Preparation and Application of Maleic Anhydride-Acylated Chitosan for Wet Strength Improvement of Paper

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Maleic anhydride-acylated chitosan (MAAC) was prepared and employed to improve the wet strength of handsheets. UV-Vis spectroscopy, elemental analysis, and chemical titration methods were used to analyze the resultant MAAC. Pretreatment and curing conditions were investigated when MAAC was used to improve the wet strength of handsheets. The results revealed that the wet strength performance was highest at a pretreatment pH of 6 and that the wet strength index and the ratio of wet to dry strength increased with increasing pretreatment temperature and MAAC dose. A higher curing temperature was beneficial and improved the wet strength performance of paper. Polyamideamine-epichlorohydrin (PAE) resin performed better than MAAC with varied soaking durations. However, MAAC also reached about 80% of the wet strength of PAE and showed its potential as an alternative to PAE.

Keywords: Chitosan; Maleic anhydride; Wet strength; Handsheets

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INTRODUCTION

Chitosan, like cellulose, is an oxygen-rich natural carbohydrate (polysaccharide) consisting of anhydroglucose units joined by an oxygen linkage to form a linear molecular chain. The structural characteristics of chitosan provide a possibility for it to be employed as a dry and wet strength additive for papermaking that facilitates strong hydrogen bonding with cellulose fibers (Qian *et al*. 2008; Gällstedt and Hedenqvist 2006). In addition to having a similar structure to cellulose, chitosan also has other special properties, such as non-toxicity, biocompatibility, biodegradability, and being antibacterial (Aranaz *et al*. 2009; Vallapa *et al*. 2011; Sun *et al*. 2010; Cai *et al*. 2009). Furthermore, as a natural biopolymer, chitosan is a renewable resource. However, its water-insolubility makes it unfavorable as a papermaking additive (Li *et al*. 2004a).

Wet strength is an important property for some household paper, packaging paperboard, and functional paper grades. Polyamideamine-epichlorohydrin (PAE) resin has been used widely as a wet strength additive. Compared with urea formaldehyde and melamine-formaldehyde resins, PAE has better wet strength performance over a wider pH range under common papermaking conditions. However, absorbable organic chlorine (AOX) emissions from paper mills and treated paper when PAE is used are unavoidable, even though new-generation PAE products contain less low-molecular weight organic chlorine compounds (Espy 1995). Therefore, the development of environmentally friendly wet strength additives without formaldehyde and AOX has attracted the attention of papermakers. Polyvinyl amine, aldehyde-containing polymers, and polycarboxylic acids have been reported as environmentally friendly wet strength additives (Saito and Isogai 2005). However, there are some problems to be noticed and solved such as negative impacts on other properties of treated paper, rigorous curing conditions, and high cost.

Chitosan can improve the wet strength of paper (Kamel *et al*. 2004). However, chitosan exhibits poor wet strength performance when it is used like PAE. It might be necessary to introduce some specific functional groups to the chitosan molecule to improve its wet strength performance. Polybasic carboxylic acids and anhydrides have been reported as environmentally friendly wet strength additives (Zakaria 2004; Xu *et al*. 1998; Xu *et al*. 1999). In this study, chitosan was modified with maleic anhydride (MA) *via* an acylation reaction, and carboxylic groups were introduced to the chitosan molecule. The wet strength performance of maleic anhydride-acylated chitosan (MAAC) under different pretreatment and curing conditions was evaluated.

EXPERIMENTAL

Materials

Chitosan (with 87% deacetylation) of about 600 kDa was supplied by Shandong Laizhou Highly Bio-product (China). PAE was kindly provided by Hangzhou Hengyuan Chemicals (China). All other chemicals used in this study were of analytical grade and used without further purification. Fully bleached softwood kraft pulp used in handsheet preparation was provided by Mudanjiang Hengfeng Paper (China) and beaten to 28 to 30° SR using a PFI mill at 10% consistency. The beaten pulp was dewatered to about 28% consistency for use.

Preparation of MAAC

One gram of chitosan was dissolved in 100 mL of 0.5% (v/v) acetic acid aqueous solution. After filtration through a sand core funnel, the solution was transferred to a 250 mL three-neck flask. A specified amount of maleic anhydride (MA) acetone solution was drop wise added to the chitosan solution over a period of 30 min at room temperature with stirring at a medium speed. The reaction was allowed to stand for another 15 h at room temperature. The reaction mixture was added slowly into 500 mL of a saturated solution of potassium hydroxide in 95% (v/v) ethanol with stirring at a medium speed. After the liquid phase was removed by a sand core funnel, the filamentous precipitate was washed with an excess amount of 95% (v/v) ethanol to neutral pH. Later, the precipitate was washed with ether in order to dewater further. The white powder MAAC was obtained after the above precipitate was dried at 55 ^{o}C under vacuum for 12 h.

The degree of substitution of MAAC (*D*s) was measured by both chemical titration and elemental analysis methods. In the chemical titration method, 0.2 g (accurate to 0.0002 g) dry MAAC sample and 25 mL of 0.1 mol/L NaOH standard aqueous solution were transferred to a conical flask. The mixture was shaken, left sitting for 2 h, and then titrated with 0.1 mol/L HCl standard aqueous solution. Phenolphthalein was employed as an indicator. The titration end-point was obtained when the red color of the mixture vanished for 30 s and did not appear again. The degree of substitution of MAAC was calculated using Eq. (1),

$$Ds = \frac{167.09 \times W}{100 \times 99 - \left(99 - 1\right) \times W} \times 100 \tag{1}$$

where *Ds* (%) is the degree of substitution of MAAC, 167.09 (g/mol) is the mean relative molecular mass of the chitosan unit with 87% deacetylation, and *W* (%) is the mass percent of the substituent. *W* is determined using Eq. (2),

$$W = \frac{\left(c_1 v_1 - c_2 v_2\right) \times 10^{-3} \times M}{m} \times 100 \tag{2}$$

where *M* is the relative molecular mass of the maleic acid group, *m* is the mass of the sample of MAAC; c_1 (mol/L) and v_1 (L) are the molar concentration and volume of NaOH standard aqueous solution, and c_2 (mol/L) and v_2 (L) are the molar concentration and consumed volume of the HCl standard aqueous solution.

In the elemental analysis method, the degree of substitution of MAAC was calculated using Eq. (3),

$$Ds = \frac{14 / N - 166.59}{98} \times 100 \tag{3}$$

where *Ds* (%) is the degree of substitution of MAAC and *N* is the nitrogen element mass content of MAAC as determined by elemental analysis (Elementar Vario Micro Cube, Germany).

UV-Vis Spectrum Analysis

MAAC was dissolved in 2% (v/v) acetic acid aqueous solution to prepare a series of known concentrations of MAAC solution. These MAAC solution samples were filtered carefully and tested by the ultraviolet and visible (UV-Vis) spectrum method, where 2% acetic acid aqueous solution was used as the reference. A calibration curve was established according to the absorbance at the maximum absorption wavelength of MAAC (232 nm). The UV-Vis spectra of MAAC and chitosan could be evidence of a reaction between chitosan and MA. The calibration curve could be used to evaluate the retention of MAAC in handsheets. The filtrate from the mixture of pulp and MAAC after pretreatment was diluted with acetic acid aqueous solution for UV-Vis spectrum analysis. The retention of MAAC in handsheets was calculated using Eq. (4),

$$R = (1 - vc / M) \times 100 \tag{4}$$

where *R* is the retention of MAAC in handsheets (%), *M* (g) is the dose of MAAC, and *v* and *c* are the volume (L) and concentration (wt%), respectively, of the filtrate from the mixture of pulp and MAAC after pretreatment.

Preparation and Strength Measurement of Handsheets

Dewatered pulp containing about 2.2 g of pulp was adjusted to a 2% consistency with distilled water in a plastic bag, and a set amount of MAAC or PAE was added to the plastic bag. The mixture in the plastic bag was pH-adjusted and cured for 30 min at a set temperature. The handsheets were prepared using a handsheet former with a target grammage of 70 g/m^2. The wet handsheets were then pressed by an oil press (ZQYC II, Northwest Institute of Light Industry Machinery Factory, China) at 0.6 MPa for 5 min on each side and air-dried for use. Prior to tensile strength measurement, the air-dried handsheets were cured at 170 ^{o}C for 10 min, unless specified otherwise. Dry and wet tensile indices of the handsheets were measured according to the China National Standard. For wet tensile indices measurement, unless specified otherwise, the sample strips were dipped in distilled water for 2 h and immediately subjected to tensile strength measurement after excess water on the surface of sample strips was absorbed by filter paper.

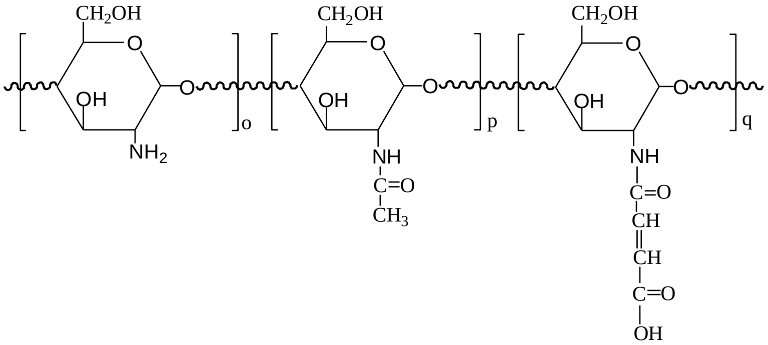
FT-IR Analysis of Handsheets

The selected handsheets were analyzed by Fourier transform infrared spectroscopy (FT-IR, Magna-IR 560 E.S.P, Nicolet Corp.) to investigate whether some new chemical bonds were formed when MAAC was used during handsheet preparation.

RESULTS AND DISCUSSION

UV-Vis Spectra Analysis of MAAC

The acylation reacton between chitosan and MA can be carried out under mild conditions (Zhu *et al*. 2010; Ranjbar-Mohammadi *et al*. 2010; Zhang *et al*. 2007). The mechanism of the reaction may be through nucleophilic substitution, with the nucleophilicity of NH_2 being more active than that of the OH in the chitosan molecule. The possible chemical structure of MAAC is shown in Scheme 1.



Scheme 1. Chemical structure of MAAC (o, p, and q are percents of these units)

Figure 1 shows the UV-Vis spectra of chitosan and MAAC. M1, M2, M3, M4, and M5 represent a 2% acetic acid aqueous solution with MAAC concentrations of 0.025%, 0.05%, 0.075%, 0.10%, and 0.125%, respectively. The concentration of 2% acetic acid aqueous solution of chitosan was 0.125%. UV-Vis absorbances of MAAC solutions with different concentrations were higher than that of the chitosan solution, which was evidence that MA had reacted with chitosan. The strong absorbance demonstrated by the MAAC UV-Vis spectra at 232 nm could be attributed to the $\pi \rightarrow \pi^*$ transition of conjugated C=C and C=O bonds. Furthermore, the UV-Vis absorbances of M1, M2, M3, M4, and M5 showed a good linear relationship with their concentrations, which could be used to quantify MAAC. The linear regression equation between UV-Vis absorbance at 232 nm and the concentration of MAAC is given as Eq. 5,

$$Y = 4.112x - 0.0038\,,\ R^2 = 0.996 \qquad (5)$$

where Y, x, and R are the UV-Vis absorbance at 232 nm, concentration of the MAAC sample, and correlation coefficient, respectively.

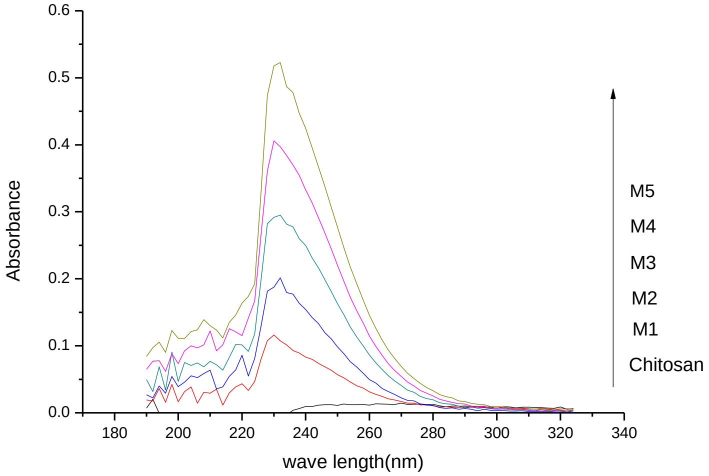


Fig. 1. UV-Vis absorbance spectra of MAAC and chitosan

Degree of Substitution of MAAC

The degrees of substitution (*Ds*) of MAAC are given in Table 1. Although chemical titration and elemental analysis methods did not obtain similar *Ds* results, they both showed that *Ds* increased with increasing MA dosage during the reaction between chitosan and MA. Our research indicated that MAAC-3 performed better than MAAC-1 and MAAC-2 when they were employed as wet strength additives, which might be due to more carboxyl groups in MAAC-3. Therefore, MAAC-3 was chosen to improve the wet strength of handsheets in further work.

Table 1. *Ds* of MAAC Samples

Sample	Chitosan (g)	MA (g)	Molar Ratio of Chitosan to MA	*Ds* (%, Element Analysis Method)	*Ds* (%, Chemical Titration Method)
MAAC-1	1.0	0.5865	1:1	45.8	37.1
MAAC-2	1.0	1.1730	1:2	49.9	43.6
MAAC-3	1.0	1.7595	1:3	63.3	56.4

Pretreatment of Pulp and Wet Strength Performance of MAAC

Figure 2 shows the dependence of the wet strength performance of MAAC on pretreatment conditions. Figure 2a shows that the wet strength index and the ratio of wet/dry strength were highest when the pH of the pulp pretreatment was 6. Dry strength was seemingly independent of pretreatment pH.

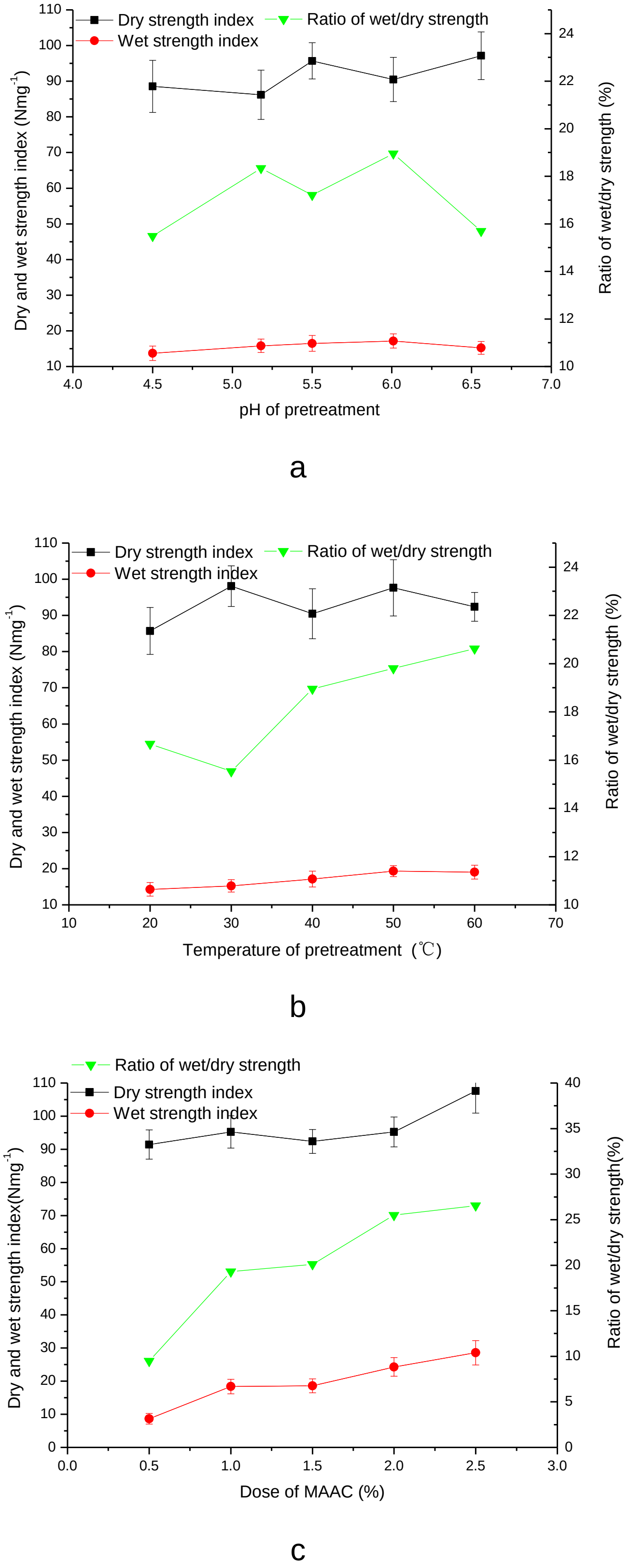


Fig. 2. Relationship between wet strength performance of MAAC and pulp pretreatment. (a) MAAC dose 1% and pretreatment temperature 40 ^{o}C; (b) Pretreatment pH 6 and MAAC dose 1%; (c) Pretreatment pH 6 and temperature 40 ^{o}C

The pulp fibers became more negatively charged when the pH of the pulp pretreatment was increased (Li *et al*. 2004b). MAAC was cationic in weak acidic solution, so higher pH perhaps improved the absorption of MAAC on pulp fibers (Myllytie *et al*. 2009; Li *et al*. 2004a). However, the cationic charge of MAAC became weaker when the pH was above 6, which was unfavorable for the absorption of MAAC onto pulp fibers. Figure 2b shows the relationship between wet strength performance and pretreatment temperature. The wet strength index and the ratio of wet/dry strength increased as the pretreatment temperature increased. Higher temperature might improve the absorption of MAAC onto pulp fibers. Figure 2c shows the relationship between wet strength performance and the dosage of MAAC. The dry and wet strength indices and the ratio of wet/dry strength increased almost simultaneously when more MAAC was added. Considering the cost and practice of paper production, relatively reasonable pretreatment conditions were pH 6, a pretreatment temperature of 40 ^{o}C, and a MAAC concentration of 1%. With the above pretreatment conditions, the wet strength index and the ratio of wet/dry strength reached 18.38 Nmg^{-1} and 19.30%, respectively, which could meet common demands for the wet strength of paper products. Higher doses of MAAC are feasible if higher wet strength is needed.

Curing Temperature

As seen in Fig. 3, the wet strength index and ratio of wet/dry strength increased as curing temperature increased. The handsheets were cured for 10 min at a set temperature before the dry and wet strength indices were measured. The dry strength index was not dependent on curing temperature. However, the wet strength performance of handsheets increased as curing temperature increased. The wet strength index and the ratio of wet/dry strength reached 33.90 Nmg^{-1} and 33.68%, respectively, at a curing temperature of 210 ^{o}C. Of course, a curing temperature of 210 ^{o}C could not be achieved in practice with the dry section of the paper machine.

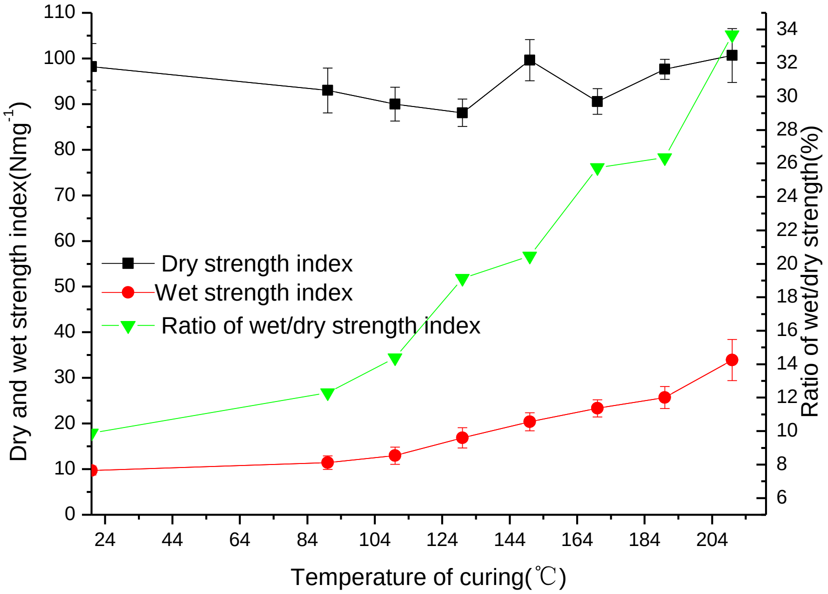


Fig. 3. Relationship between wet strength performance and curing temperature

At a temperature of 110 °C, which could be used on most paper machines, the wet strength index and the ratio of wet/dry strength reached 12.95 Nmg^{-1} and 14.39%, respectively. A likely explanation is that the esterification reaction between carboxylic groups of MAAC and hydroxyl groups of pulp fibers requires higher temperatures (Zakaria 2004). Figure 4 shows the FT-IR spectra of a blank handsheet (a), a handsheet containing MAAC without curation (b), and a handsheet containing MAAC cured under 210 °C for 10 min (c). The absorption band at 1716 cm^{-1} due to the C=O stretching vibration of ester bonds was detected in spectrum c, but not in spectra a and b (Fig. 4). The ester bonds between MAAC and pulp fibers were stable when the handsheets were saturated with water, so the handsheets had higher wet strength.

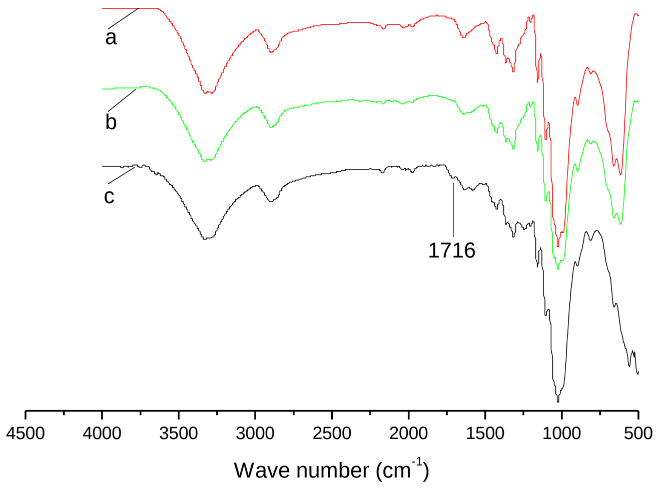


Fig. 4. FT-IR spectra of handsheets

Comparison of MAAC and PAE

Figure 5 shows the comparison of MAAC and PAE when they were used as wet strength additives with the same pretreatment conditions, that is, the pH, temperature of pretreatment, and additive dose were 6, 40 °C, and 1.0%, respectively. When the soaking duration increased, the wet strength performances of both MAAC and PAE decreased. When the soaking duration was 60 min or more, the wet strength performances of both MAAC and PAE varied little. As seen in Fig. 5, PAE achieved higher wet strength indices than MAAC at all soaking durations. However, MAAC obtained about 80% of the wet strength performance of PAE at the same soaking durations. Although PAE performed a little better than MAAC as a wet strength additive, MAAC also showed its potential as an alternative to PAE.

Retention of MAAC

Figure 6 shows the retention of MAAC in handsheets with various doses of MAAC. The retention decreased when the dose of MAAC increased. The results also indicated that MAAC did not have good retention in handsheets, especially at higher doses. However, higher wet strength indices could be achieved with lower MAAC retention. It is possible that the weaker cationic charge of MAAC compared with PAE prevented it from adsorbing onto pulp fibers. In future research, selected cationic groups will be introduced to the MAAC molecule to improve its retention and wet strength performance.

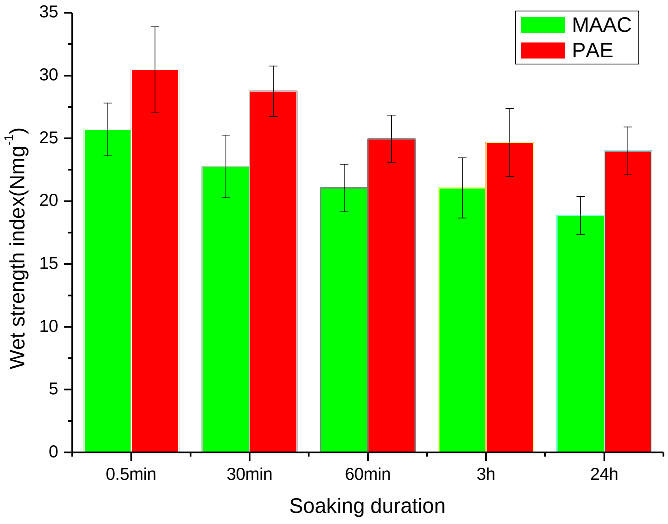


Fig. 5. Wet strength performance of MAAC and PAE at various soaking durations

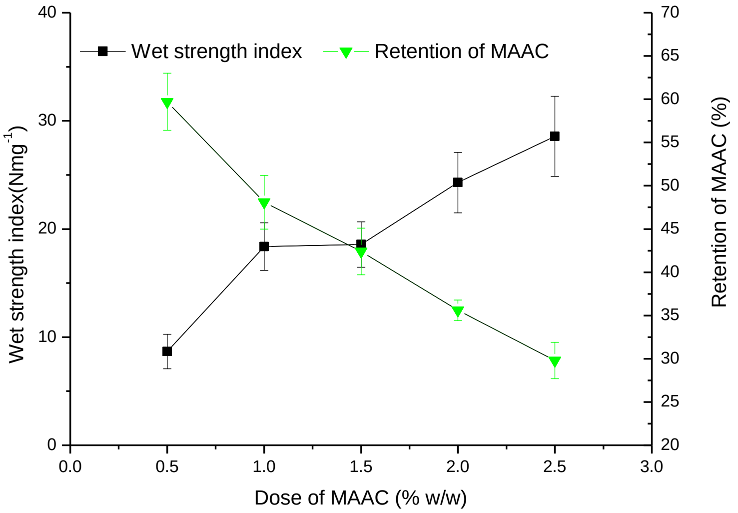


Fig. 6. Retention of MAAC in handsheets

CONCLUSIONS

1. Maleic anhydride-acylated chitosan (MAAC) was prepared and used as a wet strength additive. The results of UV-Vis spectra analysis showed that maleic anhydride could be introduced to the chitosan molecule. In addition, the UV-Vis absorbance of the MAAC solution exhibited a good linear relationship with its concentration, a result that could be used to evaluate the retention of MAAC in handsheets.

2. The wet strength index and the ratio of wet/dry strength were highest when the pretreatment pH was 6. Higher pretreatment temperatures improved the wet strength performance of MAAC. Both higher doses of MAAC and higher curing temperatures increased the wet strength indices and the ratio of wet/dry strength of MAAC.

3. The retention data indicated that MAAC did not have good retention in handsheets, especially at higher doses.

4. Although PAE achieved higher wet strength performance than MAAC, MAAC obtained about 80% of the wet strength of PAE and demonstrated its potential as an alternative to PAE.

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