

Preparation of a New Dry Strength Agent *via* Graft Copolymerization of Carboxymethyl Starch

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With the ever-increasing usage of recycled fibers, dry-strength agents play an increasingly important role in the papermaking industry. In this study, a new kind of dry-strength agent (CMS-g-PAM) was developed *via* grafting polyacrylamide onto carboxymethyl starch (CMS). Effects of the operation conditions, including the CMS-g-PAM dosage, polyaluminium chloride (PAC) dosage, and pH value of pulp system, on the properties of the paper were investigated. The contrasting effects when comparing the CMS-g-PAM and CMS were also researched. The results indicated that CMS-g-PAM had a beneficial effect on the paper properties. Compared to the control sample, when 1% CMS-g-PAM was added, the tensile index, burst index, and folding endurance of handsheets displayed noticeable increases of 38.2%, 34.7%, and 97.7%, respectively, and these properties were increased by 27.4%, 17.2%, and 46.6% when compared with the CMS-treated sample of this addition level. Scanning electron microscopy images showed that the bonding between fibers of the paper became tighter after using the CMS-g-PAM. The results demonstrated that CMS-g-PAM can be used as an effective dry-strength agent.

Keywords: Carboxymethyl starch; Polyacrylamide; Graft copolymerization; Paper dry-strength agent

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INTRODUCTION

Currently, with the rapid development of the economy and increasing awareness of energy conservation, an increased amount of recycled fibers are being used as raw materials in the pulp and paper industry (Dienes *et al.* 2004; Monte *et al.* 2009; Salam *et al.* 2015). Using recycled paper saves forest resources and significantly reduces energy consumption. However, irreversible hardening and hornification of the recycled fiber decrease its swelling capacity and beating ability, which lowers the inter-fiber bonding strength and results in the degradation of paper mechanical properties (Hubbe *et al.* 2007; Luo and Zhu 2011; Hubbe 2014; Chen *et al.* 2018). To overcome this problem, various approaches have been developed to improve the performance of the recycled fibers: mechanical beating (Gao *et al.* 2012), surface modification (Li *et al.* 2012), biological enzyme treatment (Ghosh *et al.* 2018), chemical treatment (Ma *et al.* 2014), biopulping (Pèlach *et al.* 2016), and the addition of paper-making additives (Pelton 2004).

Today, paper dry-strength agents play an important role in the papermaking industry, especially when plenty of recycled fiber is being used. To gain significant improvements in both chemical and physical properties, dry-strength agents are usually adopted to enhance the bonding strength among fibers (Arboleda *et al.* 2014; Gulsoy and Erenturk 2017; Larsson *et al.* 2018).

Addition of dry-strength agent can contribute to the quantity of hydrogen bonds, to forming chemical bonding with hydroxyl groups on the fiber surface, and to promoting the interfiber bonding to increase paper strength (Myllytie *et al.* 2009; Lindstrom *et al.* 2016; Strand *et al.* 2017; Xiang *et al.* 2017). Many dry-strength agents have been developed, and depending on the source they can be divided into synthetic organic macromolecular polymers, such as cationic polyacrylamide (CPAM) and polyamideamine-epichlorohydrin (PAE), or natural polymers, like starch, chitosan, sodium alginate, cellulose, as well as their derivatives (Hubbe 2006).

As a dry-strength agent, both natural polymers and synthetic polymers have their advantages and disadvantages. For example, CPAM can greatly improve the mechanical properties of paper compared with cationic starch, but it also has the disadvantages of high cost and environmental pollution in the process of production and its use. In recent years, with the promotion of environmental protection concepts, natural polysaccharides have attracted increased attention and are used as a new type of dry-strength agent and many of them need to be modified to gain noticeable contributions to strength (Wang *et al.* 2015; Yan *et al.* 2017; Di *et al.* 2018). Among the existing modification methods, graft copolymerization shows particular promise as a means to generate a new product with the potential of achieving advantages of both synthetic and natural polymers; these include high dry-strength performance, possible reduction in environmental impact *vs.* a completely synthetic chemical, and cost-efficiency (Salimi *et al.* 2016; Meimoun *et al.* 2018).

As one of the most abundant renewable natural polysaccharides in nature, starch has its unique advantages of good biocompatibility and biodegradability. However, the disadvantages of native starch substantially limit its application, such as its insolubility in cold water, its lack of free-flowing properties, the difficulty in controlling viscosity after gelation, and the sensitivity of cooked starch to shear forces (Gryszkin *et al.* 2017; Masina *et al.* 2017; Zia-ud-Din *et al.* 2017). Due to the presence of hydroxyl groups in a recurrent unit of the polysaccharide chain, many methods have been developed to modify native starch. One of the most common modification methods is carboxymethylation, from which carboxymethyl starch (CMS) can be obtained by converting the hydroxyl group on natural starch into a carboxyl group. The CMS is an important starch derivative with advantages of being renewable, biodegradable, and environmentally friendly; accordingly it is widely used in medicine, pharmaceuticals, cosmetics, the food industry, sewage treatment, and many other industrial applications (Spychaj *et al.* 2013; Ispas-Szabo *et al.* 2017; Xu *et al.* 2017b; Yusof *et al.* 2018).

In recent years, chemical modification of starch *via* graft copolymerization of vinyl monomers has caught many researchers' attention (Nakason *et al.* 2010; Guo and Peng 2012). Though many studies about the grafting of lactic acid, acrylonitrile, and methacrylates onto starch have been published (Lipsa *et al.* 2013; El-Hamshary *et al.* 2015), less attention has been paid to the grafting of polyacrylamide (PAM) onto CMS and its application as a paper dry-strength agent.

In this study, a CMS grafted PAM copolymer (CMS-g-PAM) was synthesized and used as a paper dry-strength agent. The effects of the operation conditions, including the CMS-g-PAM dosage, pH value of the pulp system, and additive amounts of polyaluminium chloride (PAC) on the properties of paper, were investigated.

EXPERIMENTAL

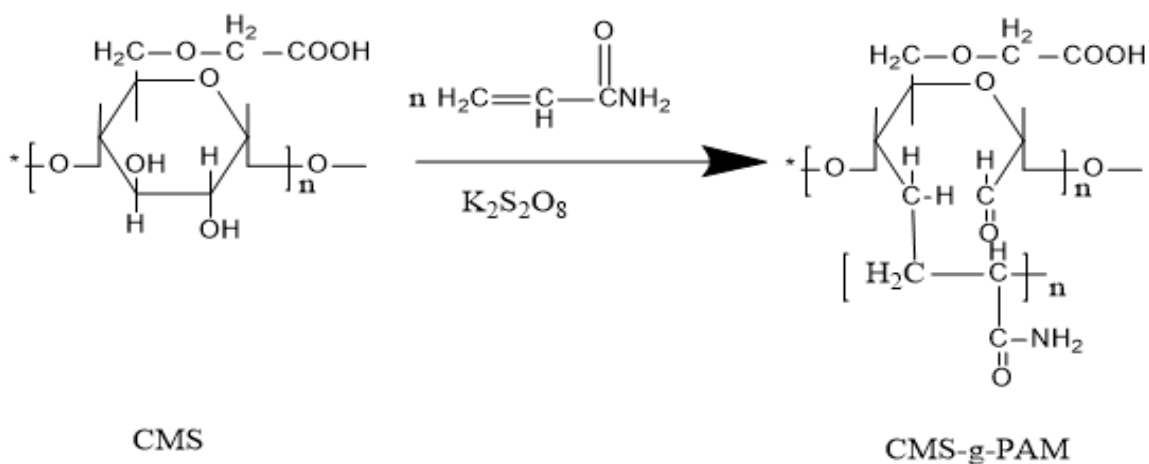
Materials

In this study, carboxymethyl starch (corn starch, substitution degree was 0.46, amylose, lipid, and protein contents were 27%, 0.6%, and 0.2%, respectively), acrylamide, potassium persulfate, and polyaluminium chloride were obtained from Beijing KeAo Biotechnology Co., Ltd. (Beijing, China). Aspen kraft pulp board was provided by Hunan Yueyang PaperGroup (Hunan, China). The pulping conditions were sulfidity of 21.8%, active alkali 15.2 g/L, maximum temperature 168 °C, heating up time 1.8 to 2 h, yield 45%, and beating degree 40° SR. All the chemicals used were of analytical or reagent grade and used without further purification.

Methods

Synthesis of CMS-g-PAM

The synthesis route is summarized in Scheme 1. A mixture of 1 g of dried CMS and 100 mL of deionized water was added to a three-necked round-bottom flask equipped with a stirrer, thermometer, and condenser, under a nitrogen atmosphere. The mixture was stirred and preheated at 80 °C for 45 min. After the CMS was completely gelatinized (starch slurry turned into a transparent solution), the mixture was cooled to 30 °C. Then, 10 mL of potassium persulfate solution with a concentration of 0.001 g/mL was added as an initiator for 10 min to facilitate free-radical formation on the starch surface and a slow stream of nitrogen was maintained to form a nitrogen atmosphere throughout the reaction. This operation was followed by the addition 50 mL of acrylamide aqueous solution (conc. of 0.02 g/mL), and then the flask's contents were rapidly heated to the 60 °C for 3 h. After that, the reaction mixture was slowly poured into anhydrous ethanol to remove the unreacted acrylamide monomer, and then the precipitated polymer was washed with acetone and vacuum-dried at 60 °C. Subsequently, acrylamide homopolymer was removed using Soxhlet extraction (HX-SS; Keao, Beijing, China) with a 60:40 (v/v) mixture of ethylene glycol and acetic acid. The purified CMS-g-PAM obtained was again washed with ethanol and then vacuum-dried at 60 °C to a constant weight (Nakason *et al.* 2010; Guo and Peng 2012). Finally, the dried CMS-g-PAM was powdered by using a mortar (C-155; Qingsheng, Jiangsu, China).



Scheme 1. The schematic representation of CMS-g-PAM reaction

Percentage grafting and grafting efficiency

The percentage grafting (PG) and grafting efficiency (GE) were calculated according to Eqs. 1 and 2,

$$\text{PG (\%)} = [(W_1 - W_0) / W_0] \times 100 \quad (1)$$

$$\text{GE (\%)} = [(W_1 - W_0) / (W_2 - W_0)] \times 100 \quad (2)$$

where W_0 , W_1 , and W_2 in the equations denote the weights (g) of the carboxymethyl starch, grafted copolymers (grafted product after extraction), and crude product before extraction, respectively.

Elemental analysis

Specific elements of the samples can be quantitatively analyzed using element analysis. The nitrogen, carbon, and hydrogen contents of CMS and CMS-g-PAM were analyzed using a Vario EL III instrument (Elementar, Frankfurt, Germany), in which approximately 3 to 5 mg samples were heated in an oxygen atmosphere.

Infrared spectroscopic analysis

The CMS and CMS-g-PAM were each mixed with a certain amount of solid KBr, and the oven-dried mixture was ground into a powder. Then, the powder was pressed into a tablet for a Fourier transform infrared (FT-IR) analysis using an FT-IR spectrometer (Spectrum-100D; Perkin-Elmer, Fremont, CA, USA), and the data were recorded from 400 to 4000 cm^{-1} .

Preparation of paper sheets

The pulp boards were shredded into small pieces and soaked in tap water for 24 h. Then, the pulp fibers were swollen, disintegrated, and beaten to the desired degrees in the beater (VB-42F; China National Pulp and Paper Research Institute, Beijing, China). An aqueous pulp suspension was obtained, and the concentration of the pulp slurry was 16 g/L.

Handsheets with a basis weight of 60 g/m^2 were prepared using a handsheet former according to GB/T 451.2 (2002). The steps were as follows: pulp suspension with the dry pulp mass of 1.88 g was added in the former, a certain amount of PAC was added to the pulp while stirring, 0.5%, 1.0%, 1.5%, or 2.0% of CMS-g-PAM based on oven-dry fiber (w/w) was added to the pulp, the pH was adjusted to the desired value using a H_2SO_4 and NaOH solution. Then, the handsheets were made after stirring at 500 rpm for 10 min.

The control handsheets were made in the same way but without any additives. After forming, the sheets were pressed at 430 kPa for 4 min and dried under a temperature of 105 $^\circ\text{C}$ for 3 min and placed in a drying apparatus with constant temperature and humidity (23 $^\circ\text{C}$ and 50% relative humidity) for at least 24 h before physical testing was performed.

Mechanical strength testing of paper sheets

Handsheets were cut into specific shapes and sizes according to TAPPI T220 sp-01 (2011) for tearing index, tensile index, and folding endurance measurements. Tensile index is a commonly applied strength indicator that is defined as the breaking force (load) per standard width of paper.

The tensile index of the handsheets was tested following the TAPPI T220 sp-01 (2011) method. It is defined as the quotient of the tensile strength (N/m) and the basis weight (g/m^2) of the paper, and thus its units are Nm/g . The tearing index is the tearing strength divided by grammage (unit is mNm^2/g), and the tearing strength of the handsheets

was tested using the ASTM D689 (2012) method. Folding endurance was measured according to the TAPPI T511 om-08 (2008) method. Density was measured based on the ISO 534 (2011) standard.

Scanning electron microscopy

The surface morphology of the samples (CMS, CMS-g-PAM, control sample paper, and experimental paper) were analyzed by obtaining the micrographs with a SU8010 (Hitachi, Tokyo, Japan) field emission scanning electron microscope (FESEM) operating at 3.0 kV. The specimens were sprayed with gold by using an EM ACE200 Ion sputter device (Leica Microsystems, Germany) to enhance the conductivity and secondary electron emission characteristics and to avoid surface charging under the electron beam.

RESULTS AND DISCUSSION

FT-IR Analysis

Figure 1 shows the FT-IR spectra of acrylamide, CMS, and CMS-g-PAM. The difference between the three curves showed evidence of the graft copolymerization of the PAM onto the CMS. It is found by the shifts in the position of the peaks characterizing the carboxyl and the hydroxyl groups and the appearance of new bands related to the acylamino groups introduced compared with CMS.

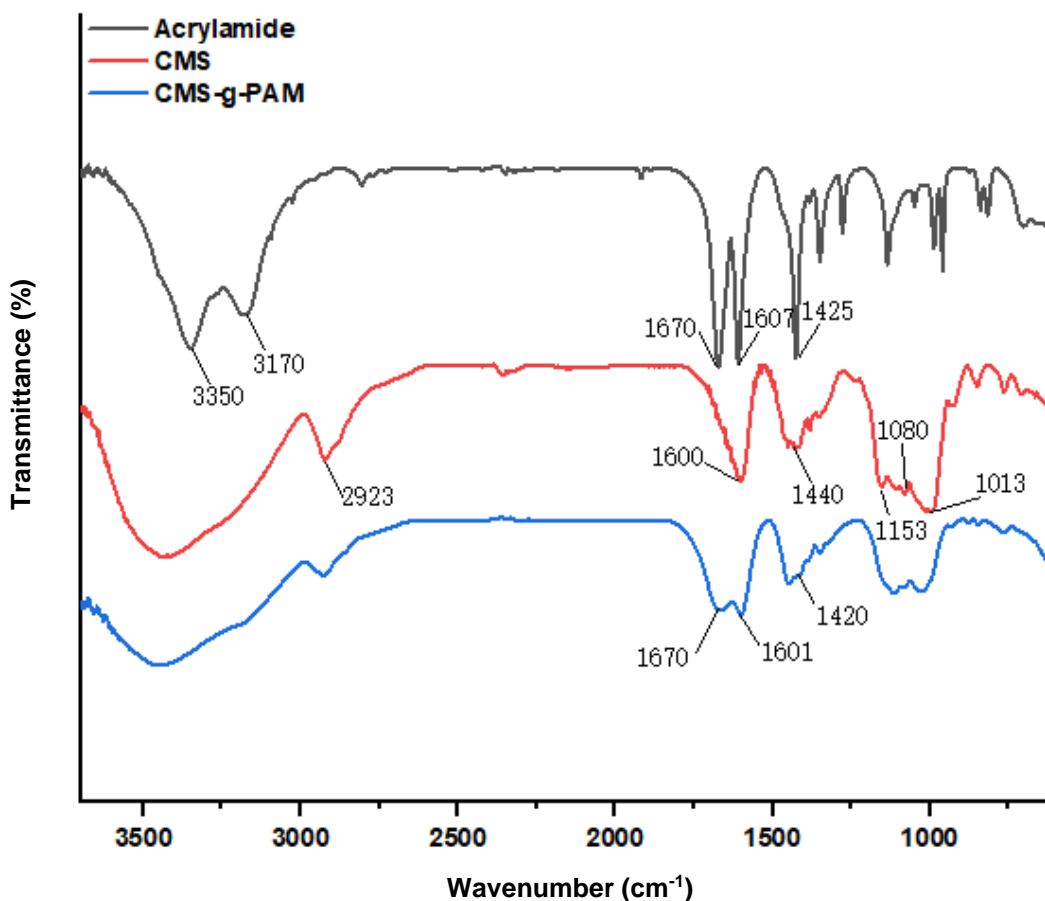


Fig. 1. FTIR spectra of the acrylamide, CMS, and CMS-g-PAM

The FT-IR spectra of acrylamide showed double absorption peaks at 3350 and 3170 cm^{-1} , which represent the N–H stretching vibration, and triplet peaks with a strong absorption at 1670, 1607, and 1425 cm^{-1} , which indicate the C=O stretching vibration, N–H bending vibration, and C–N stretching vibration of the amide groups, respectively. The broad absorption bands of the CMS curve in the region of 3550 to 3200 cm^{-1} correspond to the O–H stretching vibration, and the medium absorption peak at 2923 cm^{-1} represents the C–H stretching vibration. The CMS carboxylate (–COO–) gives the strong bands at approximately 1600 and 1440 cm^{-1} . Furthermore, the triplet peaks at 1153, 1080, and 1013 cm^{-1} indicate the presence of the C–O–C stretching vibration.

The spectra of the CMS-g-PAM showed all the absorption bands of the CMS. In addition, the bands found at 1670 cm^{-1} , 1601, and 1420 cm^{-1} of the graft copolymers indicate the characteristic C=O stretching vibration, N-H bending vibration, and C–N stretching vibration of the –CONH₂ group. The presence of these absorption peaks in the CMS-g-PAM confirmed the success of the graft copolymerization. This interpretation is supported by earlier literature on the graft copolymerization of starch with acrylamide (Sadeghi and Hosseinzadeh 2008; El-Sheikh 2016).

Reaction Efficiency and Element Analysis

The percentage grafting and grafting efficiency were 30.2% and 52.4%, respectively, which were calculated according to Eqs. 1 and 2. The results obtained through element analysis showed that the N, C, and H contents of CMS were 0.35%, 42.84%, and 6.24%, respectively, while they became 6.65%, 46.56%, and 6.45%, respectively, after the graft copolymerization. The obvious growth in the N content indicated the presence of nitrogenous compounds (AM) in the modified CMS.

SEM Analysis of CMS-g-PAM

The surface morphology micrographs of the CMS and the CMS-g-PAM with different amplifications are shown in Fig. 2, and a considerable difference between the particles of two samples was observed.

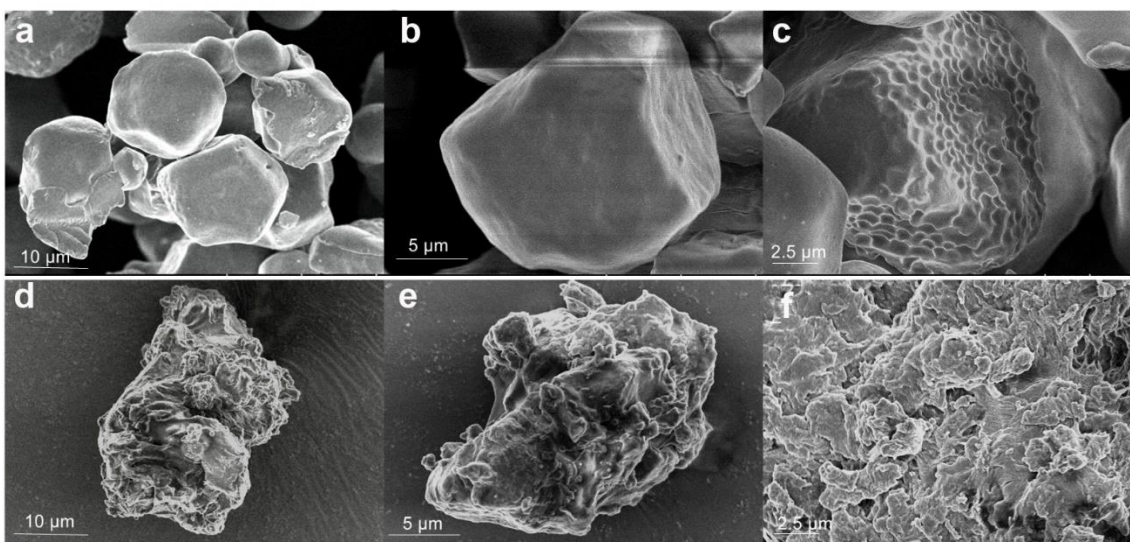


Fig. 2. The surface SEM images of CMS (a through c) and CMS-g-PAM (d through f)

Figure 2 shows that the CMS particles are cube-like and ellipsoid in shape and with small pits on the surface that range in size from 5 to 25 μm . After graft copolymerization, noticeable change of the granular structure and surface of the CMS was observed. The ellipsoid shape of CMS completely disappeared and became an irregular shape with lots of bumps and folds on the surface. This phenomenon was observed because the PAM was attached on the CMS surface and the structure of CMS was also damaged in the reaction. The SEM micrographs are morphological evidence indicating the grafting of polyacrylamide onto CMS. Similar SEM results (decrease in planarity and uniformity of the surface) were also obtained by earlier studies on the graft copolymerization of PAM onto cassava starch (Jyothi *et al.* 2010).

Effect of the Dosage of CMS-g-PAM on the Paper Properties

Table 1 reports the effect of the dosage of CMS-g-PAM on the paper properties, including density, tensile index, burst index, tearing index, and folding endurance. When the dosage of CMS-g-PAM increased, the five properties showed different variation trends: the density, tensile index, and burst index of the paper rapidly increased in the beginning, and then slightly decreased, while the folding endurance continued to rise and the tearing index gradually declined. Compared with the control sample, with the addition of 1.5% CMS-g-PAM, the density, tensile index, and burst index reached the maximum of 0.516 g/cm^3 , 68.43 Nm/g , and 5.71 $\text{kPa}\cdot\text{m}^2/\text{g}$, respectively, which represented increases of 16.5%, 41.0%, and 35.6%, respectively. As the amount of CMS-g-PAM increased from 0 to 2.0%, the folding endurance of paper increased by 109%, from 43 times to 90 times. The improvement of these properties was attributed to the bonding strength between the fibers that became stronger. When the CMS-g-PAM was added, the acylamino group on CMS-g-PAM and the hydroxyl radical on fibers formed strong intermolecular interaction and hydrogen bonds, thereby improving the strength index based on binding force, such as tensile index, burst index, and folding endurance (Yuan and Hu 2012). However, the tearing index dropped slightly (by 5.5%). There are similar results from published research that tear strength could drop slightly when a dry-strength agent is added, it is widely believed that a higher level of bonding between fibers will make the paper more brittle, which could result in a decrease in the tearing index (Song and Hubbe 2014; Di *et al.* 2018).

Table 1. Effect of Dosage of CMS-g-PAM on the Paper Properties

Dosage of CMS-g-PAM (%)	Density (g/cm^3)	Tensile Index ($\text{N}\cdot\text{m}/\text{g}$)	Burst Index ($\text{kPa}\cdot\text{m}^2/\text{g}$)	Tearing Index ($\text{mN}\cdot\text{m}^2/\text{g}$)	Folding Endurance (Double Folds)
Control	0.443	48.52	4.21	9.03	43
0	0.448	49.24	4.43	8.94	44
0.5	0.462	56.73	5.14	8.73	60
1.0	0.494	67.06	5.67	8.61	85
1.5	0.516	68.43	5.71	8.57	88
2.0	0.508	68.14	5.59	8.53	90

Note: Addition of PAC was 1% on a dry fiber basis, the pH was adjusted to 7, and handsheets were prepared after stirring for 10 min

Effect of the Dosage of PAC on the Paper Properties

The CMS-g-PAM tended to be negatively charged. Therefore, to retain such polymers efficiently onto cellulosic fibers, something cationic needs to be added to the pulp suspension. The PAC is one of the most common cationic polyelectrolytes that can be used

as a bridging agent between the anionic dry-strength agent and the cellulosic fiber. The effects of the dosage of PAC on the paper properties are described in Table 2. Compared with the control sample (without CMS-g-PAM and PAC), when only 1% CMS-g-PAM was added, all the properties except the tearing index of paper gained slight improvement. Under this condition, the density, tensile index, burst index, and folding endurance were 0.465 g/cm³, 54.0 Nm/g, 4.78 kPa.m²/g, and 62 times, respectively. Then, as the dosage of PAC increased from 0% to 2.0%, the tensile index and burst index dramatically improved from 54.03 Nm/g and 4.78 kPa.m²/g to 69.1 Nm/g and 5.83 kPa.m²/g. The density and folding endurance reached their maximum values, which were 0.511 g/cm³ and 89 times, respectively. All of the above indicated that CMS-g-PAM is capable of playing a more noticeable enhancing role in the presence of PAC. When the dosage of PAC exceeded 1%, the changes of all the properties of paper were not obvious, so the optimal dosage could be 1%; in this condition, the density, tensile index, burst index, and folding endurance were improved by 11.5%, 38.2%, 34.7%, and 97.7%, compared to the control sample.

Table 2. Effect of Dosage of PAC on the Paper Properties

Dosage of PAC (%)	Density (g/cm ³)	Tensile Index (N·m/g)	Burst Index (kPa·m ² /g)	Tearing Index (mN·m ² /g)	Folding Endurance (Double Folds)
Control	0.443	48.52	4.21	9.03	43
0	0.465	54.03	4.78	8.83	62
0.5	0.486	60.85	5.32	8.71	70
1.0	0.494	67.06	5.67	8.61	85
1.5	0.511	68.52	5.81	8.50	89
2.0	0.508	69.06	5.83	8.46	87

Notes: Addition of CMS-g-PAM was 1% on a dry fiber basis.

Effect of the pH Value on the Paper Properties

It was confirmed that the form of the hydrolytic products of PAC and the degree of carboxyl ionization on the cellulosic fiber varied with the pH value of the pulp system, so the properties of paper can also be influenced by pulp pH (Rohi *et al.* 2016). Table 3 presents the measurements of handsheets that were made under different pH values. With the addition of 1% CMS-g-PAM and 1% PAC and when the pH value was changed from 5 to 9, all of the properties except tearing index of paper improved at the beginning and then decreased slightly. When the pH was adjusted to 7, in comparison with the control sample, the density, tensile index, burst index, and folding endurance increased 11.5%, 38.2%, 34.7%, and 97.7%, respectively, which were 0.494g/cm³, 67.06 Nm/g, 5.67 kPa.m²/g, and 85 times, respectively. The tearing index of the papers were in the range of 8.6 to 8.8 mNm²/g, where minimal change was observed. Therefore, the pH value had a slight influence on this property. This was because the tearing index was mainly affected by fiber length and inherent strength of the individual fiber and had less dependency on inter-fiber bonding (Gulsoy and Erenturk 2017). When compared with the handsheets that were made at pH 5, the density, tensile index, burst index, and folding endurance were increased by 6.7%, 14.9%, 7.8%, and 30.8%. Overall, CMS-g-PAM was more effective in a neutral and alkaline environment, which was consistent with the current transformation direction of the paper industry. It is well-known that the paper produced in a neutral environment lasts a lot longer than that produced in an acidic conditions, moreover, neutral environment has less corrosion on the paper equipment.

Table 3. Effect of pH of Pulp System on the Paper Properties

pH	Density (g/cm ³)	Tensile Index (N·m/g)	Burst Index (kPa·m ² /g)	Tearing Index (mN·m ² /g)	Folding Endurance (Double Folds)
Control	0.443	48.52	4.21	9.03	43
5	0.463	58.37	5.26	8.75	65
6	0.486	62.54	5.43	8.64	76
7	0.494	67.06	5.67	8.61	85
8	0.487	66.14	5.58	8.64	82
9	0.482	63.86	5.43	8.67	78

Notes: Addition of CMS-g-PAM and PAC were both 1% on a dry fiber basis.

Comparison of Effect Between CMS and CMS-g-PAM on the Paper Properties

The effect of different CMS and CMS-g-PAM dosage on the paper properties was further explored. The results of the two additives are described in Table 4. The control sample was prepared without addition of CMS or CMS-g-PAM.

Table 4. Comparison of Effect Between CMS and CMS-g-PAM on the Paper Properties

Dosage of CMS (%)	Dosage of CMS-g-PAM (%)	Density (g/cm ³)	Tensile Index (N·m/g)	burst index (kPa·m ² /g)	Tearing index (mN·m ² /g)	Folding Endurance (Double Folds)
Control		0.443	48.52	4.21	9.03	43
0.5	0	0.451	50.82	4.64	8.85	52
0	0.5	0.462	56.73	5.14	8.73	60
1.0	0	0.468	52.63	4.84	8.79	58
0	1.0	0.494	67.06	5.67	8.61	85
1.5	0	0.472	52.34	4.81	8.82	61
0	1.5	0.516	68.43	5.71	8.57	88
2.0	0	0.460	51.53	4.78	8.84	55
0	2.0	0.508	68.14	5.59	8.53	90

Notes: Addition of PAC was 1% on a dry fiber basis.

With increased dosage, both the CMS and CMS-g-PAM increased the density, tensile index, burst index, and folding endurance of the handsheets; the CMS-g-PAM was more effective than CMS under the same addition level. As the dosage of CMS was increased from 0.5% to 2.0%, the tensile index, burst index, and folding endurance values were maximum at 52.6 Nm/g, 4.84 kPa·m²/g, and 58 times at 1.0% dosage. However, when the 1% CMS-g-PAM was added, a better result was seen; the tensile index, burst index, and folding endurance of the handsheets were 67.1 Nm/g, 5.67 kPa·m²/g, and 85 times. When the addition level was 1%, compared with the strength gains of the CMS-treated sample, the strength gains of the tensile of CMS-g-PAM-treated paper was more than quadruple and the strength gains of the burst and folding endurance were more than double. Therefore, the CMS-g-PAM can be used as a paper dry-strength agent to improve tensile index, burst index, and folding endurance of paper. Furthermore, negatively charged CMS and CMS-g-PAM can combine with the highly cationic Al³⁺, which can tie them onto the surfaces of fibers and fines and finally improve the bonding strength between the fibers (Di *et al.* 2018). As for CMS-g-PAM, a polymer with a three-dimensional network structure, in addition to hydroxyl and carboxyl groups on the main chain, it also has acylamino groups on the branch chain, which made it easier to bond with the fibers and Al³⁺; therefore, it has

a better enhancement effect (Xu *et al.* 2017a). However, when the dosage exceeded 1%, all properties of the handsheets showed minimal change with the increasing addition of CMS and CMS-g-PAM; this could have been because the dosage might have been beyond the amount that can be adsorbed on the fiber surfaces.

SEM Analysis of Handsheets

Figure 3 shows the surface morphology images of handsheets made from the control pulps and the CMS-g-PAM-treated pulps, where the state of interlacing of fibers is visible. As shown, the tightness and surface smoothness of the papers were different. The control sample had a rough surface, the fibers were loosely connected, and there were many holes. After treatment by CMS-g-PAM the paper surface was clearly different, the bonding between the fibers was more compact and appeared to be stuck together with glue and fewer holes were observed, when compared with the control sample. The changes in surface morphology were consistent with the changes in the mechanical properties of the control sample handsheets and CMS-g-PAM-treated pulps. All of the above indicate that CMS-g-PAM improved the interfiber bonding and it had a beneficial effect on the paper properties.

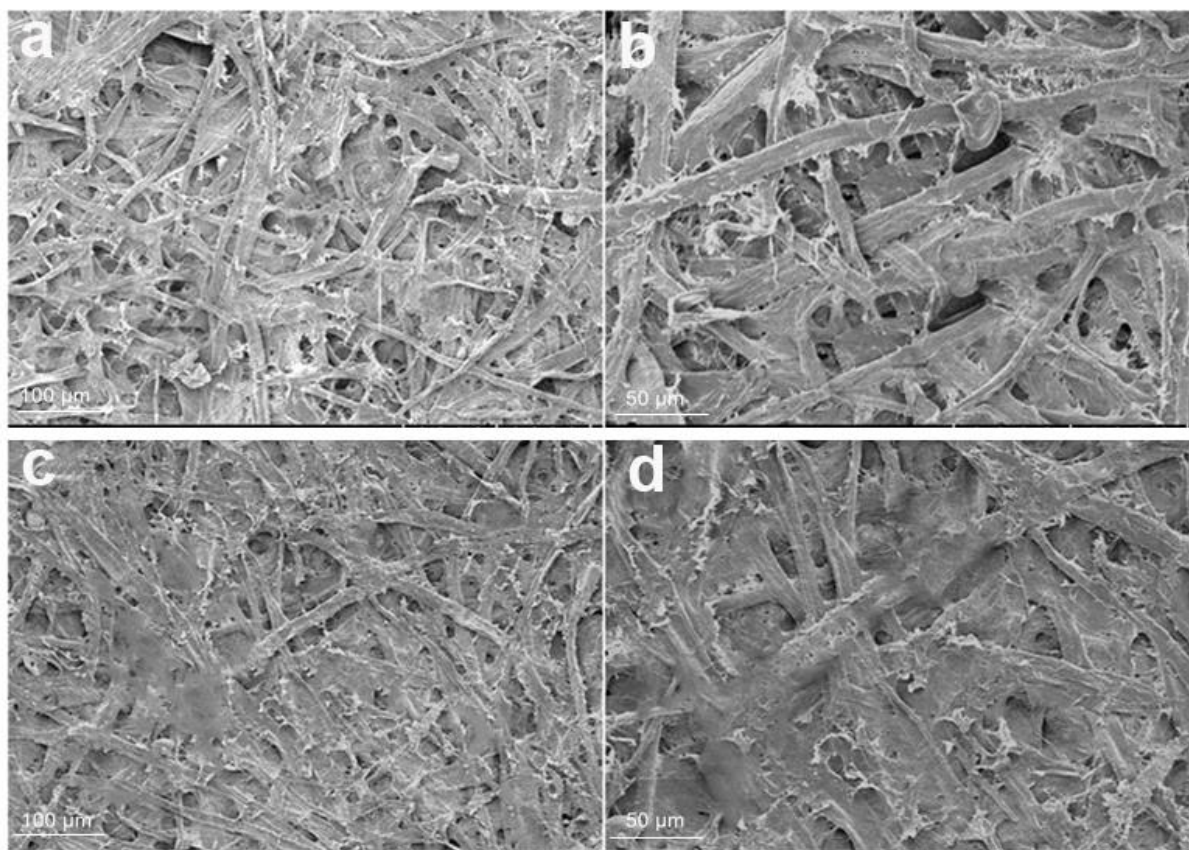


Fig. 3. The surface SEM images of control sample (a and b) and handsheet with 1% CMS-g-PAM (c and d)

CONCLUSIONS

1. In this study, the CMS-g-PAM was successfully synthesized and it had a beneficial effect on the mechanical properties of paper. When 1% of the CMS-g-PAM was added, the tensile index, burst index, and folding endurance of paper increased 38.2%, 34.7%, and 97.7%, respectively, when compared with the control sample.
2. The CMS-g-PAM showed a more obvious enhancement effect in the presence of PAC. In the same addition level, CMS-g-PAM was more efficient than CMS, when the dosage was 1%, the tensile index, burst index, and folding endurance of the CMS-g-PAM-treated paper were improved 27.4%, 17.2%, and 46.6%, when compared with the CMS-treated sample.
3. The optimal pH value of the pulp system for using CMS-g-PAM was approximately 7, and the handsheets made in a neutral environment showed better performance.
4. The SEM analysis revealed that the structure and surface morphology of CMS changed a lot after grafting polyacrylamide and that CMS-g-PAM improved the bonding strength between the fibers of the paper.

ACKNOWLEDGMENTS

The authors completed this work with financial support from the National Science Foundation of China (31470605) and the National Key Research & Development plan for the '13th Five-year Plan of China' (2017YFD0600804).

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Article submitted: April 29, 2019; Peer review completed: July 13, 2019; Revised version received: August 3, 2019; Accepted: August 7, 2019; Published: September 11, 2019.
DOI: 10.15376/biores.14.4.8470-8483