Combination of Glyoxal and Chitosan as the Crosslinking System to Improve Paper Wet Strength

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The wet strength of handsheets subjected to dipping treatment by solutions such as glyoxal with $Zn(NO_3)_2$ as a catalyst, chitosan, and the crosslinking system of glyoxal and chitosan is studied in this paper. The crosslinking system achieved better wet strength performance than glyoxal or chitosan alone and slightly better than the sum of glyoxal and chitosan in the case of a curing temperature between 90 and 130 °C. However, handsheets treated by this crosslinking system became more brittle, which was shown by the reduction of folding endurance of the handsheets with increasing wet strength. The capillary rise and contact angle of the treated handsheets showed certain relations to their wet strength when the above solutions were used to improve the wet strength of the handsheets. The physical changes of the treated handsheets can provide evidence to explain the mechanism of wet strength development.

Keywords: Glyoxal; Chitosan; Crosslinking; Wet strength; Handsheets

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INTRODUCTION

In the last few decades, papermakers have made continuous efforts to develop environmentally friendly paper wet strength agents containing less or no formaldehyde and absorbable organic chlorides (AOX) (Caulfield 1994; Hamzeh *et al*. 2013; Saito and Isogai 2006; Zakaria 2004). Glyoxal is reported as a crosslinking agent to improve the wet strength of paper in a dipping process that can provide temporary wet strength to paper without the aid of a catalyst and improve the permanent wet strength to some extent when catalysts such as $Zn(NO_3)_2$ are used (Xu *et al*. 2002). Compared with glyoxal alone, the combination of glyoxal and polyvinyl alcohol (PVA) as a crosslinking system can achieve higher folding endurance when the wet strength of paper is improved (Xu *et al*. 2004).

Chitosan is a natural dry strength paper agent and has active primary amino groups convenient for its modification as a papermaking chemical. Chitosan also is an efficient agent to strengthen the wet web of paper sheets (Lindström *et al*. 2005). Modified products and complexes of chitosan have been reported to improve the wet strength of paper (Chen *et al*. 2013; Liu and Kim 2012). However, natural chitosan as a wet strength resin is much less effective than polyamideamine epichlorohydrin (PAE) resin, which is a popular commercial wet strength agent in the papermaking industry (Niekraszewicz *et al*. 2001). As a flocculation agent, the grafted products of chitosan and other polymers have been used in the treatment of wastewater from papermaking and other industries (Saeed *et al*. 2011; Mourya and Inamdar 2008; Wang *et al*. 2008). Chitosan and its modified products can be used in other fields of papermaking because of its other special properties, which include biocompatibility, biodegradability, and antibacterial properties (Aranaz *et al*. 2009; Vallapa *et al*. 2011; Sun *et al*. 2010; Qian *et al*. 2008; Nada *et al*. 2006).

In this paper, a crosslinking system containing chitosan and glyoxal with $Zn(NO_3)_2$ as a catalyst is used to improve the wet strength of paper handsheets and is then compared with the use of glyoxal or chitosan alone. Both the temporary and permanent wet strengths of the treated handsheets are investigated. The relationship between the wet strength and brittleness of treated handsheets is studied during the development of wet strength. Some changes in the absorption and surface hydrophobicity of the treated handsheets are observed as the treated handsheets undergo wet strength measurement. To examine the possible relationships among wet strength, absorption, and surface hydrophobicity, the capillary rise and contact angle of the treated handsheets are measured.

EXPERIMENTAL

Materials

Chitosan (with 87% degree of deacetylation) of about 600 kDa was purchased from Shandong Laizhou Highly Bio-product (China). Glyoxal was 40% aqueous solution and purchased from Tianjin Bodi Chemical Co., Ltd. Acetic acid and caustic soda used in this study were of analytical grade and used without further purification. Fully bleached softwood kraft pulp used in handsheet preparation was made in Canada and kindly provided by Mudanjiang Hengfeng Paper Company (China) and beaten to 38 to 40 °SR using a Valley beater at 2% consistency. After that, the beaten pulp was thickened to about 13% consistency for use.

Handsheet Preparation and Treatment

Handsheets with a target grammage of 70 g/m^2 were prepared using a round handsheet former of diameter 200 mm. In order to maintain relatively high absorbency, the handsheets were not subjected to further pressing. After the handsheets were dried by a vacuum dryer at -0.08 MPa for 12 min at 90 ^oC, they were conditioned in a conditioning atmosphere of 50.0% ± 2.0% RH and 23.0 ± 1.0 ^oC for 24 h before further treatment. The handsheets were dipped into the treating solution for 60 s at room temperature, then carefully placed between two pieces of blotting paper on a flat rigid surface to remove the surplus solution by moving the hand roller once back and once forward over the pad without exerting any additional pressure on the roller to reach a wet pick-up of around 130%. Then, the impregnated handsheets were dried in a speed dryer (SD24D, Labtech Instruments INC. Canada) at 90 ^oC for 5 min and cured at a specified temperature for 2 min on this speed dryer. The treating solutions were 0.5% (w/w) chitosan in 2% (v/v) acetic acid aqueous solution, 0.2 mol/L glyoxal aqueous solution with 0.76% (w/w) $Zn(NO_3)_2$ as a catalyst, or 0.2 mol/L glyoxal with 0.76% (w/w) $Zn(NO_3)_2$ in combination with 0.5% (w/w) chitosan in 2% (v/v) acetic acid aqueous solution. Two percent (v/v) acetic acid and 4% (w/w) NaOH aqueous solutions were used to adjust the pH of these solutions to 4.8. In order to avoid the reaction of glyoxal with chitosan, the above third treating solution was used within one hour after preparation.

According to the test results of rotary viscosimeter (DNJ-8S), the viscosity of 0.5% chitosan solution at room temperature was 89 mPa·s, and the viscosity of the above third treating solution was almost the same as that of 0.5% chitosan solution. The control samples were treated with deionized water, subjected to the same press process, and dried at 90 ^{o}C without further curing. It is worth noting that acetic acid as an air pollutant needs appropriate treatment if the above dipping process is employed in industrial production.

Dry and Wet Tensile Strength Evaluation of the Handsheets

Dry and wet tensile strengths of the handsheets were evaluated in accordance with TAPPI standard test methods T494 om-96 and T456 om-87, respectively. The sample strips for wet tensile strength measurement were dipped in distilled water for 2 min, 30 min (correlated with the temporary wet strength), and 24 h (correlated with the permanent wet strength), respectively, and immediately subjected to tensile strength measurement after the removal of excess water on the sample strips with blotting paper. The wet strength (W/D ratio) was defined as the ratio of the wet tensile strength of treated handsheets to the dry tensile strength of the control sample. Ten strips were measured for each handsheet to obtain an average wet strength.

Determination of Capillary Rise and Contact Angle of the Handsheets

The capillary rise of the handsheets was determined according to the ISO 8787-1986 standard test method and expressed as the rise distance (mm) of water within 10 min. Five strips were measured for each handsheet to obtain an average capillary rise. The contact angle of the handsheets was evaluated in accordance with TAPPI standard test method T558 om-06. A 0.5-µL water droplet was dropped onto the surface of the samples by a micro-syringe, and the image of the water droplet was recorded and subjected to subsequent determination of contact angle. Three positions on each sample were measured to acquire an average contact angle.

RESULTS AND DISCUSSION

Wet Strength of Handsheets Treated with Glyoxal

The wet strength of the control sample was too little to measure at different dipping times (2 min, 30 min, and 24 h), indicating the control sample has little or no wet strength both temporarily and permanently. The wet strengths of the handsheets treated by 0.2 mol/L glyoxal with 0.76% $Zn(NO_3)_2$ as a catalyst are shown in Fig. 1. Obviously, the handsheets treated with higher temperature achieved better wet strength performance for not only temporary wet strength, *i.e.*, dipped in water for 2 and 30 min, but also permanent wet strength, *i.e.*, dipped in water for 24 h, from 90 to 130 ^{o}C. In comparison with the handsheets treated at 130 ^{o}C, the permanent wet strength of the handsheets treated at 140 ^{o}C was markedly improved, from 8% to 13%, and the temporary wet strength declined a little, but performed better than those treated at 90 to 120 ^{o}C. The results are similar to those of Xu *et al*. (2002), in which glyoxal and $Zn(NO_3)_2$ were employed to improve the wet strength of kraft paper. Hemiacetal bonds may form between cellulose molecules due to the reaction of glyoxal and hydroxyl groups of cellulose molecules, which could have imparted the temporary wet strength of the handsheets. When the time of dipping in water increased, the wet strength of the treated handsheets declined. However, the decline in magnitude was quite different at varied treatment temperatures. Higher temperatures achieved greater permanent wet strength. It may be that higher curing temperatures increase the acetal reaction between glyoxal and the hydroxyl groups of cellulose molecules under the catalysis of Lewis acids, which would result in handsheets with better wet strength performance (Schmitz and Eichhorn 1967).

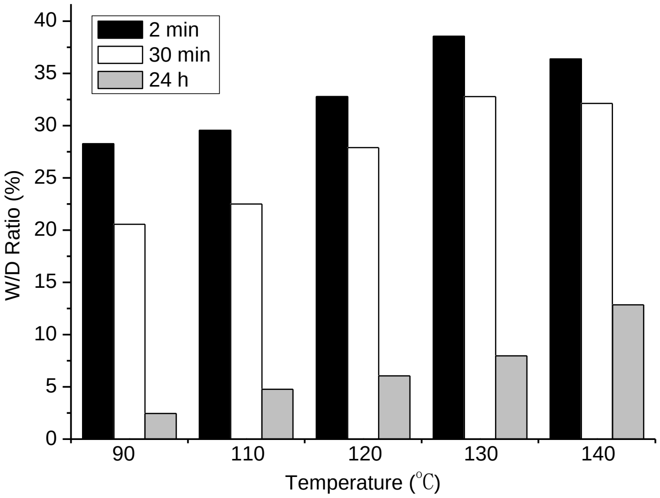


Fig. 1. Wet strength (dipped in water for 2 min, 30 min, and 24 h) of handsheets treated with 0.2 mol/L glyoxal and 0.76% $Zn(NO_3)_2$, pH 4.8, cured at different temperatures for 2 min

Wet Strength of Handsheets Treated with Chitosan

Chitosan is a dry and wet strength additive for paper. However, its working mechanism is elusive (Lindström *et al*. 2005). In this study, chitosan was employed as a wet strength additive through a dipping process. As shown in Fig. 2, the temporary wet

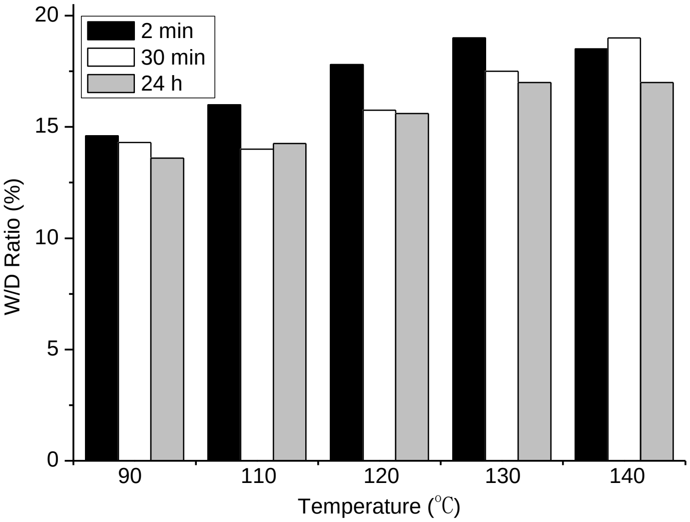


Fig. 2. Wet strength (dipped in water for 2 min, 30 min, and 24 h) of handsheets treated with 0.5% chitosan in 2% acetic acid aqueous solution, pH 4.8, cured at different temperatures for 2 min

strength, *i.e.*, dipped in water for 2 min, and permanent wet strength, *i.e.*, dipped in water for 24 h, of the treated handsheets increased when the curing temperature increased from 90 to 130 °C. Compared with 130 °C, the wet strength of handsheets cured at 140 °C varied little. The wet strength declined gradually as the dipping time was increased at different curing temperatures. However, in comparison with glyoxal, the wet strength values changed only slightly in magnitude with dipping time. In addition to hydrogen bonding and charge interactions, the Schiff bases formed between the primary amino groups of chitosan and the aldehyde groups of cellulose fibers could be an explanation for the wet strength improvement (Lindström *et al*. 2005).

Wet Strength of Handsheets Treated with the Crosslinking System of Glyoxal and Chitosan

As shown in Fig. 3, the temporary and permanent wet strengths of the treated handsheets increased as the curing temperature was increased from 90 to 130 °C. The crosslinking system of glyoxal and chitosan achieved better wet strength performance than glyoxal or chitosan alone, and slightly better than the sum of glyoxal and chitosan in the case of a curing temperature between 90 and 130 °C, according to the data from Figs. 1, 2, and 3. However, the synergy of glyoxal and chitosan could not be confirmed by the above data. The crosslinking system performed better than the sum of glyoxal and chitosan especially in temporary wet strength improvement. This could be explained by a Schiff base reaction between the primary amino groups of chitosan and glyoxal, as shown in Scheme 1 because the Schiff base was not stable in case of a long dipping time.

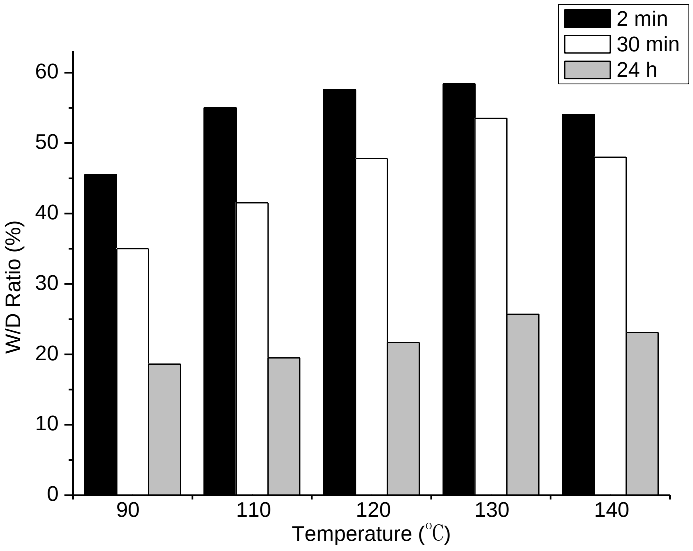
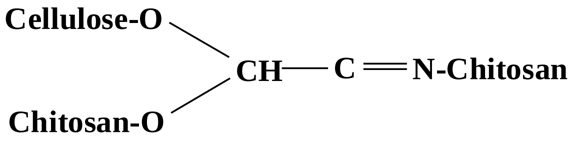


Fig. 3. Wet strength (dipped in water for 2 min, 30 min, and 24 h) of handsheets treated with the crosslinking system of 0.2 mol/L glyoxal with 0.76% $Zn(NO_3)_2$ and 0.5% chitosan in 2% acetic acid aqueous solution, pH 4.8, cured at different temperatures for 2 min



Scheme 1. Acetalization and Schiff base reactions of cellulose and the crosslinking system

Folding Endurance and Dry Strength of Treated Handsheets

Folding endurance is related to the flexibility of paper. It can be affected by the length of pulp fibers, the bonding between fibers, and the brittleness of paper sheets. In this study, the treated handsheets showed lower folding endurance compared with the control sample, exhibiting a folding endurance of 243 (times folded). As shown in Fig. 4, the folding endurance declined as a whole as the wet strength increased.

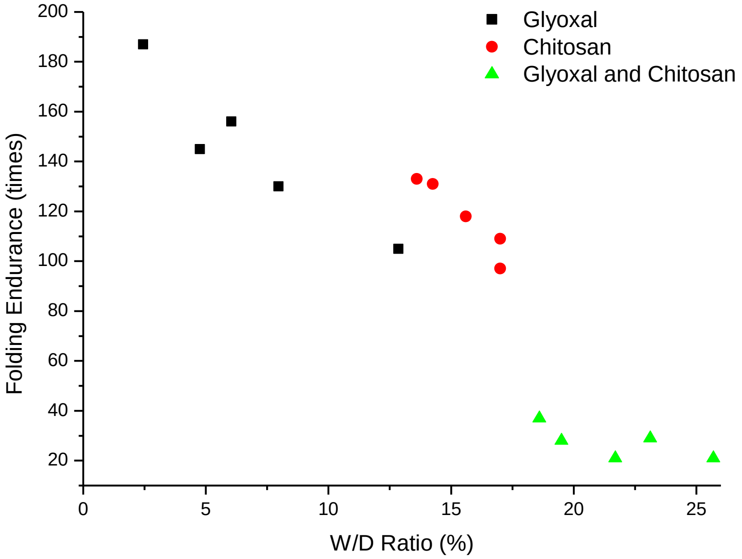


Fig. 4. Folding endurance as a function of W/D ratio (dipped in water for 24 h) for handsheets treated with 0.2 mol/L glyoxal with 0.76% $Zn(NO_3)_2$, 0.5% chitosan in 2% acetic acid aqueous solution, and the crosslinking system of glyoxal and chitosan cured at different temperatures for 2 min. The pH values of all the treating solutions were adjusted to 4.8.

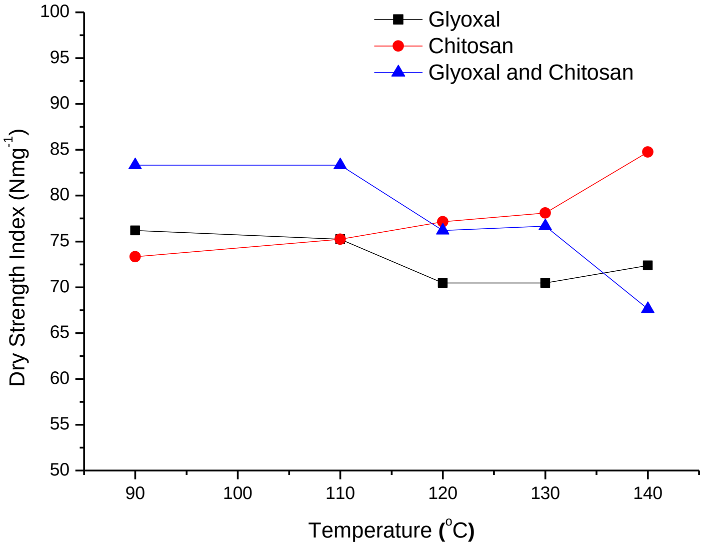


Fig. 5. Dry strength index as a function of curing temperature for handsheets treated with 0.2 mol/L glyoxal with 0.76% $Zn(NO_3)_2$, 0.5% chitosan in 2% acetic acid aqueous solution, and the crosslinking system of glyoxal and chitosan cured at different temperatures for 2 min. The pH values of all the treating solutions were adjusted to 4.8.

Dipping the sheets in different solutions improved the wet strength of the handsheets, but the treated handsheets became more brittle, especially when the crosslinking system combining glyoxal and chitosan was employed. The reduction of folding endurance is possibly a result of crosslinking between pulp fibers, which limits the mobility of cellulose molecules and thus reduces the flexibility of paper sheets (Xu *et al*. 2004). The dry strength indices of all the treated handsheets were lower than that of the control sample (96.1 Nmg^{-1}). As shown in Fig. 5, glyoxal and the crosslinking system of glyoxal and chitosan reduced the dry strength indices of the treated handsheets as the curing temperature increased. Similar to the folding endurance, the reduction of the flexibility of handsheets could be an important reason for the reduction of the dry strength. However, when chitosan was used, the dry strength indices slightly increased as the curing temperature increased. Although the handsheets treated by chitosan also became more brittle than the control samples, more hydrogen bonding between chitosan and cellulose may have counteracted the effects above to some extent (Tejado and van de Ven 2010).

Capillary Rise and Contact Angle of the Treated Handsheets

Capillary rise is related to the absorption of the paper sheet. As shown in Fig. 6, in comparison with the control sample (capillary rise of 48 mm), the treated handsheets had a lower capillary rise. Under each curing temperature from 90 to 130 ^oC, the capillary rise of sheets treated by glyoxal, chitosan, and the crosslinking system of glyoxal and chitosan declined sequentially. When the curing temperature was increased, the capillary rise of the treated handsheets changed less regularly. According to the data from Figs. 1, 2, and 3, under each curing temperature from 90 to 130 ^oC, the permanent wet strength of handsheets dipped in water for 24 h and treated with glyoxal, chitosan, and the crosslinking system of glyoxal and chitosan increased sequentially. The contact angle of the control sample was too small to measure.

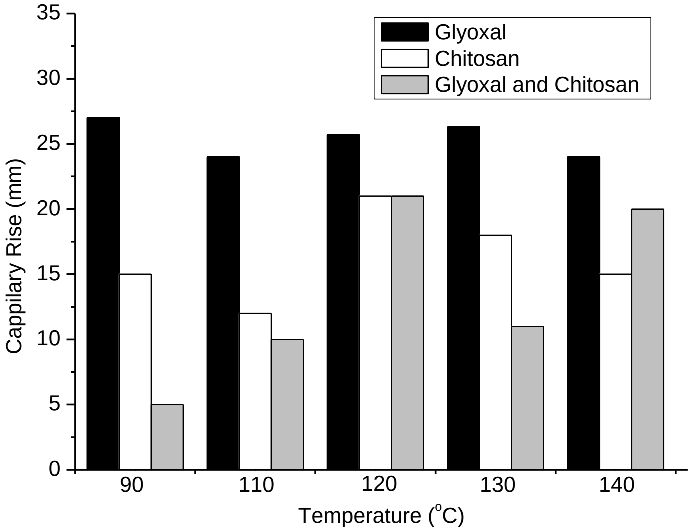


Fig. 6. Capillary rise of handsheets treated with different solutions and cured under different temperatures. (0.2 mol/L glyoxal with 0.76% $Zn(NO_3)_2$, 0.5% chitosan in 2% acetic acid aqueous solutions, and the crosslinking system of glyoxal and chitosan cured at different temperatures for 2 min. The pH values of all the treating solutions were adjusted to 4.8.)

In comparison with the control sample, the contact angle of the treated handsheets increased markedly, as shown in Fig. 7. According to the results from Figs. 1, 2, 3, 6, and 7, those treated handsheets performing better in wet strength had a higher contact angle and lower capillary rise, in general. There may be a relationship between the wet strength and the capillary rise or contact angle of the handsheets treated by these solutions. The results of capillary rise and contract angle showed that the handsheets had some changes in absorption and surface hydrophobicity when they underwent treatment in the above solutions. Although the reason for this relationship is difficult to explain, it may help to understand the mechanism of wet strength to some extent. Chemical reactions have been used to explain the wet strength mechanism by many researchers (Liu *et al*. 2009; Obokata and Isogai 2005, 2007). According to the data in Figs. 6 and 7, the physical action of the paper sheet may be one of the reasons for wet strength development in paper.

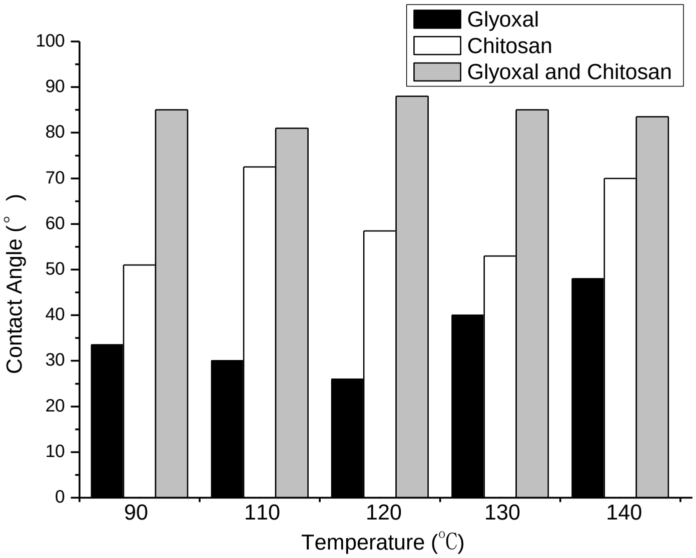


Fig. 7. Contact angles of handsheets treated with different solutions and cured under different temperatures. (0.2 mol/L glyoxal with 0.76% $Zn(NO_3)_2$, 0.5% chitosan in 2% acetic acid aqueous solutions, and the crosslinking system of glyoxal and chitosan cured at different temperatures for 2 min. The pH values of all the treating solutions were adjusted to 4.8.)

CONCLUSIONS

1. The wet strength of the handsheets made from fully bleached kraft softwood pulp was improved by dipping the handsheets into solutions such as glyoxal with $Zn(NO_3)_2$ as a catalyst, chitosan, and the crosslinking system of glyoxal and chitosan.
2. The crosslinking system achieved better wet strength performance than glyoxal or chitosan alone and slightly better than the sum of glyoxal and chitosan in the case of a curing temperature between 90 and 130 °C. However, the handsheets treated with these solutions became more brittle.

3. The changes in capillary rise and contact angle of the treated handsheets may give a hint that the physical action is one of the reasons for wet strength development in paper.

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