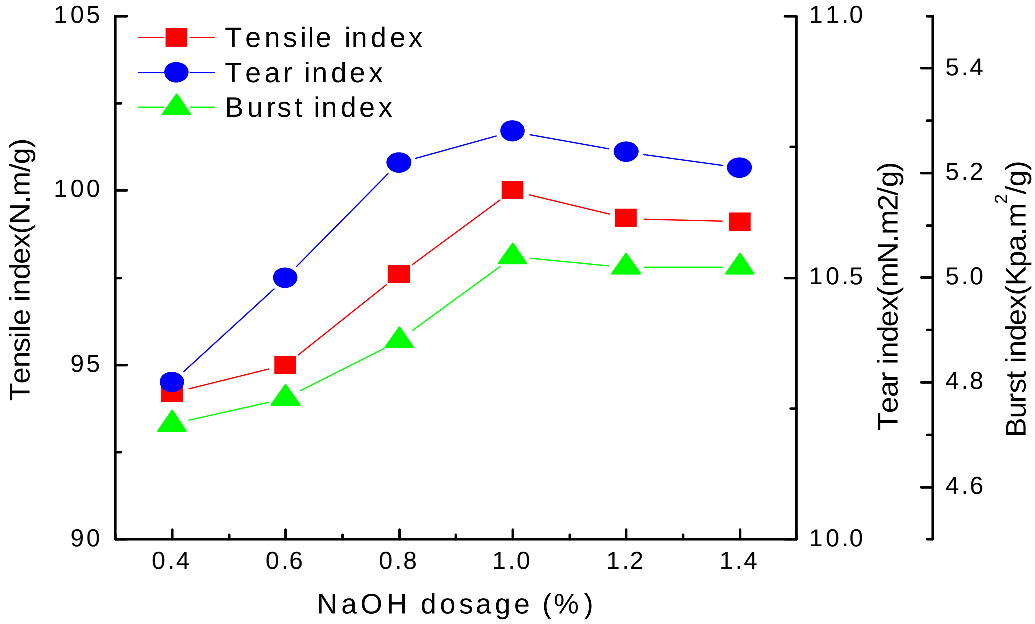

Figure 2 Effect of NaOH dosage on pulp properties (CHTAC, 0.8 %, 50 ˚C, 60 min and 10 % pulp consistency

Effect of temperature. It can be seen from Figure 3 that increasing reaction temperature from 30 ˚C to 80 °C had a slight influence on the tensile index, tear index and burst index of resulted pulp. This could be attributed to that this modification reaction was a nucleophilic reaction [12] which is insensitive to heat. The optimum temperature was 50 ˚C.

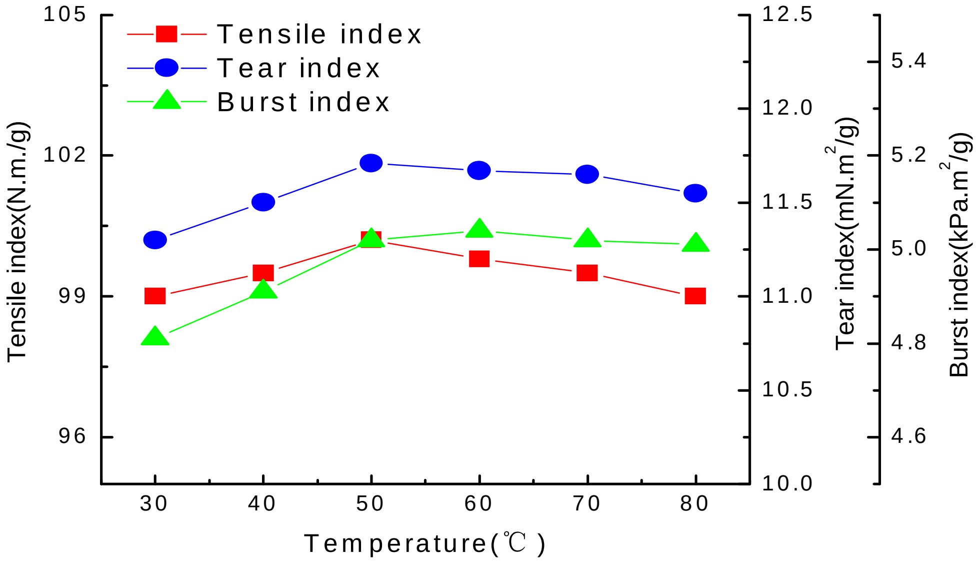

Figure 3 Effect of temperature on pulp propertise(CHTAC, 0.8 %, NaOH 1.0 %, 60 min and 10 % pulp consistency

Effect of pulp consistency. Increasing the pulp consistency usually could be beneficial in improving the efficiency of modification. However, it was difficult to mix the pulp with modification agent at a high pulp consistency, which may have a negative influence on the effectiveness of modification. Figure 4 shows that the treatment with cationic modification agent at a high pulp consistency (e.g, 8 % pulp consistency) improved the APMP strength properties, compared to that at 4 % pulp consistency. When the pulp consistency increased to 10 %, the resulted pulp properties, such as tear, tensile and burst strength, decreased, which is due to the bad mixture of pulp with modification agent at high pulp consistency. Therefore, a suitable pulp consistency in the modification treatment was 8 %

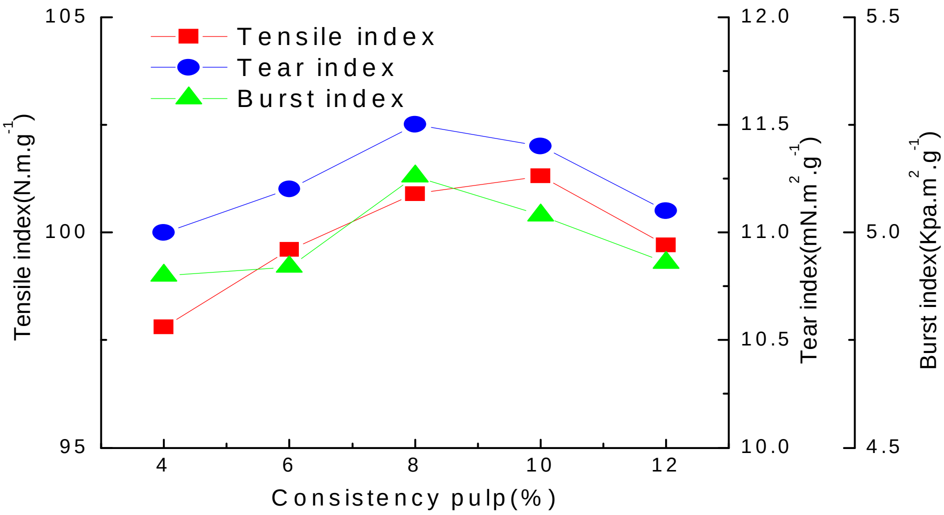

Figure 4 Effect of pulp consistency on paper propertise(CHTAC, 0.8 %, NaOH 1.0 %, 60 min and 50 ˚C)

FT-IR spectra of modified and unmodified APMP

After modification using CHTAC, the pulps were washed with the deionized water. And then the pulp fibers were dried in an oven at 50 ˚C for 24 hours. Later, measured by the infrared spectrophotometer. The spectra of modified and unmodified pulp were shown in Figure 5. The band belonging was identified based on Wang et al.[11] The broad band around 3300 cm^{-1} represented the O–H stretching vibrations. The band at 1613 cm^{-1} arose from the modification agent indicated the high amount of CH_2. The C–H stretching vibrations give a signal at 2929 cm^{-1}. The disappearance of band at 2840 cm^{-1} related to the nucleophilic substitution[12]. All these bond changes demonstrated that the structure of the modified fibers was partially changed.

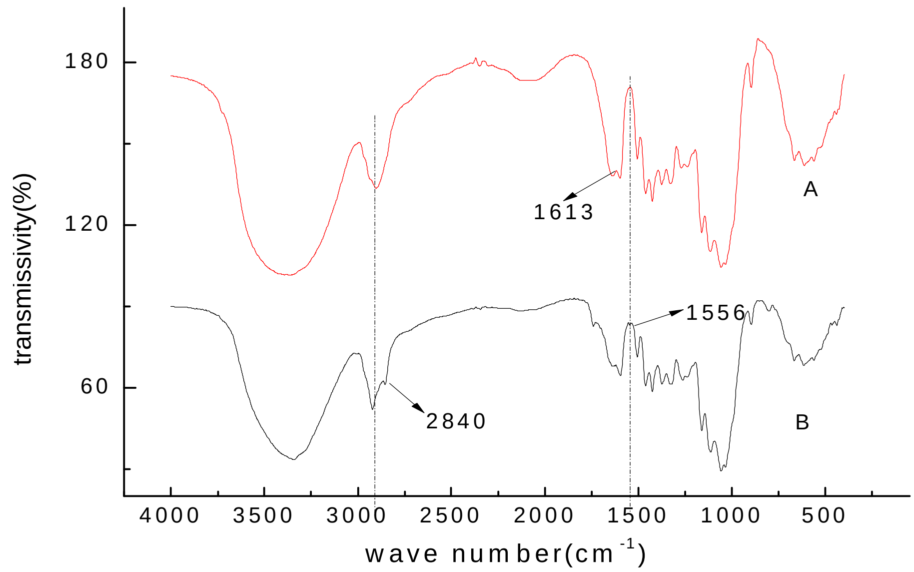

Figure 5 infrared spectrum of fiber samples (A-the modified fibers; B-the unmodified fibers)

Internal bond strength analysis of the modified fiber

Table 1 listed the internal bond strength between fibers. As list in Table 1, both of CHTAC and NaOH treatment can increase the internal bond strength to a certain extent. Furthermore, the combination of NaOH and modification agent, CHTAC, increased the internal bond strength to 125 % from the control sample, which greatly satisfied the commercial requirement for higher pulp strength. It was also a positive support for the CHTAC treatment. Similar phenomenon was obtained by Hu [13] when studying the pulp properties by laccase treatment.

Table 1Internal bond strength of different APMP.

Sample No	1	2	3	4
CHTACdosage（% oven dried pulp）	0	0	0.8	0.8
NaOH dosage（% oven dried pulp）	0	1	0	1
Internal bond strength(J/m^2)	159.1	278.2	178.3	358.0

Other conditions: 60 min, 8 % pulp consistency and 50 °C.

Conclusions

CHTAC treatment was a promising technology to enhance the pulp strength of APMP. The dosage of CHTAC, NaOH and pulp consistency were the major parameters affecting the improvement of pulp strength properties. Based on the experiments carried out in this paper, the optimal conditions were 0.8 % of CHTAC, 1.0 % of NaOH, 8 % of pulp consistency, 60 min and 50 ^{o}C. The internal bond strength and FTIR analysis further supported the conclusion of pulp strengthening capability of this technology.

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References

[1] Zhan Huaiyu. Pulping Principle and Engineering. [M], Third edition. Beijing: Chinese Light Industry Press, 2010

[2] Xu, E. C, Sabourin M. J. Process Selection for Chemimechanical Pulping Aspen [J]. Pulp &Paper Canada, 2002, 103 (3):36

[3] Zhang Quan. 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride modification of pulp on its beating nergy consumption and paper properties [D], Shan xi University of Science and Technology:2009

[4] Gruber E. Is there a future for chemically modified pulp[J]. ipw, 2002(6):73.

[5] Mao Lian Shan, Liu Gui Gan, Claude Daneault et al. Preparation of Cationic Kraft Pulp by Grafting Copolymerization[J], China Pulp & Paper,2007(4):12-15.

[6] Shi Shulan, He Fu Wang. Editor Detection and analysis of pulping and papermaking Beijing: Chinese Light Industry Press, 2010.8

[7] General Administration of Quality supervision, Inspection and Quarantine of the people's Republic of China, Standardization Administration of the people's republic of China. Editor, Fourier transform infrared Spectrometer [M], 2008,3.

[8] General Administration of Quality supervision, Inspection and Quarantine of the people's Republic of China, Standardization Administration of the people's republic of China. Editor, Paper and board—Determination of internal bond strength(Scott type)[M],2011,6.

[9] Zhou Gaijun, Yuan Zhirun, Jiang Zhihua, et al. The characteristics and application of high yield pulp [J]. International Paper, 2007, 26(1):1-10183(2015):42~46

[10] Wang Li Jun, Xie Yi Min, Han Qing.The effects of different kinds of intiator systems on copolymerzation of cellulose grafed with caprolactam[J]. The Chinese paper industry, 2010, 31(8):46-49.

[11] Po¨nni R, Kontturi E, Vuorinen T (2013) Accessibility of cellulose:structural changes and their

reversibility in aqueous media. Carbohydr Polym 93:424–429

[12] Qing Wang, Shan Shan Liu, et, al. Cationic polyacrylamide enhancing cellulose treatment efficiency of hardwood kraft-based dissolving pulp[J], Bioresource Technology.

[13] Hu Jie. Lacase-Catalyzed Improvement of Pulp hydrophobicity[D].QiLU University of technology 2013