Modified PCC used in Papermaking Processes

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Alkylketene dimer (AKD), cationic starch (CS), and polyamide epichlorohydrin (PAE) were used in the modification of precipitated calcium carbonate (PCC), and the use of the modified PCC in papermaking was investigated. It was found that after the PCC was modified, the sizing effectiveness of AKD was enhanced; when PAE was added to the filler, it had better modified effects than when CS was added. When the addition of PCC and AKD were fixed at 20% and 1% (based on the dry weight of PCC), respectively, the retention of PCC increased from 42.5% to 54.6% when modified by 5% CS, and to 56.7% when modified by 2% PAE. The strength properties (tensile indices, burst indices, and tear indices), opacity, and air permeability of the filled paper were strikingly enhanced, while the brightness was slightly negatively influenced by the addition of PAE. The results indicate that the pre-blend modified method is a promising technique for papermaking in that it enhanced the properties of paper.

Keywords: Polyamide polyamine epichlorohydrin; Cationic starch; Precipitated calcium carbonate; Modification; Papermaking

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INTRODUCTION

Paper is primarily composed of plant fibers and fillers (Shen *et al*. 2010). The proportion of fillers in paper is gradually increasing over time, and this trend allows energy and cost savings for producers and improvement in paper properties such as brightness, opacity, smoothness, ink absorption, and dimensional stability (Murray and Lyons 1956; Zhao *et al*. 2005; Chen *et al*. 2011a,b; Gupta *et al*. 2012). Currently, fillers are the second most significant portion by mass of paper stock in modern papermaking. Typical filler addition levels range from 3% to 30% (Scott 1996).

In the papermaking industry, the most popular fillers are precipitated calcium carbonate (PCC), ground calcium carbonates (GCC), kaolin clay, talc, and titanium dioxide (McKenzie and Davies 1971; Zhang *et al*. 2004; Yan *et al*. 2005; Pöykiö and Nurmesniemi 2008). The PCC is produced as rhombohedral, scalenohedral, needle shaped, or aragonite structures, with scalenohedral PCC being the most commonly used as filler in papermaking because of its relatively low price, wide availability, relatively high brightness, and opacity (Gaudreault *et al*. 2009). However, the use of fillers, especially at high dosages, has the following flaws or handicaps: (1) The strength of paper is unavoidably reduced because there are fewer fibers in a sheet. An increased

proportion of fillers in paper causes a decreased proportion of fibers and thus a reduction in the number of bonds between fibers. Stated another way, the presence of fillers reduces the contact area between fibers, which leads to a decline in paper strength (Beazley and Petereit 1975; Fairchild 1992; Gaudreault *et al*. 2009; Ibrahim *et al*. 2009); (2) Many paper properties are influenced by the competitive adsorption of chemical agents to fibers and fillers. For example, sizability of paper is very important not only to the running stability of a paper machine, but also to printing costs and the color information's reproduction from digital images to printing products. The amount of sizing agent required tends to increase with increasing surface area per unit mass of filler (Ozment and Colasurdo 1994; Hubbe 2006); (3) Use of fillers can induce abrasion to hydrofoils, the forming fabric, the table roll, press rolls, and calender rolls in a paper machine; and (4) Use of fillers can induce the degradation of an approach system's cleanliness. Low filler retention, followed by its deposition, can lead to obstruction of formation fabric, press felt, and dryer felt. According to the water treatment system, the treating difficulty and cost also tend to increase with increasing filler proportion in sheets.

To overcome these problems, much research has focused on improving the retention of fillers while avoiding the negative consequences they can have on paper properties (Hubbe 2004; Shen *et al*. 2009a,b,c,d; 2010a,b,c,d; Deng *et al*. 2010; Koivunen and Paulapuro 2010). In this study, PCC was used as the filler and alkyl ketene dimer (AKD) was used as the internal sizing agent. Polyamide epichlorohydrin (PAE) and cationic starch (CS) modifications of the filler were investigated to determine their effect on the physical and optical properties of paper.

EXPERIMENTAL

Materials

Raw materials

Northern bleached kraft pulp (NBKP) was supplied by Yongtai Co. Ltd. (Zhejiang, China). The PCC (92.3% ISO brightness), was obtained from Wuhuan Co. Ltd. (Guangxi, China). The CS had a substitution degree of 0.028 and was provided by Hengfeng Chemical Co. Ltd. (Zhejiang, China). The AKD was provided from the same source as the CS and had a solids content of 15% at pH 4.2 and ζ potential of 30.1 mV; its average diameter was determined to be 0.8 μm, and cationic starch was used as a stabilizer in the emulsion. The PAE had a solids content of 12.5% at pH 4.1 with charge density of 2.036 $mmol \cdot g^{-1}$, and was provided by Jiayun Chemical Technology Co. Ltd. (Hubei, China). The azetidinium ratio of the PAE was 80% with molecular weight of 80 thousand and viscosity of 35 mPa·s.

Mechanical refining

In this study, the pulp was refined to 31°SR by a Hollander type beater (ZQS2-23, SUST; Shanxi, China).

Preparation of pre-blended filler slurries

First, 130 mL of distilled water and 20 g of PCC filler were added together in a 500 mL four-neck round-bottom flask. This filler slurry was stirred to ensure sufficient mixing. Then, 50 g of AKD emulsion was prepared with various concentrations of the AKD sizing agent (*i.e.*, 1%, 2%, 4%, 6%, 8%, and 10%, based on the dry weight of PCC)

and distilled water. An appropriate amount of CS or PAE solution was added, and after 60 min stirring at 200 rpm the slurry was diluted to 1000 mL to facilitate its subsequent use. The final concentrations of modified filler slurries was 2% (Fig. 1). The ζ potential was measured using a Malvern Zetasizer 3000 at a stationary position. The mean size of the fillers was determined with a MS2000MU (Malvern; Worcestershire, UK) device. All the slurries were used within 12 h of preparation.

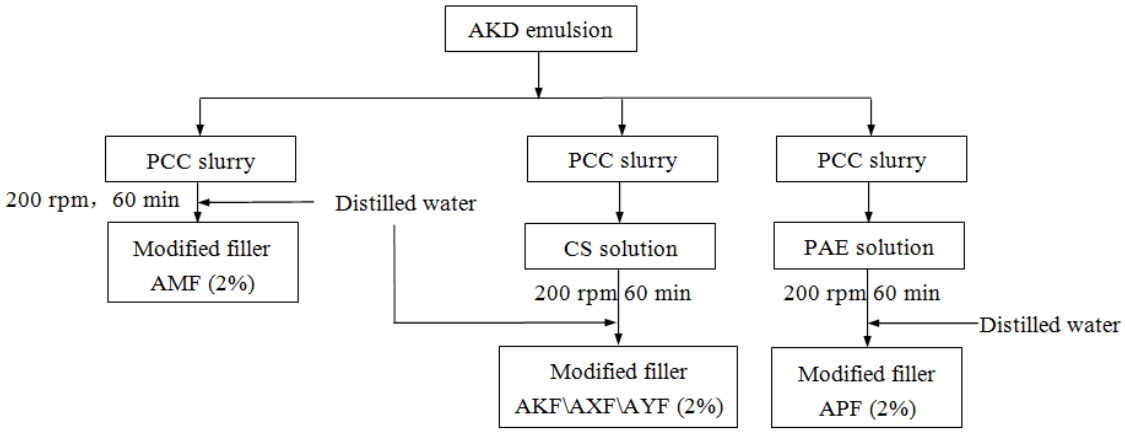

Fig. 1. Schematic diagram of preparation of pre-blended filler slurries. AMF = AKD+PCC; AKF = AKD+PCC+CS (1% to PCC); AXF = AKD+PCC+CS (3% to PCC); AYF = AKD+PCC+CS (5% to PCC); APF = AKD+PCC+PAE (2% to PCC)

Preparation of handsheets

The refined pulp was diluted to 1.2% consistency with distilled water and then was disintegrated in a standard disintegrator at 30,000 rpm until all fiber bundles were dispersed. After this, the pulp was diluted to a consistency of 0.3%. The pulp suspension was formed into handsheets with a base weight of 80 g/m^2 (Fig. 2).

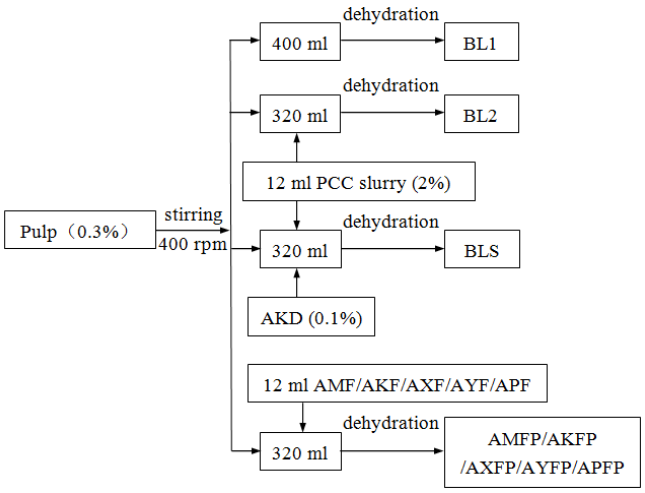

Fig. 2. Schematic diagram of preparation of handsheets. BL1 =Pulp; BL2 = Pulp+PCC; BLS = Pulp+AKD+PCC; AMFP = Pulp+AMF; AKFP = Pulp+AMF; AXFP = Pulp+AXF; AYFP = Pulp+AYF; APFP = Pulp+APF

The handsheets were prepared with a MODEL 1600 Ecno-Space automatic sheet former system (Réalisations Australes Inc., Canada) according to TAPPI T 205 sp-02 (2002) standards with the pressure modification for wet sheet pressing controlled at 200 kPa. This was followed by drying at 102 °C with a Formax 12" drum dryer (Thwing-Albert Instrument, USA). The handsheets were maintained in a controlled environment (23 ± 1 °C and relative humidity of 50 ± 1%) before analysis.

Scanning electron microscopy (SEM) analysis

Morphologies of the fracture surfaces were examined with a scanning electron microscope (SEM S3700, Hitachi, Japan) operating at an accelerating voltage of 10 kV. Before observation, the samples were coated with gold using a vacuum sputter-coater.

Fourier Transform Infrared Spectroscopy Analysis

Fourier transform infrared spectroscopy analysis (FTIR) of the samples was carried out in transmission mode using macro techniques (13 mm Φ pellet; *ca*. 1.5 mg sample with 350 mg KBr). The spectra were recorded with a Nexus Vector spectrometer made by Thermo Nicolet (Nexus 670, Thermo Nicolet Company, USA) under the following specifications: Apodization: triangular; Detector: DTGS/KBr; Regulation: 4 cm^{-1}; Number of scans: 32.

X-ray Diffraction Analysis

The X-ray powder diffraction patterns of the samples were recorded on Bruker D8 Advance X-ray diffractometer (step size 0.02°, 17.7 s per step). A generator with 40 kV and current of 40 mA was employed as a source for CuKα radiation.

Property measurement

The sizing degree of the handsheets was determined according to TAPPI Useful Method UM-429 (1991), and the contact angle of a water droplet on a sheet surface was measured on DSA 30S (Kruss, Germany) by drop method (The sheets were dried in a forced air circulation oven at 105 °C for 2 min before measurement). The tensile indices, burst indices, tear indices, brightness, opacity, and air permeability of the papersheets were determined according to TAPPI T 494 om-01, T 403 om-10, T 414 om-04, T 525 om-06, T 425 om-06, and T 460 om-11. The optical properties (brightness and opacity) were determined using a Micro TB-1C (Technidyne Corporation, USA). The strength properties (tensile, burst, and tear indices) of the paper sheets were determined using a CE 062 Tensile Strength Tester (Lorentzen & Wettre, Sweden), a CE180 Bursting Strength Tester (Lorentzen & Wettre, Sweden), and a Elmendorf Tear Tester (TMI, USA). The air permeability was determined using a Bendtsen ME-113 Roughness and Air Permeance Tester (Messmer Instruments Ltd., Testing Machines Inc., USA). Ash content of the fibers was measured according to ISO 2144 (1997) standards, and ash contents of the pulp and paper sheets were determined according to TAPPI T 413 om-85 (1985) standards. The retention efficiency of the fillers was calculated with Eq. (1):

$$R = \frac{(A-B)\cdot(1-L-C)}{(L-B)\cdot(1-A-C)} \times 100\% \quad (1)$$

where *A*, *B*, and *L* represent the ash content of the paper sheets, fiber, and pulp, respectively, and *C* represents the loss on ignition of the PCC (44%).

All samples were tested three times, with relative standard deviations of about 5%.

RESULTS AND DISCUSSION

Characterization of Fillers

The particle sizes of the fillers are shown in Table 1, which indicates that the sizes were slightly increased after modifications. The ζ potential of the suspension is also shown in Table 1. The original PCC filler was negatively charged in water. After modification the negative ζ potential of PCC was reduced in magnitude and even reversed to positive because AKD, CS, and PAE have high ζ potentials, which are more positive than that of the PCC.

Table 1. Characterization of PCC Fillers

Sample	Extension	Particle size(μm)	ζ potential（mV）
PCC	100PCC	2.40	-18.32
AMF	6AKD+100PCC	2.42	-15.58
AKF	6AKD+100PCC+1CS	2.46	-8.42
AXF	6AKD+100PCC+3CS	2.48	7.28
AYF	6AKD+100PCC+5CS	2.53	19.35
APF	6AKD+100PCC+2PAE	2.51	24.27

SEM Images of Fillers and Paper-sheets

The PCC can be produced in scalenohedral and rhombohedral morphologies of the calcite crystalline form, or as needle-shaped structures having the aragonite crystalline form. An SEM image of PCC particles used in this research is shown in Fig. 3a. It can be seen that the particles manifested a scalenohedral structure, which is the most widely used PCC structure in wet end papermaking (Gaudreault *et al*. 2009). SEM images of the paper-sheet without AKD sizing (Fig. 3b), the paper-sheet with unmodified PCC (Fig. 3c), and filled paper-sheets with modified PCC (Fig. 3d - Fig. 3f) are also shown in Fig. 3. It was found that the particles of modified PCC particles were more firmly adhered and bonded to the surfaces of fiber.

Function Group Analysis of Fillers

Figure 4 shows the FTIR spectra of the above mentioned samples. In spectra a, the 705 cm^{-1} and 875 cm^{-1} peak were attributed to the bending vibrations of C-O. The peak at 1425 cm^{-1} indicates the asymmetric stretching vibration of C-O, whereas the band at 1792 cm^{-1} might be assigned to the vibration of C=O.

In spectra b, c, and d, the weak peaks at 2920 cm^{-1}, 1016 cm^{-1} or 2380 cm^{-1} represent the stretching vibration of C-H, the stretching vibration of C-O and the characteristic stretching vibration of N-H. Those weak peaks indicating that the PCC particles were enveloped by AKD, CS or PAE molecules by physical adsorption.

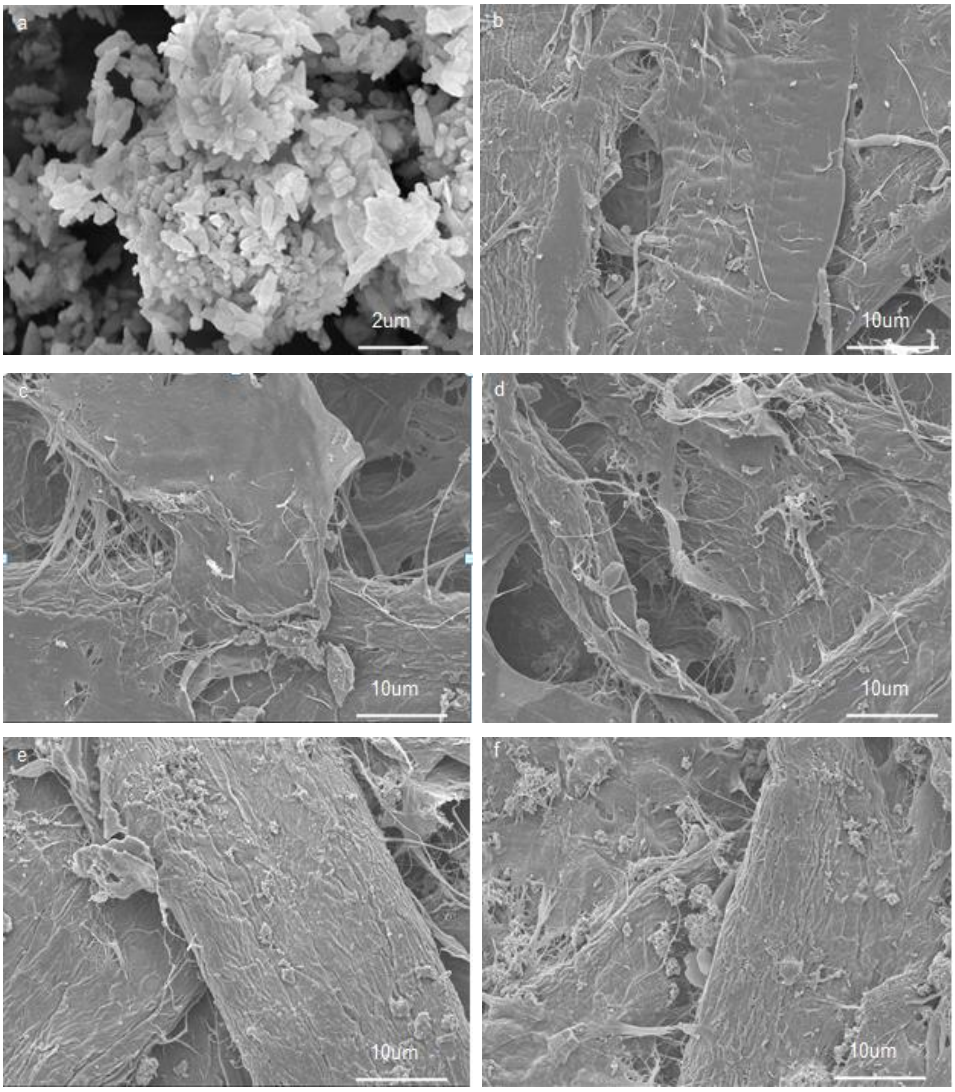

Fig. 3. SEM images of fillers and paper-sheets： (a) PCC; (b)BL2; (c) BLS; (d) AMFP; (e)AXFP; (f)APFP.(The dosage of bone dry AKD to PCC in corresponding sample was fixed on 6:100)

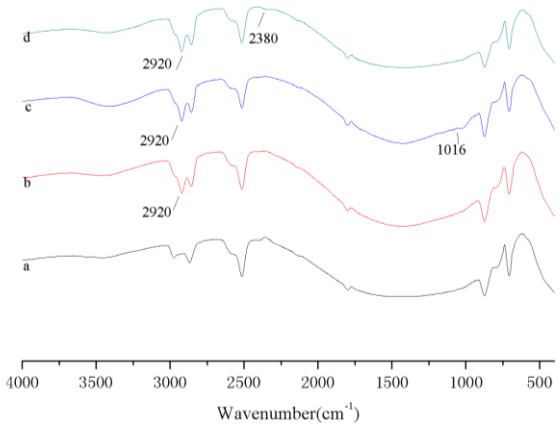

Fig. 4. FTIR spectra of different samples: (a) reference PCC; (b)AMF; (c) AXF; (d) APF.(The dosage of bone dry AKD to PCC in corresponding sample was fixed on 6:100)

XRD Patterns of Fillers

The XRD patterns of different samples are shown in Fig. 5. In patterns a, it can be found that the crystal of PCC is calcite, for which the diffraction peaks at 23.04°, 29.40°, 36.00°, 39.40°, 43.16°, 47.48°, and 48.50° represent the {012}, {104}, {110}, {113}, {202}, {018}, and {116} crystal planes, respectively. The relative intensity of {104} to other crystal planes was obviously weaker compared with pattern a, indicating that the morphology of PCC particles was significantly changed in modified processes.

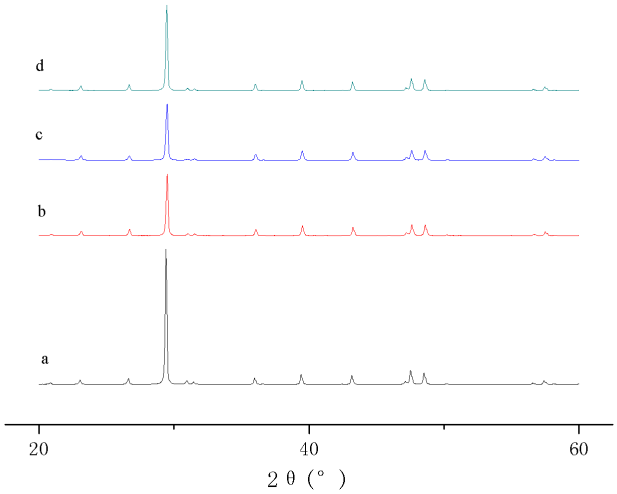

Fig. 5. XRD patterns of different samples: (a) reference PCC; (b)AMF; (c) AXF; (d) APF. (The dosage of bone dry AKD to PCC in corresponding sample was fixed on 6:100)

Sizing Degree of Paper Sheets

The sizing degree and the contact angle of water on the paper sheets are shown in Table 2 and Fig. 6. When the addition level of AKD to PCC was raised from 0% to 10%, the sizing degree of the paper sheets was increased accordingly. Compared with the control sample (BLS), the sizing degree of AMFP decreased slightly because during this processing, the AKD particles tended to drain with the filler particles instead of retaining themselves in the paper sheets. Although this was shown to have a negative influence on AKD sizing, the sizing degree of the paper sheets improved obviously when CS was used as a retention aid. The optimal CS addition amount was 3% (AXFP). When the CS addition was increased from 3% (AXFP) to 5% (AYFP), the sizing degree of the paper sheets was unchanged except for the samples for which the dosage of AKD was fixed at 8% (decreased for 1 s).

In contrast to the addition of CS, the addition of PAE enhanced the sizing effectiveness obviously when the dose of AKD was at 2%. The contact angle of different paper sheets also shows that PAE was able to achieve a better modified effect (Fig. 6). The open loop of epoxy groups in PAE molecules, which leads to the alkylation of secondary amines, is suggested as a major reason for this increase.

The lactone ring of the AKD was attacked by the PAE, which resulted in the opening and fixation of the lactone ring on the molecular chain of the PAE. The PAE molecules were irreversibly fixed on the surface of the fibers because of its strong adsorption bridging capabilities (Drahl *et al*. 2005). Because of this, the retention of AKD particles was also enhanced.

Table 2. The Sizing Degree of Paper Sheets

Dosage of AKD (%)	1	2	4	6	8	10
BLS	0	0	2	4	6	6
AMFP	0	0	2	3	5	5
AKFP	0	0	2	4	7	10
AXFP	0	0	3	5	9	11
AYFP	0	0	3	5	8	11
APFP	0	3	4	7	11	13

BLS = Pulp+AKD+PCC; AMFP = Pulp+AMF; AKFP = Pulp+AMF; AXFP = Pulp+AXF; AYFP = Pulp+AYF; APFP = Pulp+APF
unit: second

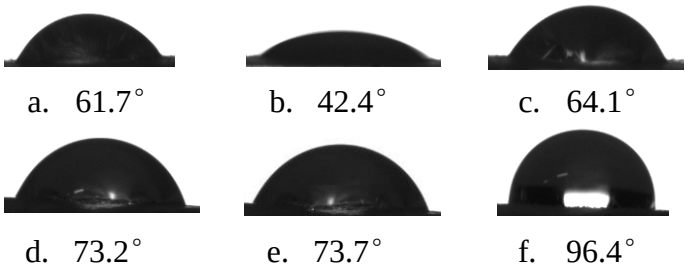

Fig. 6. Paper-sheet contact angles: (a) BLS; (b)AMFP; (c) AKFP; (d) AXFP; (e) AYFP; (f) APFP. (The ratio of dosages of bone dry AKD to PCC in corresponding sample was fixed at 6:100)
BL1 =Pulp; BL2 = Pulp+PCC; BLS = Pulp+AKD+PCC; AMFP = Pulp+AMF; AKFP = Pulp+AMF; AXFP = Pulp+AXF; AYFP = Pulp+AYF; APFP = Pulp+APF

Filler Retention

The influence of unmodified PCC and modified PCC fillers is shown in Table 3. The retention efficiency of fillers increased as the dosage of AKD increased because the formulation of the AKD emulsion needed not only to achieve high activity and easy hydrolysis, but also to render the emulsion stable relative to coagulation. Currently, commercial AKD emulsifiers include lignin sulfonate and natural polymers such as cationic starch. In papermaking processes, cationic starch can increase the adsorption of filler particles onto fibers so that they are retained with the fibers. In contrast to CS addition, PAE addition showed better retention effects in this study.

Table 3. Filler Retention

Dosage of AKD (%)	0	1	2	4	6	8	10
BL2 (no AKD added)	41.16						
BLS		42.50	42.88	43.21	43.95	44.51	46.16
AMFP		47.27	49.93	52.93	54.34	56.75	58.63
AKFP		49.39	51.27	53.23	55.36	58.36	61.63
AXFP		52.91	53.41	55.23	57.07	59.27	63.25
AYFP		54.64	55.27	56.45	57.69	61.64	65.52
APFP		56.68	58.30	59.21	62.79	64.75	67.79

BL2 = Pulp+PCC; BLS = Pulp+AKD+PCC; AMFP = Pulp+AMF; AKFP = Pulp+AMF; AXFP = Pulp+AXF; AYFP = Pulp+AYF; APFP = Pulp+APF; **unit: %**

Compared with the control sample (BL2), the retention rate of the APFP sample was increased by 64.7% (10% AKD). After the addition of PAE, fibers, fines, and PCC particles can be cross-linked to PAE molecules to form larger flocculation bodies by charge neutralization and the charged patch effect (Hsieh and Yoo 2010). The primary retention mechanism of cationic starch is electrostatic adsorption, which produces microfloc-enclosing fines and PCC particles (Kela *et al*. 2007).

Strength Properties of Paper Sheets

The influences of different fillers on the tensile and burst indices of the paper sheets are shown in Tables 4 and 5, respectively. Compared to the control group (BL1), strength properties of other groups were remarkably reduced because the addition of filler in papersheet reduces the fiber-fiber bonding area. When the addition of PCC and AKD were fixed at 20% and 1%, respectively, the following was found: the tensile index of the paper sheets was increased from 60.82 N•m/g to 64.74 N•m/g (modified by 5% CS) and 65.65 N•m/g (modified by 2% PAE), and the burst index of the paper sheets was increased from 4.44 kPa•m²/g to 5.23 kPa•m²/g (modified by 5% CS) and to 5.25 kPa•m²/g (modified by 2% PAE).

Table 4. Tensile Indices of Paper Sheets

Dosage of AKD (%)	0	1	2	4	6	8	10
BL1 (no AKD added)	69.31						
BL2 (no AKD added)	53.82						
BLS		60.82	60.07	58.63	57.94	55.39	55.25
AMFP		56.34	55.76	54.94	54.65	53.86	51.45
AKFP		62.21	62.06	58.58	58.17	57.19	56.20
AXFP		62.54	62.15	61.71	61.08	60.03	59.45
AYFP		64.74	62.81	62.32	61.95	60.86	57.39
APFP		65.65	65.35	65.07	64.83	62.31	59.46

BL1 =Pulp; BL2 = Pulp+PCC; BLS = Pulp+AKD+PCC; AMFP = Pulp+AMF; AKFP = Pulp+AMF; AXFP = Pulp+AXF; AYFP = Pulp+AYF; APFP = Pulp+APF
unit: N•m/g

Table 5. Burst Indices of Paper Sheets

Dosage of AKD (%)	0	1	2	4	6	8	10
BL1 (no AKD added)	5.92						
BL2 (no AKD added)	4.77						
BLS		4.44	4.42	4.37	4.34	4.16	4.09
AMFP		4.85	4.75	4.50	4.44	4.39	4.29
AKFP		5.18	4.73	4.64	4.44	4.36	4.30
AXFP		5.13	5.08	5.02	4.87	4.76	4.75
AYFP		5.23	5.04	4.95	4.84	4.74	4.66
APFP		5.25	5.22	5.07	4.96	4.95	4.67

BL1 =Pulp; BL2 = Pulp+PCC; BLS = Pulp+AKD+PCC; AMFP = Pulp+AMF; AKFP = Pulp+AMF; AXFP = Pulp+AXF; AYFP = Pulp+AYF; APFP = Pulp+APF
unit: kPa·m²/g

As for the strengthening mechanisms of PAE, covalent bond formation between the 3-hydroxy-azetidinium (AZR) groups of PAE and the carboxyl groups slightly present in pulps have been researched (Su *et al*. 2012). The retention and reactivity of PAE could be influenced by the introduction of carboxyl groups to fibers through sulfate pulping, bleaching, and other processes (Li *et al*. 2013; Ma and Zhai 2013; Wang and Song 2013). In the role of electrostatic attraction, cationic heterocyclic butadiene in PAE was attracted by negatively carboxyl groups on the surface of fibers, so insoluble covalent bonds between fibers may have been formed.

Table 6 shows the relationship between different fillers and tear indices of the paper sheets. When the addition level of AKD increased from 1% to 10%, the tear indices of paper sheets increased first, and then decreased when the addition level reached a certain percent. The tear indices were not only affected by the length and strength of the fibers individually, but also by the number and strength of the fibers combined. When the addition level of AKD increased, bonds between the fibers were hindered by hydrophobic AKD particles (Roberts 1996). However, the tear indices of the paper sheets increased because of the increased number of fibers pulled out of the paper sheets. When higher levels of AKD were applied, the tear indices of the paper sheets decreased. The loss of bond strength between the fibers plays a major role in this decrease in tear indices.

Table 6. Tear Indices of Paper Sheets

Dosage of AKD (%)	0	1	2	4	6	8	10
BL1 (no AKD added)	29.10						
BL2 (no AKD added)	26.82						
BLS		25.06	25.86	27.34	29.27	27.29	26.23
AMFP		27.55	28.34	28.57	28.63	29.72	27.01
AKFP		24.75	25.61	26.65	27.06	28.28	26.42
AXFP		26.04	26.43	27.87	32.06	33.69	29.18
AYFP		24.21	24.94	26.26	26.42	31.27	30.14
APFP		26.93	27.35	27.82	27.97	30.66	28.83

BL1 =Pulp; BL2 = Pulp+PCC; BLS = Pulp+AKD+PCC; AMFP = Pulp+AMF; AKFP = Pulp+AMF; AXFP = Pulp+AXF; AYFP = Pulp+AYF; APFP = Pulp+APF
unit: mN .m²/g

Optical Properties of Paper Sheets

As can be seen in Table 7 compared with the blank group (BL1), addition of 20% natural PCC (BL2) led to an increase in brightness (about 2.3%). The addition of PCC modified by CS resulted in a slight increase in brightness, and brightness increased as the CS addition levels increased. The major reason behind this was the increased filler retention rate. The addition of AKD had little or no effect on brightness, and the addition of PAE to the PCC resulted in a small decrease in brightness because of the yellowish color of the PAE aqueous solution (Fang *et al*. 2010).

From Table 8, it can be seen that compared with the blank group (BL1), addition of 20% natural PCC (BL2) led to an increase in opacity (about 4.3%). In groups BLS, AMFP, AKFP, AXFP, and AYFP, the opacity of the paper sheets increased as the CS dosage increased. In each group, the opacity increased when higher levels of AKD were applied due to the emulsifiers in the AKD latex (Mohlin *et al*. 2006). In contrast with the

CS groups (AKFP, AXFP and AYFP), the PAE group (APFP) displayed higher opacity because it retained PCC better.

Table 7. Brightness of Paper Sheets

Dosage of AKD (%)	0	1	2	4	6	8	10
BL1 (no AKD added)	85.06						
BL2 (no AKD added)	86.99						
BLS		87.42	87.42	86.93	86.89	86.93	86.63
AMFP		87.45	87.75	87.78	86.25	87.17	87.23
AKFP		87.56	87.71	87.80	88.12	87.38	87.83
AXFP		88.37	88.31	88.33	87.69	87.81	87.52
AYFP		87.89	87.69	87.42	87.79	88.40	88.27
APFP		83.22	84.15	84.12	84.39	84.69	84.14

BL1 =Pulp; BL2 = Pulp+PCC; BLS = Pulp+AKD+PCC; AMFP = Pulp+AMF; AKFP = Pulp+AMF; AXFP = Pulp+AXF; AYFP = Pulp+AYF; APFP = Pulp+APF
unit: %ISO

Table 8. Opacities of Paper Sheets

Dosage of AKD (%)	0	1	2	4	6	8	10
BL1 (no AKD added)	69.70						
BL2 (no AKD added)	72.71						
BLS		73.04	73.12	73.75	74.53	74.86	75.55
AMFP		73.39	73.44	74.19	75.25	75.27	75.86
AKFP		73.76	73.83	74.21	76.10	76.36	77.74
AXFP		73.92	74.86	74.90	76.57	77.17	77.97
AYFP		74.39	75.60	76.49	77.09	78.01	78.38
APFP		75.15	76.10	76.76	77.41	78.50	78.92

BL1 =Pulp; BL2 = Pulp+PCC; BLS = Pulp+AKD+PCC; AMFP = Pulp+AMF; AKFP = Pulp+AMF; AXFP = Pulp+AXF; AYFP = Pulp+AYF; APFP = Pulp+APF
unit: %

Table 9. Air Permeability of Paper Sheets

Dosage of AKD (%)	0	1	2	4	6	8	10
BL1 (no AKD added)	2.12						
BL2 (no AKD added)	3.32						
BLS		3.35	3.41	3.55	3.62	3.74	3.88
AMFP		3.43	3.55	3.61	3.74	3.85	3.98
AKFP		3.50	3.64	3.75	3.82	3.91	3.96
AXFP		3.63	3.77	3.85	3.91	3.98	4.09
AYFP		3.76	3.89	4.05	4.18	4.29	4.32
APFP		3.84	3.93	4.14	4.27	4.35	4.47

BL1 =Pulp; BL2 = Pulp+PCC; BLS = Pulp+AKD+PCC; AMFP = Pulp+AMF; AKFP = Pulp+AMF; AXFP = Pulp+AXF; AYFP = Pulp+AYF; APFP = Pulp+APF
unit: um/Pa·s

Air Permeability of Paper Sheets

Table 9 shows the influence by different fillers on air permeability of the paper sheets. Compared with the blank group (BL1), addition of 20% natural PCC (BL2) led to the increase of air permeability (about 56.6%). The air permeability of the paper sheets was enhanced obviously by CS and PAE modifications because of the increase of retention rate of the fillers. This result concurs with earlier reports in that fillers increase air permeability and porosity of paper (Shen *et al*. 2010a).

CONCLUSIONS

1. In the presence of cationic starch (CS) or polyamide-epichlorohydrin wet-strength agent (PAE), the sizing effectiveness of alkylketene dimer (AKD) was enhanced, and the addition of PAE had better modified effects than when CS was added.
2. The retention rate of precipitated calcium carbonate (PCC) can be enhanced by the addition of CS and PAE. When the addition of PCC and AKD were fixed at 20% and 1%, respectively, the retention of PCC can be increased from 42.5% to 54.6% (modified by 5% CS) and to 56.7% (modified by 2% PAE).
3. The strength properties (tensile indices, burst indices, and tear indices), opacity, and air permeability of the modified, filled paper was strikingly enhanced, but the brightness was negatively influenced slightly by the addition of PAE.

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