INFLUENCE OF CARBOXYMETHYLATED HOLOCELLULOSE AND PAE BINARY SYSTEM ON PAPER PROPERTIES

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In this paper, corncob, as raw material, was delignified with sodium chlorite. The residue holocellulose was modified with sodium chloroacetate to prepare paper strengthening agents. The influence of carboxymethylated holocellulose (CMH), polyamide-epichlorohydrin (PAE), cationic starch (CS) and their mixture on paper properties was evaluated. The results showed that PAE, CMH and CS could significantly increase the tensile index, burst index and folding endurance of paper. After adding 0.6% PAE, the dry tensile index, burst index and folding endurance of paper increased as the dosage of CMH changed from 0.3% to 1.2%. Compared with adding PAE separately, dry tensile index, wet tensile index, and burst index of paper increased by 15.03%, 43.22%, and 11.38%, respectively, when the dosage of CMH was 0.6%. The binary system of CMH and CS had similar results. FTIR-ATR analysis of the paper surface indicated that modification with all of PAE, cationic starch, the binary systems of CMH/PAE and CMH/CS could increase C-O bond intensity, which drew the fibers closer to each other in the handsheets. This was also proved by the results of SEM analyses.

Keywords: carboxymethylated, holocellulose, PAE, wet-strengthening agent, paper properties

INTRODUCTION

With the improvement in people's living standards, the demand for paper is increasing. Due to the shortage of raw materials for paper and the increase in environmental pressures, straw and recycled paper have been used by many paper companies, which caused the decrease of paper properties. In this case, in order to improve paper properties, paper dry-strength agents have become widely used in the paper industry to increase the bond strength between the fibers.[1-3]

Paper strengthening agents include dry-strength additives, which increase dry paper strength, and wet-strength additives, which increase wet paper strength. Their action is based on different mechanisms. Wet-strength additives can form a crosslinking network structure on the fiber interfaces, limit the activity between fibers, reduce the fiber wetness-swelling, and improve the humidity of paper's fine chemicals. Wet-strength additives include urea formaldehyde (UF), melamine formaldehyde (MF), polyamide epichlorohydrin (PAE), *etc*. PAE is generally used in alkaline papermaking. Widely used dry strengthening agents include products based on polyacrylamide, starch, emulsion polymers, and resin glue, including anionic, cationic and amphoteric strengthening agents, to improve the dry strength of paper.[4-13] Nanocellulose and carboxymethyl cellulose also can improve paper's dry-strength.[14,15]

Corncob is an agricultural by-product, which contains higher hemicellulose content than other plants. It was found that corncob holocellulose could be used to prepare paper dry-strength additives optionally by carboxymethylation.[16] However, no reports have been found about the use of carboxymethylated holocellulose (CMH) with other additives, such as polyamide-epichlorohydrin (PAE) or cationic starch (CS) .[17-19] In this paper, we compared CMH with PAE and CS, and evaluated the influence of CMH, PAE, CS and their mixture on paper properties. The results provide a new application for carboxymethylated corncob holocellulose.

EXPERIMENTAL

Materials

Corncob was obtained from Shandong province, with 5.26% moisture content. The corncob was split into about 20 mm × 10 mm × 10 mm pieces, then the pieces were ground into a fine powder and the powder particles under 80 mesh size were collected. Aspen Kraft pulp was obtained from Hunan Yueyang Paper Group. The pulping conditions were as follows: active alkali – 15.2 g/L, sulfidity – 21.8%, maximum temperature – 168 ºC, heating up time – 1.8-2 h, soaking time – 90 min, yield – 45%, and beating degree – 40 °SR.

Holocellulose preparation and carboxymethylation

Holocellulose was prepared by treating corncob powder with sodium chlorite. Carboxymethylated holocellulose was obtained by processing holocellulose with sodium chloroacetate under alkaline conditions. The conditions have been described in detail in our previous study.[16] Carboxymethylated holocellulose (carboxymethylation time – 100 min) had the following characteristics: degree of substitution – 0.752, carboxyl content – 196 $mmolkg^{-1}$, nitrogen content – less than 0.3%, contents of carbon, hydrogen, and oxygen – 29.06%, 3.76%, and 66.88%, respectively.

Polyamide-epichlorohydrin (PAE) preparation

An amount of 41 g diethylenetriamine, 7.5 g H_2O, and 0.5 g p-toluenesulfonic acid were put into a three-necked flask. An impeller stirring apparatus and a steam flow device were used. 55 g of adipic acid was added into the flask after stirring. The temperature of the mixture immediately rose to 125 ºC and the water was distilled off. The mixtures was heated to 150~160 ºC and reacted for 3 h. When the distilled liquid of water and amine was about 17.5 g, heating was stopped and the temperature was decreased to less than 100 ºC. 80 g of water was put into the flask and stirred to uniformity. 200 g water was added into the flask, then 40 g epichlorohydrin was added under stirring. The temperature was controlled at 70 ºC and the reaction time was 1-2 h, when the viscosity increased to 30-150 mPa·s, the pH was adjusted to 3-5 with acetic acid, and then the PAE sample was obtained.

Pulp beating and papermaking

The pulp was beaten to 40 °SR. 1.88 g (o.d.) kraft pulp handsheets were prepared and determined according to the appropriate China GB standard methods.

Scanning electron microscopy (SEM)

An S-3000N type of SEM device (Hitachi Ltd., Japan) was used for analyzing handsheet surface, fracture surfaces by tensile force and cut sections of paper. Sample images were obtained after gold sputtering.

Fourier Transform Attenuated Total Reflection Infrared Spectroscopy (FTIR-ATR)

Fourier Transform Attenuated Total Reflection Infrared Spectroscopy (FTIR-ATR) analysis of the paper surface was carried out using a Bruker FT-IR Tensor 27 Spectrometer. The transmittance between 4000 cm^{-1} and 400 cm^{-1} was studied.

RESULTS AND DISCUSSION

Dosage of CMH

Table 1 indicates the effects of dosage of CMH on physical properties of paper. As shown, with increasing dosage of CMH, the dry tensile index, burst index, and folding endurance increased at first and then decreased. It indicated that a proper quantity of CMH has an important strengthening effect on paper properties. When the dosage was excessive, the paper properties were impaired, because an increasing negative charge decreased the bond force among the fibers.[20-22] The dry tensile index, burst index, and folding endurance of paper made with 0.9% CMH increased by 42.40%, 18.60%, and 81.77%, respectively, compared to the control sample.

Effects of PAE dosage on paper properties

As shown in Table 2, with increasing the PAE dosage, the dry tensile index, wet tensile index, and folding endurance of the handsheets increased at first and then decreased, while burst index increased gradually, tear index decreased at first and then increased. When the PAE dosage was less than 0.9%, the bonding force between PAE and fibers increased gradually, resulting in increasing paper properties.

When the PAE dosage was increased to exceed 1.2%, the increasing positive charge of PAE caused the bonding force between PAE and the fibers to decrease, so the paper properties decreased. The dry tensile index, burst index, and folding endurance of paper made with 0.9% PAE increased by 58.50%, 21.40% and 91.38%, respectively, compared with corresponding properties of the control sample. At the same time, the wet tensile index increased to 20.1N·m/g.

Effects of CMH and PAE binary system

The effects of the binary system of CMH and PAE on paper properties are shown in Table 3. As shown, after adding 0.6% PAE, varying the dosage of CMH from 0.3% to 1.2%, the wet tensile index, burst index, and folding endurance increased at first and then decreased.

Table 1
Effects of CMH dosage on paper properties

Dosage of CMH (%)	Density (g/cm^3)	Dry tensile index (N·m/g)	Tear index ($mN·m^2/g$)	Burst index ($kPa·m^2/g$)	Folding endurance (double folds)
control	0.49	55.9	15.6	5.86	406
0.3	0.51	77.4	11.5	6.31	483
0.6	0.49	80.6	11.8	6.56	524
0.9	0.49	79.6	11.6	6.95	738
1.2	0.49	77.0	10.8	6.92	616

Note: Carboxymethylation time – 100 min. The handsheets were prepared with a certain amount of CMH, 0.5% $Al_2(SO_4)_3·18H_2O$ on a dry fiber basis. After alum addition, the pH was adjusted to 5. Standard deviation <4%

Table 2
Effects of PAE dosage on paper properties

Dosage of PAE (%)	Density (g/cm^3)	Dry tensile index (N·m/g)	Wet tensile index (N·m/g)	Tear index ($mN·m^2/g$)	Burst index ($kPa·m^2/g$)	Folding endurance (double folds)
control	0.49	55.9	0.100	15.6	5.86	406
0.3	0.46	65.3	8.67	12.3	6.10	636
0.6	0.47	78.5	11.8	11.7	6.50	729
0.9	0.44	88.6	20.1	10.4	7.04	777
1.2	0.46	82.3	17.4	11.6	7.11	631

Note: Standard deviation <4%

Table 3
Effects of CMH and PAE binary system on paper properties

Dosage of PAE (%)	Dosage of CMH (%)	Density (g/cm^3)	Dry tensile index (N·m/g)	Wet tensile index (N·m/g)	Tear index ($mN·m^2/g$)	Burst index ($kPa·m^2/g$)	Folding endurance (double folds)
0.6	0	0.47	78.5	11.8	11.7	6.50	729
0.6	0.2	0.44	77.9	12.9	11.7	6.39	497
0.6	0.4	0.45	77.7	13.8	11.9	6.40	521
0.6	0.6	0.50	90.3	16.9	10.0	7.24	543
0.6	0.8	0.52	89.9	16.3	10.4	7.05	529

Note: Standard deviation <5%

When the dosage of CMH was 0.6%, the dry tensile index, wet tensile index, and burst index increased by 15.03%, 43.22%, and 11.38%, respectively, compared with those of the paper with 0.6% PAE only. The main reason was that the carboxymethyl of CMH could form cross-linkages among fibers, which increased the bonding force among the fibers.

SEM analysis

Figure 1 shows SEM images of paper fracture during tensile testing. Most fibers in the original paper were intact when the paper was torn by the tensile force, while the majority of fibers were fractured in the paper with CMH and CMH/PAE. These results proved that there was sufficient inter-fiber bonding in the paper containing CMH and the CMH/PAE binary system, so that the fibers failed rather than were separated from the inter-fiber bonding.

SEM cross-section images of handsheets are also shown in Figure 1, revealing that the cross-section of the control paper was thicker than that of the paper with CMH and CMH/PAE. It indicated that paper strengthening additives could improve the bonds among the fibers, which joined the fibers closer together in the handsheets.

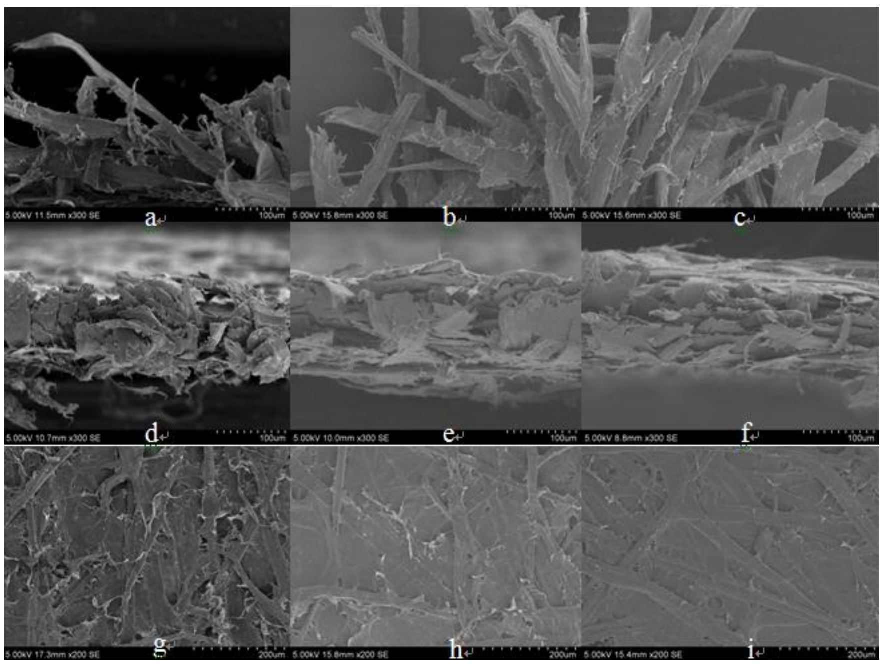

Figure 1: SEM images of handsheet fracture, section and surface of control paper (a, d and g), paper modified with CMH (b, e and h) and paper modified with the binary system (c, f and i)

Table 4
Effects of CS dosage on paper properties

Dosage of CS (%)	Density (g/cm^3)	Tensile index (N·m/g)	Tear index ($mN·m^2/g$)	Burst index ($kPa·m^2/g$)	Folding endurance (double folds)
control	0.49	55.9	15.60	5.86	406
0.3	0.49	56.87	13.05	6.28	478
0.6	0.47	61.89	13.41	6.28	522
0.9	0.47	63.91	14.46	6.31	457
1.2	0.46	68.22	15.46	6.33	443

Note: Standard deviation <4%

Table 5
Effects of CMH and CS binary system on paper properties

Dosage of CS (%)	Dosage of CMH (%)	Density (g/cm^3)	Tensile index (N·m/g)	Tear index (mN·m^2/g)	Burst index (kPa·m^2/g)	Folding endurance (double folds)
0.6	0	0.47	61.89	13.41	6.28	522
0.6	0.2	0.47	63.28	14.24	6.30	1121
0.6	0.4	0.47	68.73	14.43	6.30	1131
0.6	0.6	0.48	72.74	15.03	6.49	1996
0.6	0.8	0.48	69.86	15.17	6.35	2327

Note: Standard deviation <5%

Figure 1 also shows the SEM surface images of a handsheet surface. As may be observed, there were many pores on the control paper surface, while there were relatively few pores in the paper containing CMH (Fig. 1h) and CMH/PAE (Fig. 1i). Meanwhile, there were fewer pores on the surface of the paper with CMH/PAE, compared to that with CMH alone.

Effects of CS dosage on paper properties

Table 4 shows the effects of CS dosage on paper properties. The tensile index, burst index, and folding endurance increased when cationic starch was added into the paper. However, when increasing the dosage of CS, the tensile index increased gradually, the burst index changed a little, while folding endurance increased at first and then decreased, and the density decreased gradually.

This behavior can be explained by the fact that with an increasing dosage of CS, the CS combined with pulp fiber, which improved the bond among the fibers. However, when the amount CS was excessive, the fiber surface obtained a positive charge, which increased the repulsion among fibers and led to decreases in density and folding endurance.

Effects of CMH and CS binary system

The effects of the binary system of CMH and CS on paper properties are shown in Table 5. After adding 0.6% CS, with an increasing dosage of CMH, the tensile index and folding endurance of paper increased significantly. When the dosage of CMH was 0.6%, the tensile index, burst index and folding endurance increased by 17.53%, 3.34%, and 282.38%, respectively, compared with those of the paper containing 0.6% CS only. These results demonstrate that CMH and CS had a synergistic effect.

FTIR-ATR analysis

Figure 2 shows the FTIR-ATR spectrograms of the surface of the paper samples (control, PAE and CMH/PAE modified samples).

The spectrograms of the three samples are similar. Thus, the peak at around 3400 cm^{-1} is assigned to hydroxyl groups, the peak at 2896 cm^{-1} is a CH_2 stretching vibration peak, the peak at 1640 cm^{-1} is a combining water peak and the peak at 1050 cm^{-1} is a C-O stretching vibration peak.

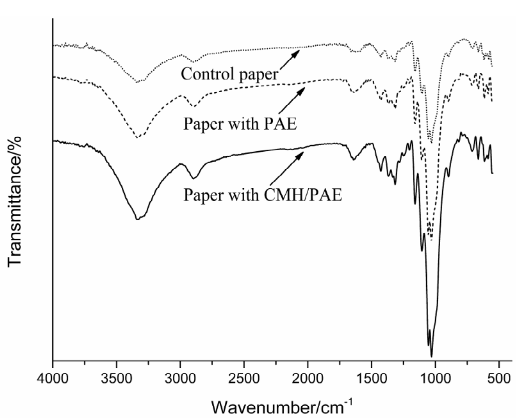

Figure 2: Surface FTIR-ATR spectra of paper with PAE and CMH/PAE

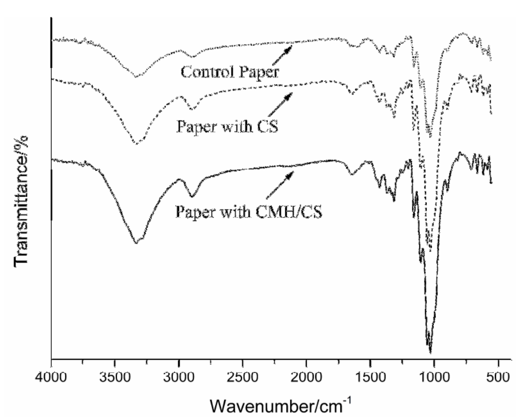

Figure 3: Surface FTIR-ATR spectrogram of paper with CS and CMH/CS

The hydroxyl peak and C-O stretching vibration peak increased significantly in the spectra of the paper samples containing PAE and CMH/PAE. Moreover, the increase of these two peaks is even more pronounced in the spectrum of the paper with the binary system of CMH and PAE. This suggests that both PAE and CMH/PAE can increase C-O bonds among fibers, thus leading to an increase in the paper properties.[23]

The FTIR-ATR spectrograms of the paper modified with CS and CMH/CS, as well as that of the control, are shown in Figure 3. The peaks assigned to the hydroxyl groups and C-O stretching vibration are significantly higher in the spectra of the paper samples containing CS and CMH/CS. However, the hydroxyl peak is lower in the spectrum of the paper with the binary system of CMH and CS, compared to that in the spectrum of the paper containing only CS. This can be explained by the fact that the hydroxyl content is higher in CS than in CMH. The latter covered the fiber surface, which decreased the content of the hydroxyl groups on the paper surface. The C-O stretching vibration peak increased evenly in the spectra of both modified paper samples, which indicated that C-O bonds increased on the paper surface after adding strength additives.

CONCLUSION

The present investigation allowed drawing a number of conclusions. Thus, CMH was found able to improve paper properties. The dry tensile index, burst index and folding endurance of the paper modified with 0.9% CMH increased by 42.40%, 18.60% and 81.77%, respectively, compared with the corresponding properties of the control sample.

CMH and PAE demonstrated a synergistic effect in improving paper properties. When 0.6% CMH and 0.6% PAE were used, the dry tensile index, wet tensile index and burst index increased by 15.03%, 43.22% and 11.38%, respectively, compared with the case when only 0.6% PAE was used.

CMH and CS also demonstrated a synergistic effect in improving paper properties. When 0.6% CMH and 0.6% CS were used, the dry tensile index, burst index and folding endurance increased by 17.53%, 3.34% and 282.38%, respectively, compared with the use of 0.6% cationic starch only.

FTIR-ATR analyses of the paper surface indicated that CMH, PAE and CS, as well as their binary systems, could increase C-O bonds on the paper surface, which led to improved paper properties. This was also proved by SEM analyses of the paper surface, cross-section and fracture.

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