

# The Retention and Drainage Behavior of Cross-linked Gelatin with Glutaraldehyde in a Papermaking System

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A type of novel retention aid, cross-linked gelatin, was prepared using low-grade industrial gelatin as the raw material and glutaraldehyde as the crosslinking agent. The structure of cross-linked gelatin was characterized according to the crosslinking degree, isoelectric point, Fourier transform infrared spectroscopy, and ultraviolet-visible spectroscopy. The results indicated that the crosslinking reaction was successfully performed between the primary amine group of gelatin and the aldehyde group of glutaraldehyde, resulting in the formation of a Schiff base structure. The retention test showed that the addition of cross-linked gelatin remarkably improved the retention of filler. This effect was mainly attributed to the fact that cross-linked gelatin, with a high molecular weight and highly branched structure, exhibited favorable bridging flocculation and induced filler aggregation into the flocs, which were retained in the paper sheet. The drainage test showed that the cross-linked gelatin exhibited a poor drainage effect, which was attributed to the synergic effects of excellent hydrophilicity, film forming property, and sealing property.

*Keywords:* Low-grade industrial gelatin; Cross-linked gelatin; Retention; Drainage

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## INTRODUCTION

In recent years, a trend toward higher filler content in paper has been driven by a reduction in papermaking cost and the improvement in optical performance, printing performance, paper formation, *etc.* (Yoon and Deng 2006). However, in the absence of additives, filler retention mainly depends on mechanical entrapment, and the retention rate is lower because the diameter of filters is considerably larger than the fillers (Forsberg and Ström 1994). To improve the filler retention rate, it is necessary to add retention aids to the pulp suspension before the filtration process. The retention aid promotes the flocculation of fillers and the adsorption of flocs on the network of cellulose fibers (Blanco *et al.* 2005, 2009). Additionally, most retention aids improve the dewatering of fibers and fillers by decreasing the polarity and specific surface area.

The most common retention aids are inorganic salts (alum, polymeric aluminum, *etc.*) and natural or synthetic polymers (cationic starch, polyacrylamide, *etc.*) (Hubbe *et al.* 2009). Synthetic polymers, such as polyacrylamide, exhibit good performance at low cost, but they do not degrade easily and can harm the environment. Among the natural polymers, cationic starch has favorable biodegradability and renewability; however, it requires a higher additive quantity (1 to 3 wt.%, based on dry fiber) to meet the performance requirement (Khosravani *et al.* 2010). Chitosan has good performance, but it is expensive and cannot be used in neutral or alkaline conditions. In addition, this material is high-cost because of the chemical modifications required during its processing (Allen *et al.* 1999; Li

*et al.* 2004). Cationic micro-fibrillated cellulose has been used as a retention aid (Diab *et al.* 2015). Although cationic microfibrillated cellulose has some beneficial effects, the synthetic procedures are seemingly impractical because of the stepwise nature of this method (the preparation of micro-fibrillated cellulose and cationic reaction), and the expensive cationic reagent. Hence, there is an urgent need to explore efficient, low-cost, and environmentally friendly retention aids.

Gelatin, a denatured form of collagen, derived from connective tissue, is an abundant renewable biomass resource. Gelatin is a mixture of polypeptide chains, with molecular weights ranging from a few thousand to several hundred thousand Da (Li *et al.* 2005), and it has abundant reactive amino, carboxyl, hydroxyl, and acylamino groups, which implies that gelatin possesses flocculation abilities (Lefebvre and Antonov 2001; Piazza and Garcia 2010).

The flocculation ability is an important indicator of a retention aid; thus, it is reasonable to hypothesize that gelatin can be used for this purpose. Moreover, cross-linked gelatin may be a more promising retention aid because its flocculation ability would be improved upon higher molecular weight. In this study, cross-linked gelatin was prepared as a retention aid using low-grade industrial gelatin as the raw material and glutaraldehyde as the crosslinking agent. The performance and mechanism of cross-linked gelatin on retention and drainage were investigated.

## EXPERIMENTAL

### Materials

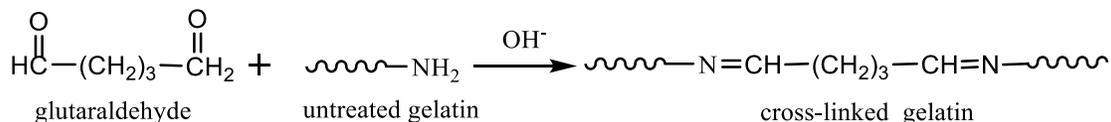
Low-grade industrial gelatin (30 Bloom strength) was obtained from a local market (Sichuan, China). Commercial stock glutaraldehyde (50% concentration) was purchased from the Kelong Chemical Reagent Factory (Sichuan, China). Bamboo-bleached kraft pulp, with a 31 °SR beating degree, cationic starch (DS = 0.03), and cationic polyacrylamide (CPAM; DS = 0.5,  $M_w = 8000$  kDa) were obtained from a local paper mill (Sichuan, China). Before application, the cationic starch was gelatinized at 95 °C for 20 min.

Kaolin was purchased from the Fengcheng Chemical Reagent Factory (Shanghai, China). Polyaluminum chloride (PAC) was prepared using a slow alkalinity titration method at 80 °C. Under rapid stirring, an aluminum chloride ( $AlCl_3$ ) solution was titrated using NaOH to the target ratio (OH/Al) of 1:2 within 3 h. The final concentration was 51  $g \cdot L^{-1}$  (mass concentration of aluminum oxide). All other chemicals were of analytical grade.

### Methods

#### *Preparation and characterization of cross-linked gelatin*

The cross-linked gelatin was synthesized using glutaraldehyde as the crosslinking agent (Fig. 1). First, 5 g of gelatin was dissolved in 100 mL of distilled water, and the pH of the gelatin solution was adjusted to 7.5 using 0.5 M NaOH. Subsequently, the gelatin solution was incubated at 40 °C for 30 min, when 0.5 mL of 50% glutaraldehyde solution was added to the gelatin solution. The crosslinking reaction was performed at 40 °C for 3 h until a viscous liquid with a light yellow color was obtained.



**Fig. 1.** Synthesis of cross-linked gelatin

The properties of crosslinked gelatin were analyzed by determining the crosslinking degree, isoelectric point, Fourier transform infrared (FT-IR) spectrum, and ultraviolet-visible (UV-Vis) spectrum. To analyze the crosslinking degree, the primary amine content of the cross-linked gelatin and untreated gelatin were measured as previously described (Sarin *et al.* 1981; You *et al.* 2014). Briefly, 0.5% (w/v) ninhydrin solution in 0.5 mol·L<sup>-1</sup> phosphate buffer (pH 6.0) was prepared and stored in a sealed brown volumetric flask at room temperature. The ninhydrin reaction was performed by incubating 2 mL of 1.0 g·L<sup>-1</sup> untreated gelatin/cross-linked gelatin solution with 1 mL of the ninhydrin solution in boiling water for 15 min. Subsequently, the mixture was diluted with 40% (v/v) ethanol to 10 mL and was then measured at 570 nm by UV-Vis spectroscopy (UV2800, Hitachi, Ltd., Tokyo, Japan). The primary amine content was calculated according to the calibration curve of glycine:  $y = 0.01864 + 2.19823x$ ,  $R^2 = 0.9949$ , where  $y$  and  $x$  are the absorbance of the diluted solution and the glycine concentration (mmol·L<sup>-1</sup>), respectively. The crosslinking degree was calculated as follows:

$$\text{crosslinking degree} = \frac{-\text{NH}_2 \text{ content of untreated gelatin} - \text{NH}_2 \text{ content of cross-linked gelatin}}{-\text{NH}_2 \text{ content of untreated gelatin}} \quad (1)$$

The isoelectric point (pI) was estimated according to the change in the zeta potential, which was measured using a Zetasizer instrument (Nano ZS90, Malvern Instruments, Malvern, UK). The cross-linked gelatin and untreated gelatin were diluted to 1.0 g·L<sup>-1</sup> with varying pH. The test samples were equilibrated at room temperature for 30 min prior to analysis. The structures of the cross-linked and untreated gelatins were analyzed by FT-IR spectroscopy (Nicolet iS10, Thermo Scientific, Waltham, MA, USA) in the range of 500 to 4000 cm<sup>-1</sup>. The cross-linked and untreated gelatin solutions (800 mg·L<sup>-1</sup>) were analyzed by UV-Vis spectroscopy (UV2800, Hitachi, Ltd., Tokyo, Japan). The spectra were recorded in the range of 230 to 450 nm.

#### *Retention and drainage test*

The filler retention performances were conducted using a self-made dynamic drainage jar (SDDJ). The SDDJ suspensions consisted of 0.2 wt.% fiber and 30 wt.% (based on dry fiber) kaolin, and the pH of the suspensions was adjusted to 7.0, with a stirrer speed of 500 rpm for the entire experimental procedure. Subsequently, a certain amount of retention aid (based on dry fiber) was added, and the filtrate was collected after 20 sec. The kaolin amount in the filtrate was tested by FT-IR spectroscopy (Ma *et al.* 2015), and the filler retention (%) was calculated as follows:

$$\text{filler retention (\%)} = \frac{\text{initial kaolin concentration} - \text{kaolin concentration of filtrate}}{\text{initial kaolin concentration}} \quad (2)$$

The drainage performance was evaluated by Schopper-Riegler degree ( $^{\circ}\text{SR}$ ), an important parameter to evaluate the drainage performance of pulp suspensions. When the  $^{\circ}\text{SR}$  is low, the dewatering of the pulp suspension is favorable (Chi *et al.* 2007). The  $^{\circ}\text{SR}$  was measured using a YT-DJ-100 beating degree tester (Yante Science & Technology Co. Ltd., Hangzhou, China), according to the China national standard ISO 5267-1 (1999). The zeta potential of the pulp suspension was determined with a pulp zeta potential instrument (Mütek SZP-06, BTG Instruments, Germany, UK). In this test, the concentration of fiber was 1 wt.%, and the proportion of kaolin and retention aid (based on dry fiber) was consistent. The morphology of the hand-sheets was observed using field emission scanning electron microscopy (FESEM; S-4800, Hitachi, Tokyo, Japan).

## RESULTS AND DISCUSSION

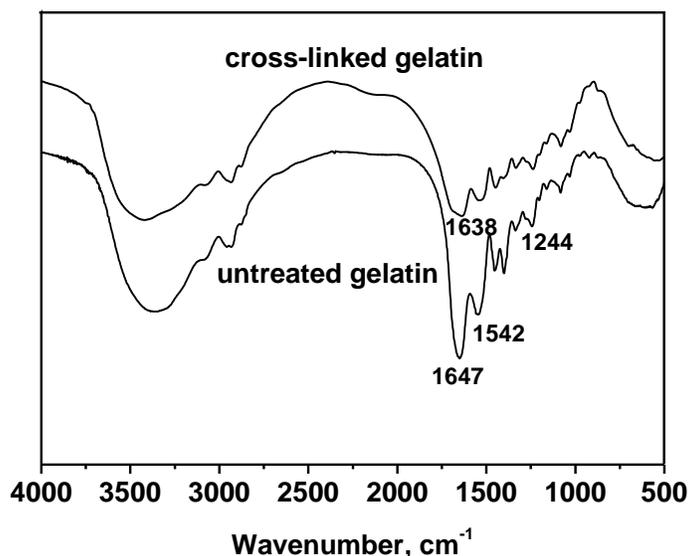
### Characteristics of Crosslinked Gelatin

Because the crosslinking reaction mostly occurs at the site of the primary amine groups in gelatin (Farris *et al.* 2010), the primary amine content of untreated gelatin and cross-linked gelatin were analyzed (Table 1). The primary amine content of cross-linked gelatin was appreciably less than that of untreated gelatin, which indicated that the primary amine reacted with the aldehyde group. Meanwhile, the solution of cross-linked gelatin exhibited a higher viscosity than the solution of untreated gelatin, also suggesting that the crosslinking reaction was successful.

**Table 1.** Content of Primary Amine Groups and the Crosslinking Degree

Samples	-NH <sub>2</sub> Content (mmol 100 g <sup>-1</sup> )	Crosslinking Degree	Viscosity (mPa·s)
Untreated gelatin	29	0	2.8
Cross-linked gelatin	7	0.76	26.5

The structures of untreated and cross-linked gelatins were characterized by FT-IR spectroscopy (Fig. 2).



**Fig. 2.** FTIR spectra of untreated gelatin and cross-linked gelatin

The absorption bands around  $1647\text{ cm}^{-1}$ ,  $1542\text{ cm}^{-1}$ , and  $1244\text{ cm}^{-1}$  represented the amide I, II, and III bands of gelatin, respectively (Sionkowska *et al.* 2004). The absorption band of a Schiff base is located at approximately  $1620\text{ cm}^{-1}$  (Cai *et al.* 2011), which is similar to that of the amide I band of gelatin. Hence, the FT-IR spectrum of cross-linked gelatin exhibited a changed peak at  $1638\text{ cm}^{-1}$ , suggesting a red shift, as compared with the amide I band of gelatin. This result implied that the gelatin reacted with glutaraldehyde, resulting in the formation of a Schiff base (Liu *et al.* 2011).

The UV-Vis spectra of untreated gelatin and cross-linked gelatin solutions are shown in Fig. 3. Cross-linked gelatin showed a new absorption band at 265 nm, which was ascribed to the formation of a Schiff base structure between the aldehyde group and the primary amine group (Bowes and Cater 1968; Damink *et al.* 1995). This result is additional evidence of the crosslinking reaction between gelatin and glutaraldehyde.

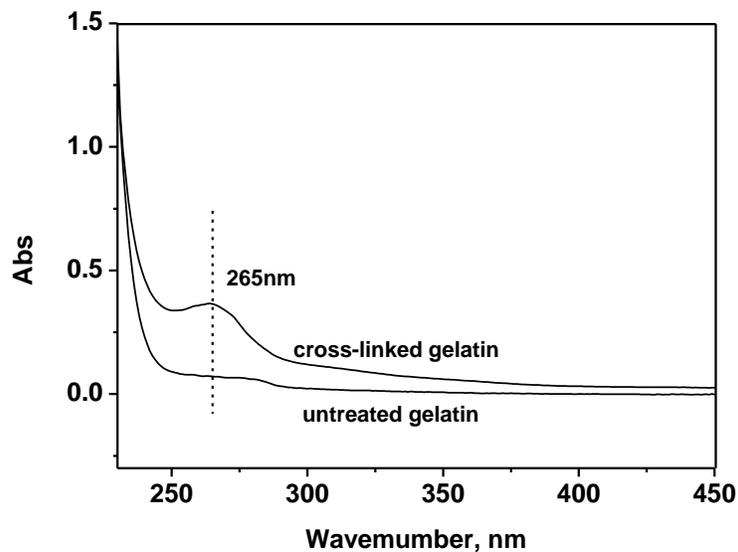


Fig. 3. UV-Vis spectra of untreated gelatin and cross-linked gelatin

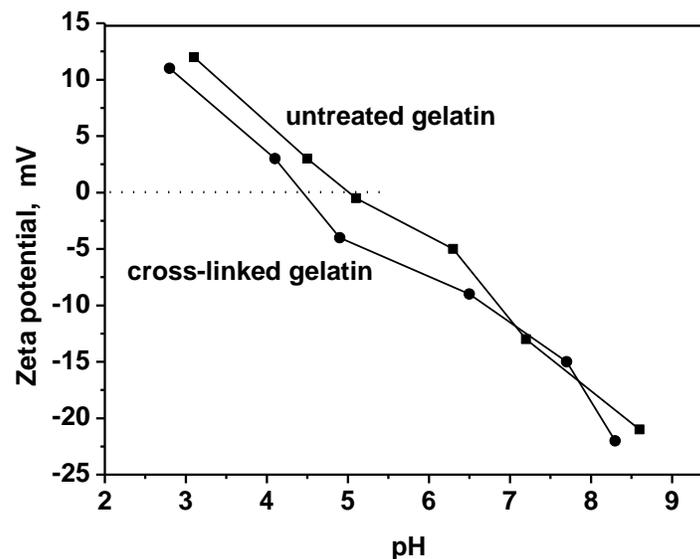


Fig. 4. The isoelectric point of untreated gelatin and cross-linked gelatin

The zeta potential of untreated and cross-linked gelatin solutions, at varying pH, are shown in Fig. 4. Gelatin is an amphoteric polymer, and the pH of the gelatin solution at which the zeta potential is zero is referred to as the isoelectric point. The amino group of gelatin can bind to a proton to become positively charged in an acidic environment. With increasing pH, the zeta potential decreases and finally becomes negative. The pI of untreated gelatin (approximately 5) was slightly higher than that of cross-linked gelatin (approximately 4.5). This result was expected because the crosslinking reaction leads to a decline in primary amino groups. The above results strongly suggest that the crosslinking reaction was successfully performed.

## Retention Results

The influences of varying untreated gelatin and cross-linked gelatin dosages on the filler retention are shown in Fig. 5. The retention rate of the filler was only 43% in the absence of a retention aid, suggesting that filler retention depended on mechanical entrapment. When using untreated gelatin as the retention aid, the retention rate of the filler exhibited no considerable improvement, which could be explained because normal gelatin has a relatively low molecular weight, insufficient to result in bridging flocculation. In contrast, cross-linked gelatin positively impacted the retention of filler; the retention rate of filler was considerably improved with increasing dosage of cross-linked gelatin, with an optimum retention rate of greater than 63% when the dosage was 0.4 wt.%. This result was attributed to the fact that cross-linked gelatin has a high molecular weight and highly branched structure, which is beneficial for inducing the aggregation of kaolin particles into the flocs with large size and retention in the paper sheet (Shin *et al.* 1997; Antunes *et al.* 2008). When the dosage of cross-linked gelatin was greater than 0.4 wt.%, the retention performance tended to decrease, potentially because excess cross-linked gelatin plays a role in dispersion (Wu *et al.* 2012).

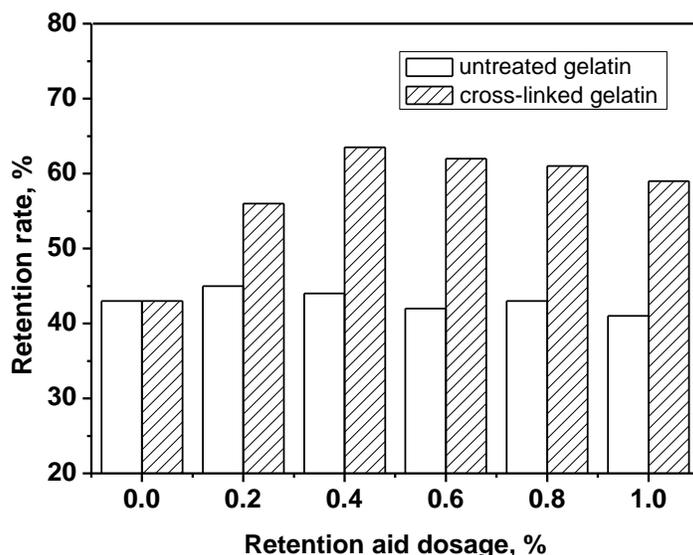


Fig. 5. Retention performances of untreated gelatin and cross-linked gelatin

To evaluate the practicability of cross-linked gelatin, several commercial retention aids (PAC, cationic starch, and CPAM) were selected as controls, and the optimized dosage of PAC, cationic starch, and CPAM were 0.80 wt.%, 1.00 wt.%, and 0.05 wt.%, respectively. Figure 6 shows a comparison of the commercial retention aids and cross-

linked gelatin. The retention rate of cross-linked gelatin was better than PAC and cationic starch but not as good as CPAM. However, the safety risk and ethical issues of these papers using cross-linked gelatin as retention aid should be fully evaluated before being used in the food industry. Overall, cross-linked gelatin was a very promising retention aid.

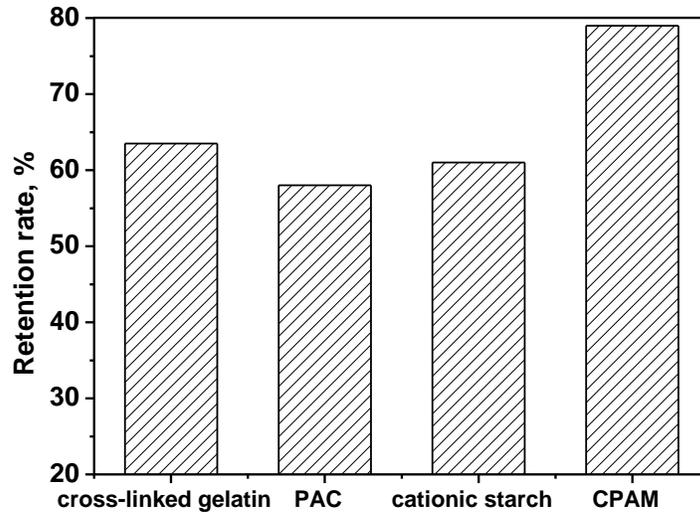


Fig. 6. Comparison of cross-linked gelatin and the commercial retention aids

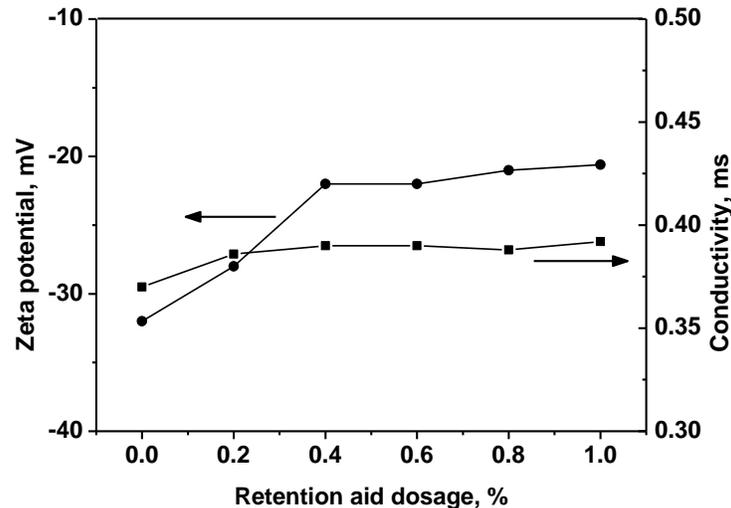


Fig. 7. The effect of cross-linked gelatin dosage on the zeta potential and conductivity of pulp

### Retention Mechanism

To study the retention mechanism of cross-linked gelatin, the zeta potential and conductivity of the pulp suspensions were tested (Fig. 7). The conductivity of the pulp slightly increased after adding cross-linked gelatin. Because cross-linked gelatin is a weak electrolyte, its addition increased the conductivity of the pulp. In contrast, the zeta potential of the pulp notably increased with the addition of cross-linked gelatin. This result can be explained in two ways. First, the pI of cross-linked gelatin was higher than that of the pulp; therefore, the addition of cross-linked gelatin improved the zeta potential of the pulp. Secondly, the decrease in the absolute value of the zeta potential means that the pulp was

unstable and favored aggregation (Zhang *et al.* 2010); thus, the results are consistent with the retention result. When the dosage of cross-linked gelatin was greater than 0.4 wt.%, the zeta potential was stabilized. Nevertheless, the zeta potential of pulp never reached a positive value because the cross-linked gelatin is anionic under neutral conditions, such that the charge neutralization of crosslinked gelatin is poor. The zeta potential analysis tentatively suggested that the retention mechanism of cross-linked gelatin included bridging flocculation.

To verify this hypothesis, the effect of pH on the retention performance of cross-linked gelatin was investigated (Fig. 8). There was no difference in the retention performance between the different pH conditions. The cross-linked gelatin exhibited a wide applied range. If the retention mechanism of cross-linked gelatin was mainly dependent on charge neutralization, then the change in pH would strongly influence its retention performance. Hence, it was confirmed that the retention mechanism of cross-linked gelatin was mainly bridging flocculation.

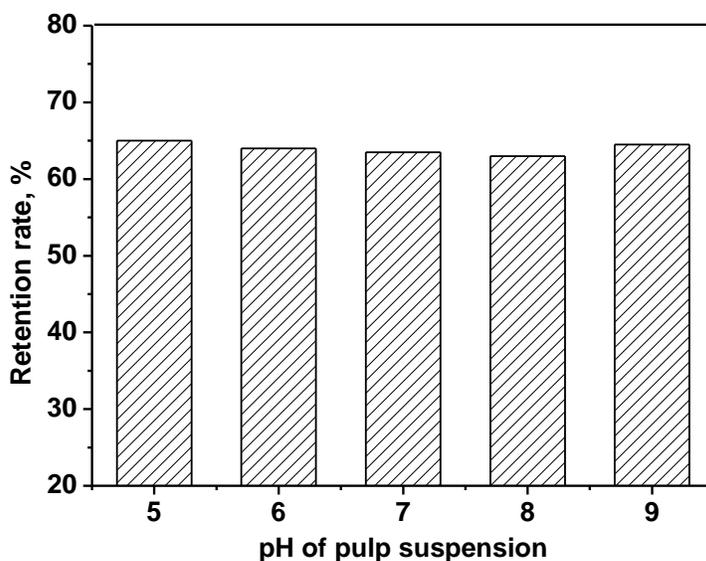


Fig. 8. The effect of pH on the retention performances of cross-linked gelatin

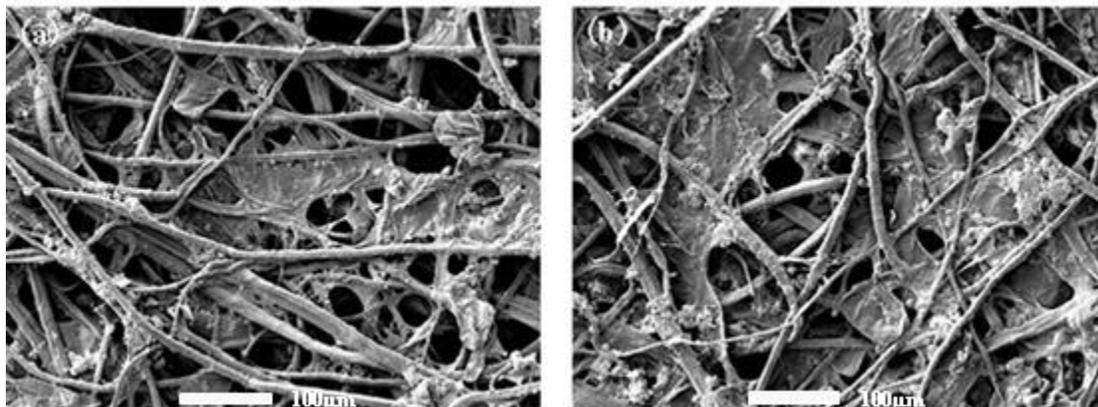


Fig. 9. Scanning electron microscopy of hand sheets: (a) without additives and (b) with cross-linked gelatin

## Morphology Analysis

The surface morphology of the hand-sheets was observed by SEM (Fig. 9). In the absence of additives, there were very few small kaolin flocs on the paper sheet. When the cross-linked gelatin was present, the aggregates were larger and more numerous than in the control group. Thus, cross-linked gelatin participated in bridging flocculation, which proved helpful in the conglomeration of kaolin particles and improved the retention efficiency. Besides, the addition of cross-linked gelatin did not significantly change the color of the handsheets.

## Drainage Results

The dewatering of the pulp suspension is an important parameter that has a direct influence on the speed of the paper machine and the energy consumption of the drying process. Hence, as the evaluating index of drainage performance, the °SR was measured (Fig. 10). When adding untreated gelatin as the drainage aid, the drainage performance gradually worsened with the increasing dosage. Compared with untreated gelatin, the drainage performance initially improved and then gradually worsened with an increasing dosage of cross-linked gelatin. Overall, the drainage performances of untreated gelatin and cross-linked gelatin were poor. This result could be explained as follows. First, untreated gelatin and cross-linked gelatin, with excellent hydrophilicity and film-forming property, easily form a film on the fiber and floc surface, enhancing water retention (Peña *et al.* 2010). Secondly, the film seals the pores of the fiber and floc to prevent dewatering of the area. Based on this scenario, an optimized process to improve the drainage performance of cross-linked gelatin warrants further investigation.

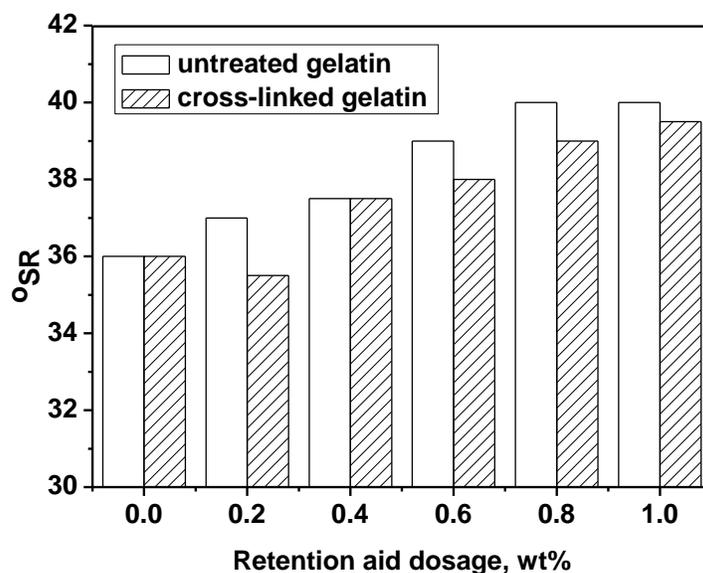


Fig. 10. Drainage performances of untreated gelatin and cross-linked gelatin

## CONCLUSIONS

1. Low-grade industrial gelatin was used as a raw material for preparing a novel biomass-based retention aid through a crosslinking reaction. This method is low-cost, simple, and requires mild reaction conditions.

2. The retention rate of filler was improved with increasing dosages of cross-linked gelatin, and the optimum retention rate was greater than 63% at 0.4 wt.%. The retention mechanism of cross-linked gelatin mainly included bridging flocculation. Compared with commercial retention aids, cross-linked gelatin exhibited better retention than PAC and cationic starch but worse performance than CPAM.
3. The drainage performance of cross-linked gelatin was poor.

## ACKNOWLEDGMENTS

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