Reinforcing Paper Strength by Dual Treatment of a Cationic Water-soluble Polymer and Cellulose Nanofibril

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Abstract: Cellulose nanofibril (CNF) was used as the anionic component of two dual strengthening systems wherein polyamidopolyamine epichlorohydrin resin (PAE) or cationic starch (CS) was used as the cationic component. Their strengthening effects were investigated for low-basis-weight (30 g/m^2) paper composed of a mixture of fully bleached softwood and hardwood pulp in a 4:1 mass ratio. Using the PAE/CNF or CS/CNF dual system, it was generally easier to achieve higher wet and dry tensile strengths of paper compared to the paper using the single PAE or CS system. For example, the paper using the PAE (0.4%)/CNF (0.3%) dual system exhibited 89% higher wet tensile strength than the paper using the single PAE (0.4%) system, and the paper using CS (1.3%)/CNF (0.3%) dual treatment showed 21% higher dry strength than that using the single CS (1.3%) system. However, the PAE/CNF system only showed small improvement in the dry strength of paper (11% higher than that of paper using the single PAE system), so did the CS/NFC system on wet strength improvement (only 17% higher than that of paper using the single CS system).

Keywords: cellulose nanofibril; polyamidopolyamine epichlorohydrin; cationic starch; dual treatment

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1 Introduction

The dry and wet strengths of paper are important for the grading of paper for subsequent use as tissues, towels, and liquid packaging base paper, where the wet strength is a significant property[1]. Cationic starch (CS) and polyamidopolyamine epichlorohydrin resin (PAE) are effective dry and wet strengthening agents, respectively. However, in isolation, these chemicals are prone to reach strength ceilings that may be insufficient to meet certain paper grades. The dual treatment of papermaking fibers with a cationic and a anionic polymer is a possible method for achieving higher strength properties.

Cellulose nanofibril (CNF) is a promising natural nanocellulose material that has attracted significant research interests recently due to its biodegradability, barrier properties, chemical tunability, and robust mechanical properties[2]. It is commonly prepared from plant fiber via enzymatic and/or chemical treatments followed by physical treatment such as grinding or homogenization[3]. CNFs have been used as reinforcing agents for paper products and their practical effects have been quite remarkable[4-6].

In contrast, compared to single strengthening system such as cationic starch (CS) for dry strength or polyamidopolyamine epichlorohydrin (PAE) for wet strength, preparation of dual strengthening system of papermaking fibers with cationic and anionic polymers remains popular due to its cost-effectiveness. Wang et al[7] reported that a dual PAE/carboxymethyl cellulose (CMC) strengthening system exhibited more significant effect on the dry-wet strength properties than the single PAE or CMC system. In addition, the addition order did not significantly influence the strengthening effect. Yao et al[8-10] explored the application of cellulose nanocrystalline (CNC)/CS dual system in papermaking with two addition modes, adding CNC/CS complexes or pre-adsorbing CS onto the cellulose prior to CNC-adsorption. The paper strength improvement was more efficient when the components were prepared using the latter sequence. Ahola et al[11] studied the effect of CNF/PAE addition strategies on the wet and dry strength of paper by comparing layer-structures and nano-aggregates formed by the nanofibril and PAE using a quartz crystal microbalance with dissipation (QCM-D) and atomic force microscopy (AFM). Using the bi-layer system, both the wet and dry strengths of paper can be increased even with low PAE contents and the nanofibril could replace some dry strength additives commonly used in the paper industry.

This study was performed to determine the dry and wet strengths of low basis weight papers prepared using a mixture of fully bleached softwood and hardwood pulp in a 4:1 mass ratio. At a basis weight of 30 g/m^2, the wet/dry strengths would be improved by using the PAE/CNF and CS/CNF dual strengthening systems.

2 Experimental

2.1 Materials

Bleached hardwood and softwood Kraft pulp were provided by Langfang Sinolight Specialty Fiber Products Co., Ltd. with beating degrees of 42°SR and 41°SR, respectively. The softwood and hardwood pulps were initially mixed at a mass ratio of 4:1 and stored for further use.

CNF was obtained from Guilin Qihong Technology Co., Ltd. with a diameter of 3~5 nm, length of 1~3 μm, and surface charge of −0.339 mmol/g. PAE (25%) and CS were purchased from Transfar Chemicals Co., Ltd. and Papermate Science & Technology, respectively, in Hangzhou, China.

For the CS solution preparation, 2.0 g of CS was first dissolved in 200 mL of deionized water and placed in a water bath. The solution was stirred at 95℃ for 1.5 h and subsequently maintained at 60℃ for at least 30 min. The resulting gelatinized CS solution was diluted to a final concentration of 0.1%. PAE and CNF were also diluted to 0.1% with deionized water before being added to the pulp.

2.2 Methods

2.2.1 Zeta potential measurements

The Zeta potentials of the suspensions were measured in triplicate using a streaming Zeta potential meter (model SZP-04, BTG instruments GmbH; Herrsching, Germany).

The cationic component, PAE or CS solution, was first added stepwise in predetermined amounts (percentage, based on dried weight of the chemicals to dried weight of the pulp) to the mixed pulp to determine the proper dosage in the dual strengthening system. Special attention was paid to the amount of cationic component that turned the Zeta potential of the fiber slurry from negative to positive. During the measurements, the mixed pulp was first diluted to 0.8% and the PAE or CS solution was added to the fiber slurry via different batch addition, each time in an increment of 0.1% (for PAE) or 0.2% (for CS). The corresponding data were recorded after thorough mixing.

In the dual strengthening system, the desired amount of cationic component was first added to the fiber slurry under stirring for 5 min and 0.1% CNF was added successively at defined intervals.

2.2.2 Handsheet preparation

Handsheets with a basis weight of 30 g/m^2 were prepared using a semi-auto sheet machine (KRK, KOGYO Co., Ltd.) according to the TAPPI standard method (T 205 sp-02). The cationic component and CNF suspension were added to the mixed pulp successively at a 5 min interval and the final consistency was adjusted to 3.0%. After further mixing for 5 min, the fiber slurry was used to form handsheets.

2.2.3 Mechanical properties of handsheet

The mechanical properties of handsheets were measured under standard conditions of temperature (23±1)℃ and humidity (50±2)% RH. The dry and wet tensile mechanical properties of the handsheets were measured using a horizontal tensile tester (Frank-PTI GmbH) equipped with a 500 N load cell according to Tensile Test ISO 1924-2 and Tissue (wet) EN 12625-5, respectively. After data collection, the mean values and standard errors were calculated. Statistical t-tests were used to determine the significance of the differences between two data sets. A p-value of less than 0.05 was judged to be statistically significant[12]. The p-values were calculated using WPS software following its “Formula-Insert Functions-Statistics-TTEST” steps.

3 Results and discussion

3.1 Determination of the additive content

The effect of PAE or CS on the Zeta potential of fiber suspension is shown in Fig.1. The initial Zeta potential of fiber suspension was as low as −60 mV, indicating that the fiber may contain a significant amount of carboxyl groups. This allowed the cationic strengthening agents to adsorb onto the negatively-charged fiber surface and neutralize the negative charge due to electrostatic attraction, leading to a gradual increase of Zeta potential of the fiber suspension with increasing addition of PAE or CS.

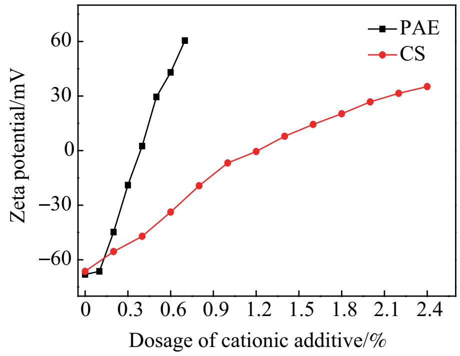

Fig.1 Effects of cationic additives on the Zeta potential of the fiber suspension in single systems

The Zeta potential of the fiber suspension changed from negative to positive when at PAE and CS contents of 0.4% and 1.3%, respectively. Based on the above results, it was determined that a dosage of 0.4% PAE or 1.3% CS would be optimal for the following studies both in the single and dual systems.

Setting the dosage of PAE at 0.4% or CS at 1.3%, the optimal dosage of CNF was determined, as shown in Fig.2, for further Zeta potential determination. The Zeta potential of the treated fiber suspension was drastically reduced and electronegativity significantly enhanced with increasing CNF dosage, but the trend plateaued at approximately 0.3% of CNF.

In subsequent dual treatments, the CNF dosage was

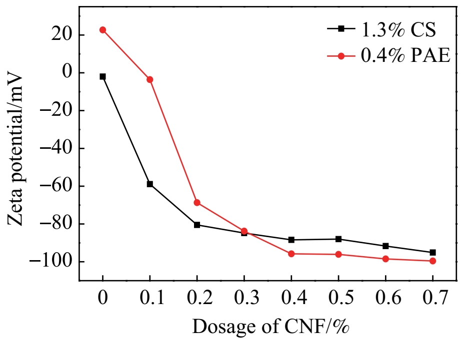

Fig.2 Effect of CNF dosage on the Zeta potential of the fiber suspension in the dual systems

0.3%, and was supplemented at 0.6% to investigate the effect of CNF at elevated dosage.

3.2 The effects of additives on the dry tensile strength of handsheets

Handsheets were prepared from the 4:1 mixture of bleached softwood and hardwood pulps which was treated with the two dual systems, where the cationic component (PAE or CS) was first mixed into the pulp and subsequently CNF was added.

Fig.3 shows that the dry tensile index of handsheet in the single system increased by approximately 12.8% (p-value of 4.256×10^{-3}) when 1.3% CS was added compared to the control handsheet. CS, as a widely used reinforcing agent, contains a significant amount of free glucose hydroxyl groups which participate in the formation of hydrogen bonding with cellulose molecules on the fiber surface. This increased the number of hydrogen bonds between the fibers and improved bonding strength.

For the CS/CNF dual system, when CS content was 1.3%, the dry tensile strength of handsheets were 36.9% and 21.2% (p-values of 2.776×10^{-6} and 6.632×10^{-6}, respectively) higher than the control handsheet at CNF dosages of 0.3% and 0.6%, respectively. The surface of the CNF has a large number of carboxyl groups, therefore it can electrostatically attract and form complexes with the CS molecules either being adsorbed on the fiber or remaining in the aqueous phase of the pulp. It can also be inferred that the complexes existed in a state that is adsorbed on the fiber surface or another state that is filled in the fiber network. In either case, the formed complex contributes to the bonding force between fibers and improves the paper dry strength.

However, increasing the dosage of CNF from 0.3% to 0.6% did not further increase the dry tensile strength (p-value of 0.3466). The electrostatic repulsion between the over-dosed CNFs, or that between CNF and negatively charged fibers, may be the underlying mechanism of this phenomenon.

Fig.4 shows that dry strength enhancement was small (8.9%) when 0.4% PAE was used in isolation as compared to the control handsheet (p-value of 2.419×10^{-2}). For the dual system, when PAE content was 0.4%, the dry tensile strength of handsheets at CNF addition of 0.3% and 0.6% were increased by 20.8% and 18.3% (p-values of 1.635×10^{-4} and 3.981×10^{-4}, respectively) compared to the dry tensile strength of control handsheet, and 11.0% and 8.7% higher than that of the handsheet with 0.4% PAE added alone (p-values

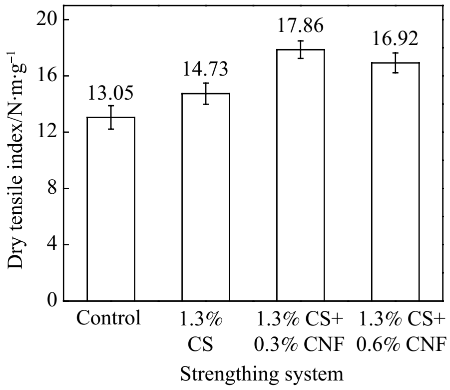

Fig.3 Effect of CS/CNF dual treatment on the dry tensile index of the resulting handsheets

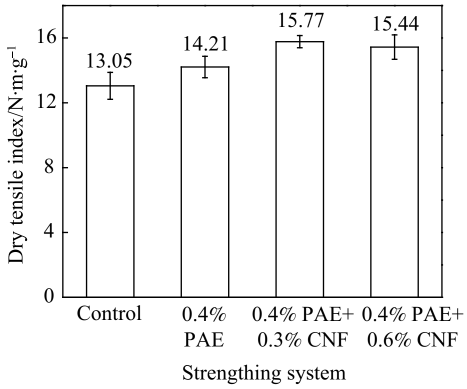

Fig.4 Effect of PAE/CNF dual treatment on the dry tensile index of the resulting handsheets

of 1.046×10^{-4} and 1.333×10^{-2}, respectively).

In summary, the effect of the CS/CNF dual system on the dry strength of handsheet was more significant than the PAE/CNF system. CS is known to enhance dry strength by hydrogen bonding between fibers. In contrast PAE, a typical wet strengthening agent, affects the dry strength to some extent by covalent bonding between the PAE azetidinium group and its amine groups or the hydrogen groups of cellulose molecules. Therefore, to enhance dry strength, hydrogen bonding provides more significant contributions than covalent bonding[13-15].

3.3 The effect of additives on the wet tensile strength of handsheets

Fig.5 shows the effect of the CS/CNF dual system on the wet tensile index of the prepared handsheets. CS alone has significant but not very large effect on the wet strength of handsheet. When only 1.3% CS was added, the wet strength of handsheet was only 21.7% (p-value of 9.200×10^{-4}) higher than that of the control handsheet. For the CS/CNF dual system, 0.3% CNF following the 1.3% CS addition contributed another 24.6% increase (p-value of 1.892×10^{-8}) to the wet strength. However, increasing CNF addition (to 0.6%) did not further contribute to the wet strength (p-value of 0.9556).

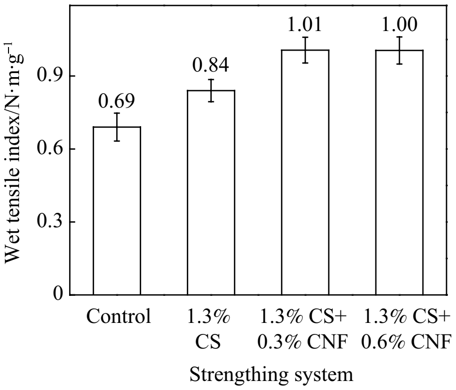

Fig.5 Effect of CS/CNF dual treatment on the wet tensile index of the resulting handsheets

Fig.6 shows the effect of PAE/CNF dual system on the wet tensile strength of handsheets. As expected, 0.4% PAE significantly increased the handsheet wet strength (more than 4.0-fold increase compared to that of the control handsheet, p-value of 3.305×10^{-11}). The wet-strength development from PAE to cellulose sheets is primarily due to covalent bond formation between the PAE azetidinium groups and hydroxyl groups of cellulose fibers[1].

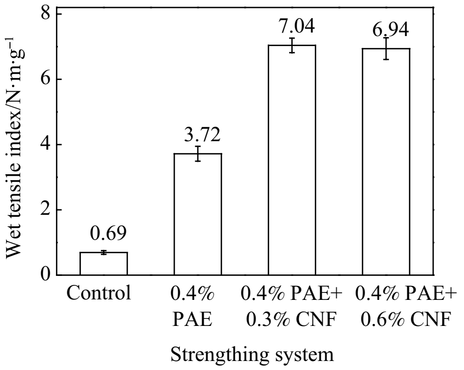

Fig.6 Effect of PAE/CNF dual treatment on the wet tensile strength of the resulting handsheets

For the PAE/CNF dual system, with the addition of 0.3% CNF, the wet strength of handsheet increased by more than 9 times (p-value 1.602×10^{-12}) compared to that of the control sample and 0.89 times (p-value 8.796×10^{-15}) compared to that of the 0.4% PAE treated sample. The additional increasing wet strength of PAE/CNF dual system on handsheet was mainly attributed to the improved retention of PAE by addition of CNF and improved chemical interactions between the PAE and hydroxyl groups of the nanofibrils. However, increasing CNF addition (to 0.6%) did not further increase the wet strength (p-value of 0.4989).

4 Conclusions

Using cellulose nanofibril (CNF) with polyamidopoly amine epichlorohydrin (PAE) or cationic starch (CS) as part of dual strengthening system, both the wet and dry tensile strengths of handsheet were improved compared to isolated PAE or CS even at a low CNF content. In addition, the PAE/CNF system significant affected the wet strength of the resulting paper sheets, while the effect of CS/CNF on the dry strength was more significant.

Generally, the use of CNF as a component of dual strengthening system enables paper to achieve higher strengths at a low basis weight, which can reduce fiber use. In addition, the additives have the potential to be used in special tissues, wipers, towels, and liquid packaging base paper, for which the wet strength is the most significant property.

Acknowledgments

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