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Carboxymethyl cellulose/alum modified precipitated calcium carbonate fillers: Preparation and their use in papermaking

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ABSTRACT

Carboxymethyl cellulose and alum were used in the modification of precipitated calcium carbonate filler, and the use of modified fillers in papermaking was investigated. The alum dosage was found to be much critical to the effective precipitation and encapsulation of carboxymethyl cellulose on filler surfaces. When the dosages of carboxymethyl cellulose and alum were 4% and 12% (based on the dry weight of precipitated calcium carbonate), respectively, filler modification significantly improved filler retention by as much as 71.5%, and the brightness and opacity of the filled paper were strikingly enhanced; however, paper strength was practically unchanged, indicating improved affinity of filler particles to fibers in the aqueous papermaking wet end system. XPS analysis and SEM observations of the fillers confirmed the surface encapsulating effect of the modifiers on the filler. SEM images of the paper-sheets indicated that modified filler particles were more effectively adhered and bonded to the pulp fibers, in comparison to unmodified filler particles.

1. Introduction

Paper is mainly made of cellulosic pulp fibers derived from renewable natural bioresources including wood and non-wood lignocellulosic materials. For most paper grades such as printing and writing papers, fillers are usually the second most important component of the paper stock (Zhao et al., 2008) as far as their added amounts are taken into consideration. Globally, the use of fillers in papermaking is now a very common practice to meet the needs of papermakers. Many benefits can be achieved as a result of filler addition, which mainly include cost and energy savings (Dong, Song, Patterson, Ragauskas, & Deng, 2008), increased furnish drainage rate, and improvement in optical properties, printability, and appearance of paper products. Also, as claimed by Ragauskas and Deng (2009) at IPST (Institute of Paper Science and Technology at Georgia Institute of Technology) in their GA TIP3 Projects Review of 2009, the substitution of pulp fibers with fillers can potentially reduce the carbon footprint of papermaking. Moreover, it is worth noting that, by use of specialty or functional fillers with certain unique attributes, paper can possibly be functionalized, engineered, or even "smartized" to suit specific end uses. Obviously, for the entire papermaking industry, the benefits associated with filler addition seen self-evident.

However, the use of fillers, especially at high loading levels, is usually considered to have certain disadvantages, obstacles, or limitations, such as deteriorated paper strength, poor filler retention, decreased sizing efficiency and bending stiffness, increased wire abrasion, and "dusting" during printing. In order to overcome or alleviate at least one of the drawbacks associated with filler addition, many methods have been reported or industrially practiced, which generally include fiber loading by incorporating fillers into the lumens and/or cell walls of pulp fibers (Klungness, Ahmed, Ross-Sutherland, & AbuBakr, 2000), pulp fines-filler complexation by premixing fillers with fines/fibrils or in situ precipitation of filler particles on fines/fibrils (Silenius, 2003; Subramanian, Fordsmand, Paltakari, & Paulapuro, 2008; Subramanian, Fordsmand, & Paulapuro, 2007; Subramanian, Maloney, Kang, & Paulapuro, 2006; Subramanian, Maloney, & Paulapuro, 2005), substitution of traditional fillers with novel fillers (such as starch-based biodegradable organic fillers, and fibrous/high-aspect-ratio inorganic fillers) with specifically desired attributes (Hu & Deng, 2004; Mathur, 2004; Mollaahmad, 2008; Peltonen, Mikkonen, & Qvintus-Leino, 2006; Shen, Song, & Qian, 2010), use of functional strengthening agents before the wet

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web formation of paper (Chen, Huang, & Pelton, 2005; Fahmy & Mobarak, 2008a, 2009), fiber modification (Bratskaya, Schwarz, Petzold, Liebert, & Heinze, 2006; Kang, 2007), and filler modification (Gill, 1992; Ibrahim, Mobarak, El-Din, Ebaid, & Youssef, 2009; Laleg, Collins, Gagne, & Middleton, 2008; Shen, Song, Qian, & Liu, 2009a; Shen, Song, Qian, Liu, & Yang, 2010; Song, Dong, Ragauskas, & Deng, 2009a,b; Zunker, 1985).

In recent years, filler modification for papermaking has been frequently reported. In some sense, among the numerous filler modification methods available in the literature, the use of biodegradable and renewable carbohydrate polymers (such as starch, cellulose, and chitosan) as modifiers is a very interesting and promising research topic (Deng, Yoon, Ragauskas, & White, 2008; Fairchild, 2008; Kurrle, 1996; Lambert & Lowes, 1975; Myllymäki, Aksela, Sundquist, & Karvinen, 2006; Nelson & Deng, 2008; Shen, Song, & Qian, 2009; Shen, Song, Qian, & Song, 2008; Song et al., 2009a,b; Yan, Liu, & Deng, 2005; Yoon, 2007; Yoon & Deng, 2006a,b, 2007; Zhao, Hu, Ragauskas, & Deng, 2005; Zhao et al., 2008). It is well known that, the main component of paper, i.e., pulp fibers, is closely related to carbohydrate polymers, and certain carbohydrate polymers are widely considered to be suitable for use in papermaking to optimize the manufacturing processes, and/or to improve paper properties (Fahmy, 2007a,b; Fahmy & Mobarak, 2008b; Fahmy, Mobarak, Fahmy, Fadl, & El-Sakhawy, 2006; Fatehi, Kititerakun, Ni, & Xiao, 2010; Fernandes et al., 2009; Li, Du, Xu, Zhan, & Kennedy, 2004; Lima, Oliveira, & Buckeridge, 2003; Nada, El-Sakhawy, Kamel, Eid, & Adel, 2006; Ren, Peng, Sun, & Kennedy, 2009). As the commonly used fillers are generally not capable of forming bonds with fibers, filler modification with carbohydrate polymers can potentially enhance the compatibility between fillers and fibers, and can possibly confer certain beneficial attributes of carbohydrate polymers to fillers. Based on the available scientific publications, the advantages associated with the use of carbohydrate polymers in filler modification can at least include such aspects as low cost, easy availability and environmental friendliness of the modifiers, enhanced paper strength, improved filler retention, or increased filler loading levels, and the successful commercialization of the relevant technologies can undoubtedly provide numerous benefits to the papermaking industry.

In this work, the use of a very common carbohydrate polymer with natural compatibility and affinity with cellulosic pulp fibers, i.e., carboxylmethyl cellulose, in combination with alum (a widely used papermaking additive), in the modification of a papermaking grade precipitated calcium carbonate filler, was explored for the first time, and the use of the resulting modified fillers in papermaking was investigated.

2. Experimental

2.1. Materials

Carboxymethyl cellulose with the trademark of Finnfix® 5 was supplied by CP Kelco (a Huber company), and its degree of substitution was claimed to be 0.60–0.95. The macroscopic photo of carboxymethyl cellulose taken with a canon camera is shown in Fig. 1(a). Papermaking grade precipitated calcium carbonate filler with ISO brightness of 92.4% was supplied by Guangxi Guilin Wuhuan Co., Ltd., China, and its mean diameter was tested to be 2.3 μm using a Laser Diffraction Particle Size Analyzer (LS320, Beckman Coulter, Miami, FL, USA). The carboxymethyl cellulose and precipitated calcium carbonate were all used as received.

Commercial bleached chemical pulp (softwood) with ash content of 0.86% was provided by Heilongjiang Mudanjiang Hengfeng Paper Co., Ltd., China, and was refined in a Valley beater to beating degree of 39.0° SR. The pulp characteristics were measured using a KajaaniFS300 Fiber Analyzer (Metso Automation Inc., Finland), and the results are listed in Table 1. Alum was an analytical reagent produced by Tianjin Kaitong Chemicals Co., Ltd., China.

2.2. Filler modification

20 g precipitated calcium carbonate filler and 130 mL distilled water were added into a 500 mL four-neck round-bottom flask. The filler slurry was stirred to ensure sufficient mixing. 200 mL freshly prepared polymer solution containing 0.8 g carboxymethyl cellulose was added to the slurry, and the mixture was stirred for 30 min. The freshly prepared alum solution was then instantly poured into the above mixture, and the resulting mixture was further stirred for 10 min. The modified filler slurry was then diluted to 1000 mL to facilitate its subsequent use.

After sufficient agitating, a portion of the 1000 mL slurry was added to a 250 mL beaker, and macroscopic optical photograph was taken after storing the slurry (in a stationary manner) for 24 h to roughly investigate and demonstrate the influence of alum dosage on filler modification. As shown in Fig. 1(b), the supernatant was quite clear at relatively high alum dosages, i.e., above 10%, based on the dry weight of precipitated calcium carbonate filler, possibly indicating the effective precipitation and encapsulation of carboxymethyl cellulose on the filler surfaces. As illustrated in Fig. 1(c), in addition to the encapsulation of one single filler particle, the simultaneous encapsulation of several particles to bind them together was also thought to be possible. This presumption of the schematic structures of modified filler particles was generally referenced from the available publications on filler modification using the starch or regenerated cellulose encapsulation/coating methods (Deng et al., 2008; Nelson & Deng, 2008; Song et al., 2009a,b; Yan et al., 2005; Yoon, 2007; Yoon & Deng, 2006a,b, 2007; Zhao et al., 2005, 2008).

2.3. Paper-sheet preparation and determination of paper properties

Paper-sheets with target basis weight of 60 g/m^2 were prepared using MODEL 1600 Econo-Space Automatic Sheet Former System (Réalisations Australes Inc., Canada) according to TAPPI T 205 (except that the pressure for wet sheet pressing was controlled at 200 kPa), and the sheets were dried at 103 °C using a Formax 12″ Drum Dryer (Thwing-Albert Instrument Company, USA). The target loading level was controlled at 20% (based on the total dry weight of pulp and filler), and no retention agent was used during the sheet formation processes. For the use of unmodified precipitated calcium carbonate in combination with carboxymethyl cellulose in sheet formation, the amount of carboxymethyl cellulose was 0.8%, based on the total dry weight of filler and pulp, i.e., 4%, based on the dry weight of the filler. The paper-sheets were conditioned

Table 1
Characteristics of pulp fibers.

Item	Fiber length (mm)	Projection length (mm)	Fines content (%)	Fiber width (μm)	Fiber kink (1/m)	Fiber curl (%)
Length-weighted	1.98	1.51	4.41	22.85	1362.86	25.24
Weight-weighted	2.80	2.15	–	24.14	1095.93	32.67
Arithmetic	0.78	0.63	35.76	21.03	1975.18	19.06

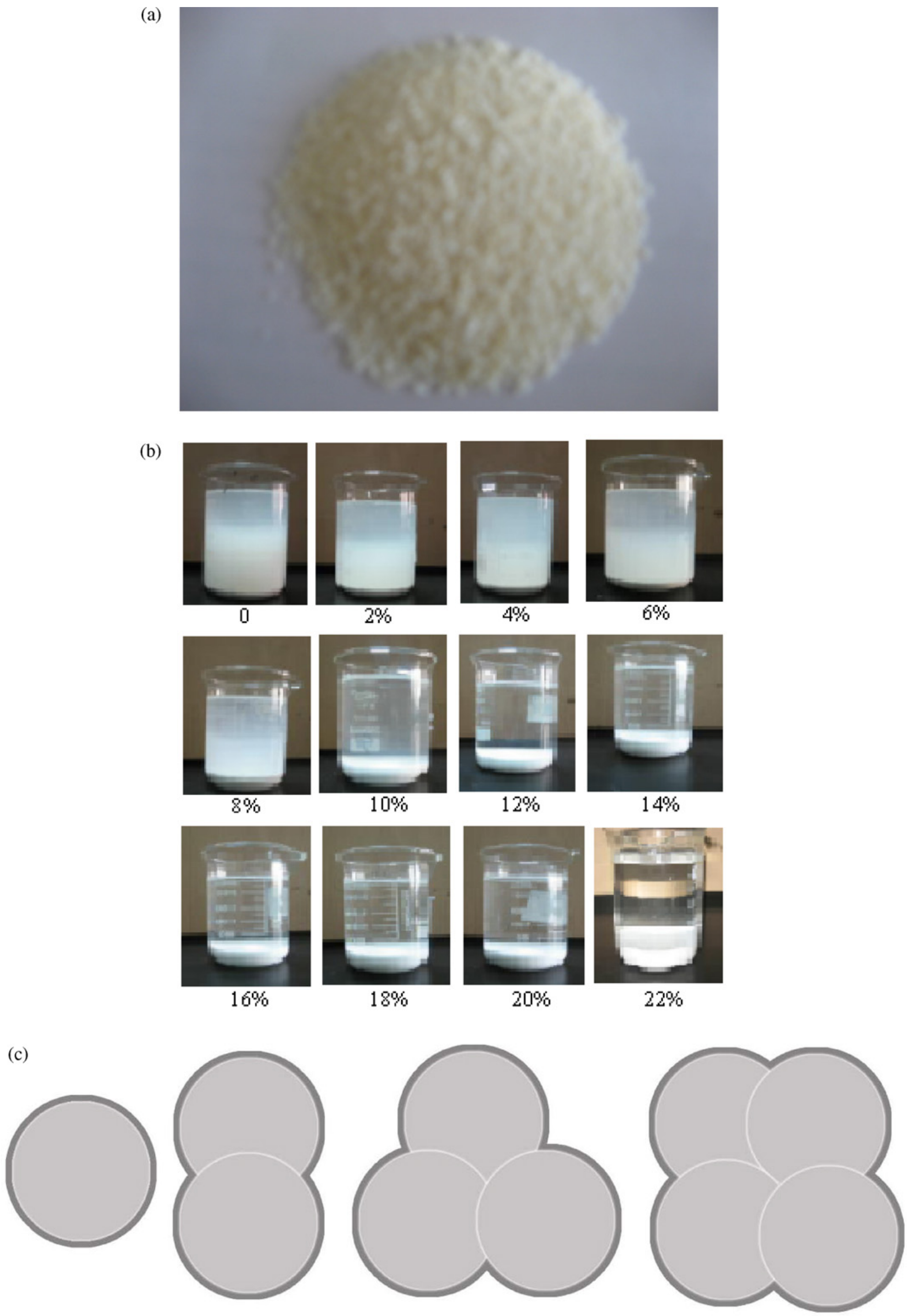

Fig. 1. Macroscopic optical photographs of (a) carboxymethyl cellulose and (b) modified filler slurries (at different alum dosages) taken with a digital camera (Canon), and presumed illustrative structures of the modified filler particles at high alum dosages of above 10% (c).

under controlled environment (temperature of 23 ± 1 °C and relative humidity of 50 ± 1%) before analysis.

The strength properties (tensile, burst, and tear indices) of the paper-sheets were determined using the L&W CE062 Tensile Strength Tester (Sweden), L&W Bursting Strength Tester with the code of 180 (Sweden) and TMI Elmendorf Tear Tester (USA). The optical properties (brightness and opacity) of the paper-sheets were determined using a Technibrite Micro TB-1C optical tester (New Albany, IN, USA). The air permeability values of the paper-sheets were measured using a Bendtsen ME-113 Roughness and Air Permeance Tester (Messmer Instruments Ltd., Testing Machines Inc., USA), and the thickness values were measured using a ZH-4 paper/paperboard thickness tester (China), and the values of apparent density was then calculated based on thickness and grammage. The paper-sheet properties were all determined according to the standards.

Table 2
Filler retention in the paper-sheets.

Sample	Alum dosage (%)	Filler retention (%)	Increased percentage of filler retention (%)
Unmodified precipitated calcium carbonate filler	–	36.5	–
Unmodified precipitated calcium carbonate filler used in combination with carboxymethyl cellulose	–	41.3	13.2
Modified precipitated calcium carbonate filler	0	46.7	27.9
	6	48.2	32.1
	8	50.9	39.5
	10	54.0	47.9
	12	62.6	71.5
	14	56.8	55.6
	20	53.8	47.4

2.4. Evaluation and estimation of filler retention

At 525 °C, the paper-sheets with the target amount of filler incorporated in each sheet of 0.24 g were incinerated in a muffler oven according to TAPPI T 211, and the ash weight values were calculated. Filler retention (R) was evaluated and estimated using the following equation:

$$R(\%) = \frac{A_1 - A_2}{A} \times 100$$

where A_1 is the total weight of ash in the sheet, A_2 is the weight of ash in the sheet originating from pulp fibers, and A is the weight of filler incorporated in each sheet.

2.5. XPS analysis and SEM observations

X-ray photoelectron spectroscopy (XPS) analysis of fillers was performed with a Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, UK), AlKα X-ray was used as the X-ray source (1486.6 eV, 15 kV, 10 mA). Scanning electron microscopy (SEM) observations of fillers and paper-sheets were performed with a scanning electron microscopy (SEM, QUANTA 200).

3. Results and discussion

3.1. Filler retention

The retention of fillers has always been a hot topic in the research area of papermaking wet end chemistry, and the retention efficiency strongly influences the cost of the product, cleanliness of the papermaking system, and pollution load of the disposal system (Vengimalla, Chase, & Ramarao, 1999). Therefore, it is quite necessary to firstly investigate the retention performances of modified precipitated calcium carbonate fillers.

The retention of unmodified precipitated calcium carbonate filler and modified precipitated calcium carbonate fillers is shown in Table 2. The use of unmodified precipitated calcium carbonate filler only resulted in filler retention of as low as 36.5%. When carboxymethyl cellulose with amount of 0.8% (based on the total dry weight of pulp and filler) was added, the retention of unmodified precipitated calcium carbonate filler was increased by 13.2%. Thus, under our experimental conditions, the addition of carboxymethyl cellulose can give certain positive effect on the retention of unmodified precipitated calcium carbonate filler.

Compared with the use of unmodified precipitated calcium carbonate filler as well as the combined use of unmodified precipitated calcium carbonate filler and carboxymethyl cellulose, modified precipitated calcium carbonate fillers all gave higher filler retention. Most strikingly, the modification of precipitated calcium carbonate filler with carboxymethyl cellulose and alum with dosages of 4% and 12% (based on the dry weight of precipitated calcium carbonate filler), respectively, improved filler retention by as much as 71.5%.

With the increasing dosage of alum in the range of 0–12%, the retention performance of modified precipitated calcium carbonate was improved gradually. However, further increase in alum dosage lowered the retention performance.

3.2. Optical properties of the papers

Besides cost reductions, the improvement in optical properties of the papers is generally the most important contribution of fillers to papermakers. When considering the development of new filler technologies, the effect of filler addition on the optical properties of the papers should always be taken into consideration. For calcium carbonate fillers, their optical properties and low cost are always the main considerations of worldwide papermakers when switching from acid papermaking to neutral-to-alkaline papermaking.

Table 3
Optical properties of the paper-sheets.

Sample	Alum dosage (%)	Brightness (%ISO)	Opacity (%)
Paper-sheets with no filler added	–	82.63	71.91
Paper-sheets filled with unmodified precipitated calcium carbonate filler	–	84.83	73.90
Paper-sheets filled with unmodified precipitated calcium carbonate filler with carboxymethyl cellulose added	–	83.09	69.31
Paper-sheets filled with modified precipitated calcium carbonate filler	0	85.12	70.60
	6	85.25	71.73
	8	86.35	72.35
	10	86.32	72.35
	12	87.65	75.25
	14	87.15	73.40
	20	87.12	75.54

Table 4
Strength properties of the paper-sheets.

Sample	Alum dosage (%)	Tensile index (N m/g)	Burst index (kpa m^2/g)	Tear Index (mN m^2/g)
Paper-sheets with no filler added	–	78.02	6.63	24.43
Paper-sheets filled with unmodified precipitated calcium carbonate filler	–	62.60	4.83	24.31
Paper-sheets filled with unmodified precipitated calcium carbonate filler with carboxymethyl cellulose added	–	67.04	5.43	23.15
Paper-sheets filled with modified precipitated calcium carbonate filler	0	70.63	5.58	25.86
	6	69.17	5.49	26.23
	8	68.84	5.63	37.24
	10	68.54	5.62	37.26
	12	60.19	4.71	27.34
	14	64.91	5.15	34.60
	20	60.92	4.82	33.43

The brightness and opacity of the unfilled paper and the papers filled with unmodified precipitated calcium carbonate filler and modified precipitated calcium carbonate fillers are shown in Table 3.

The brightness values of the filled papers were all higher than that of the unfilled paper, as a result of the incorporation of high brightness fillers in the sheets. Among the paper samples, the brightness of the paper filled with modified precipitated calcium carbonate filler prepared with alum dosage of 12% was the highest. As shown in Tables 2 and 3, among the seven modified precipitated calcium carbonate fillers, the use of modified precipitated calcium carbonate filler prepared with alum dosage of 12% simultaneously gave the highest filler retention and highest paper brightness, indicating high consistency of filler retention with paper brightness.

For opacity, the papers filled with modified precipitated calcium carbonate fillers with alum dosages of 12% and 20% gave much similar values, and the values were much all higher than that of other paper samples.

Therefore, among the fillers used in this work, modified precipitated calcium carbonate filler prepared with alum dosage of 12% generally gave the best contribution to the improvement in brightness and opacity of the paper. Generally, the optical properties of the filled paper depend on many factors such as chemical composition of the filler, particle morphology, particle size, and filler content. The significant improvement in brightness and opacity of the paper as a result of the use of modified filler prepared with alum dosage of 12% was principally thought to be due to its highest filler retention, in comparison to other fillers used in this work.

3.3. *Strength properties of the papers*

It has been widely accepted that, when mineral fillers are used in papermaking, especially at relatively high loading levels, they can usually result in strikingly reduced paper strength (Deng et al., 2008; Fahmy & Mobarak, 2008a, 2009; Fairchild, 2008; Kurrle, 1996; Ibrahim et al., 2009; Laleg et al., 2008; Silenius, 2003; Song et al., 2009a,b; Subramanian et al., 2005, 2006, 2007, 2008; Yan et al., 2005; Yoon, 2007; Yoon & Deng, 2006a,b, 2007; Zhao et al., 2005, 2008), which can be manifested in the following two aspects:

- Mineral fillers can undoubtedly interfere with fiber-to-fiber bonding due to the poor bondabilities of filler matrices.
- Substitution of fibers with mineral fillers results in reduced number or amount of fibers in the paper matrix, which can inevitably play a negative role in the development of paper strength.

The strength properties (tensile, burst, and tear indices) of the unfilled paper and the papers filled with unmodified precipitated calcium carbonate filler and modified precipitated calcium carbonate fillers are shown in Table 4.

The tensile and burst indices of the filled papers were all lower than that of the unfilled paper due to the incorporation of fillers in the fiber matrices. On the other hand, generally, tearing strength was not negatively influenced as a result of filler addition.

As shown in Tables 2 and 4, the incorporation of carboxymethyl cellulose and unmodified precipitated calcium carbonate filler in the sheet improved the tensile/bursting strength of paper and filler retention simultaneously, and the tearing strength was practically unaffected. Thus, the direct wet end addition of carboxymethyl cellulose possibly improved the bonding capacity of the filler, resulting in improved paper strength and filler retention. When alum dosages were 0, 2%, 4%, 6%, 8%, 10%, and 14%, the use of modified precipitated calcium carbonate fillers all gave better paper strength and higher filler retention, in comparison to the single use of unmodified precipitated calcium carbonate filler, and the combined use of unmodified precipitated calcium carbonate filler and carboxymethyl cellulose. When the alum dosages were 12% and 20%, the use of modified precipitated calcium carbonate fillers

Table 5
Air permeability and apparent density of the paper-sheets.

Sample	Alum dosage (%)	Air permeability (μm/Pa s)	Apparent density (g/cm^3)
Paper-sheets with no filler added	–	1.41	0.66
Paper-sheets filled with unmodified precipitated calcium carbonate filler	–	2.99	0.63
Paper-sheets filled with unmodified precipitated calcium carbonate filler with carboxymethyl cellulose added	–	2.79	0.62
Paper-sheets filled with modified precipitated calcium carbonate filler	0	2.78	0.63
	6	3.35	0.61
	8	3.45	0.61
	10	2.90	0.61
	12	4.00	0.62
	14	3.99	0.60
	20	3.51	0.62

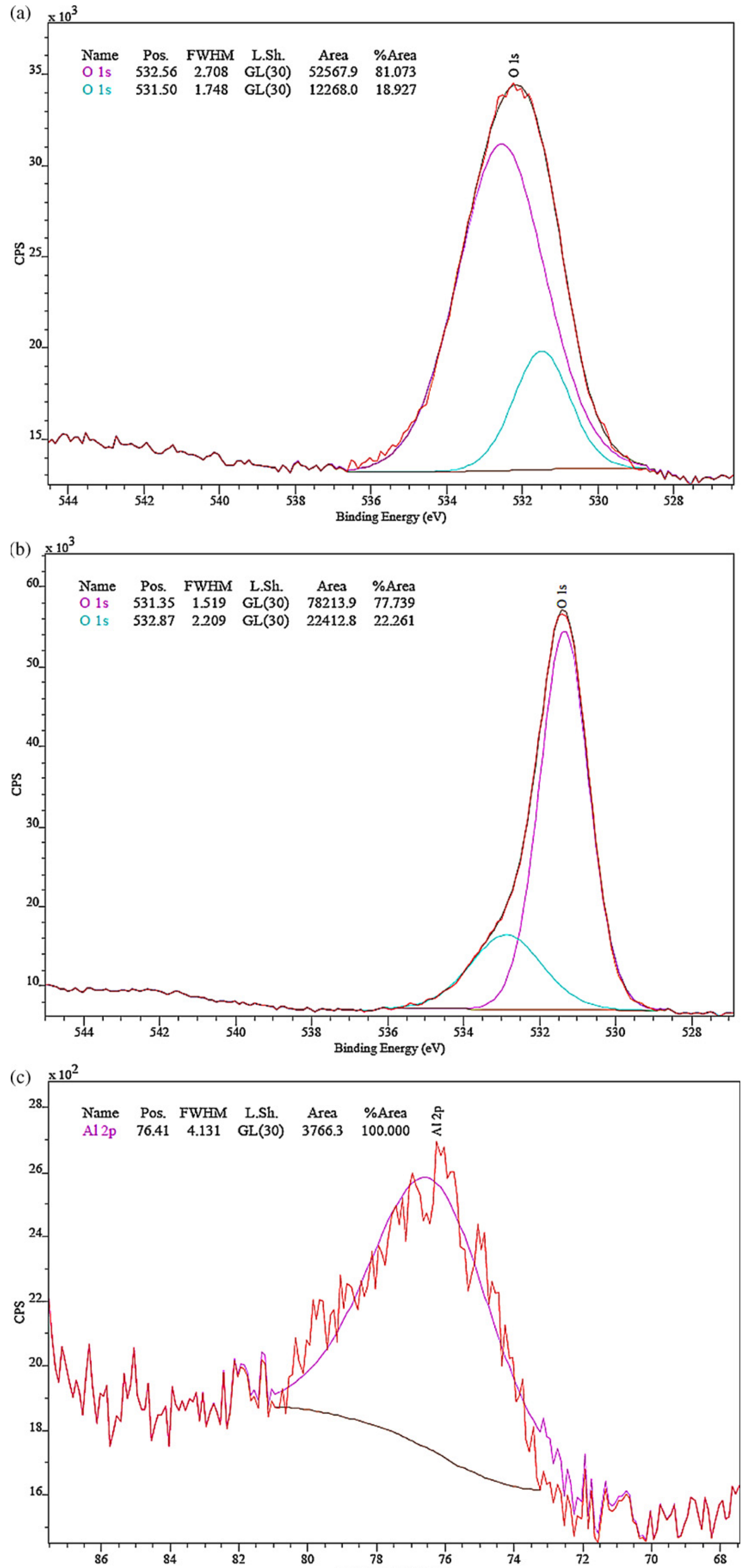

Fig. 2. X-ray photoelectron spectra: (a) O1s spectra of modified precipitated calcium carbonate filler; (b) O1s spectra of modified precipitated calcium carbonate filler; (c) Al2p spectrum of modified precipitated calcium carbonate filler.

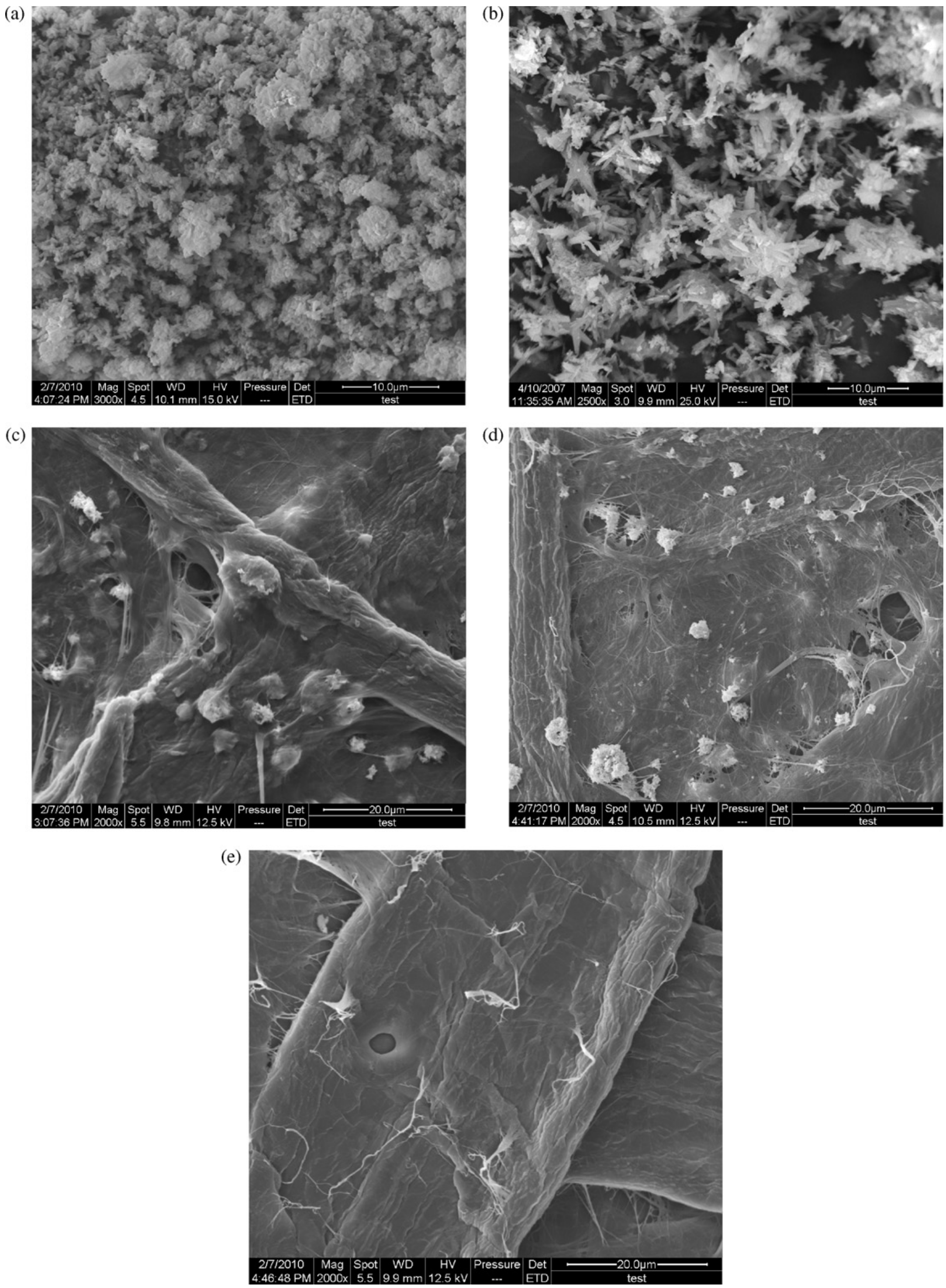

Fig. 3. SEM images of fillers and paper-sheets: (a) modified precipitated calcium carbonate; (b) unmodified precipitated calcium carbonate; (c) paper-sheet filled with modified precipitated calcium carbonate; (d) paper-sheet filled with unmodified precipitated calcium carbonate; (e) unfilled paper-sheet.

gave similar tensile/bursting strength and better tearing strength as compared with the unmodified precipitated calcium carbonate filler.

Most notably, when the alum dosage was 12%, filler modification using carboxymethyl cellulose and alum improved filler retention by as high as 71.5%, while paper strength was generally or almost not negatively affected (see Tables 2 and 4).

3.4. Air permeability and apparent density of the papers

For papermakers, besides the above mentioned parameters regarding paper properties, air permeability (also always referred to as porosity) and apparent density of the papers are another two indispensable parameters. Different categories of fillers may have different influences on the two parameters. The investigation into the effect of filler addition on air permeability and apparent density can be beneficial to the better understanding of the influence of fillers on paper properties.

The air permeability and apparent density of the unfilled paper and the papers filled with unmodified precipitated calcium carbonate filler and modified precipitated calcium carbonate fillers are shown in Table 5.

The air permeability values of the filled papers were all higher than that of the unfilled paper, indicating the increase in paper porosity as a result of filler addition. For the modified precipitated calcium carbonate fillers prepared with alum dosages of 12% and 14%, the air permeability values of the resulting papers were higher than those of other paper samples.

The apparent density values of the filled papers were generally or practically similar to that of the unfilled paper. Also, for different paper samples containing fillers, the apparent density values were almost similar to each other. Thus, under our experimental conditions, filler modification did not strikingly affect the apparent density of the filled paper.

3.5. XPS analysis and SEM observations

As indicated from the above discussions, based on our experimental results, the modification of precipitated calcium carbonate filler using carboxymethyl cellulose and alum could contribute a lot to the improvement of the use of filler in papermaking.

Most strikingly, when the dosages of carboxymethyl cellulose and alum were 4% and 12%, respectively, filler modification using carboxymethyl cellulose and alum provided increment in filler retention by as much as 71.5%, and the optical properties (brightness and opacity) of the filled paper were strikingly enhanced; however, paper strength was practically unchanged. Thus, after modification, the bonding capacity of filler was strikingly improved, resulting in alleviated negative effect of increased filler content on paper strength. As seen from Fig. 1(a), when alum dosage was 12%, carboxymethyl cellulose was possibly effectively precipitated and anchored on the filler surfaces, resulting in very clear supernatant. The benefits associated with filler modification might be achieved as a result of the surface encapsulation of the filler. In order to confirm the encapsulating effect of the modifiers, and to understand the bonding of fillers to fibers, XPS analysis and SEM observations were conducted.

X-ray photoelectron O1s spectra of modified precipitated calcium carbonate filler and unmodified precipitated calcium carbonate filler are shown in Fig. 2(a) and (b). For unmodified precipitated calcium carbonate filler, there was a striking peak at 531.35 eV associated with $CaCO_3$ (Briggs & Seah, 1990; Shen et al., 2009; Shen, Song, Qian, & Liu, 2009b), and the relatively weak peak at 532.87 eV might possibly be attributed to C-OH located on filler surfaces (Shen et al., 2009, 2009b). After modification, the peak (531.50 eV) characteristic of $CaCO_3$ became weaker, and the corresponding area percentage (%Area) was strikingly reduced (from 77.739 to 18.927), indicating the occurring of surface encapsulation when the relevant modifiers were used.

X-ray photoelectron Al2p spectrum of modified precipitated calcium carbonate filler is shown in Fig. 2(c). The peak at 76.41 eV might possibly be associated with the carboxymethyl cellulose–Al(III) complexes and $Al(OH)_3$ (Nylund & Olefjord, 1994). It should be noted that, for unmodified precipitated calcium carbonate filler, the Al element was not detected by XPS. Thus, when carboxymethyl cellulose and alum were used as modifiers during the filler modification process, carboxymethyl cellulose–Al(III) complexes and $Al(OH)_3$ precipitates were possibly formed and then anchored on the filler surfaces.

SEM images of modified precipitated calcium carbonate filler and modified precipitated calcium carbonate filler are shown in Fig. 3(a) and (b). Obviously, the surface morphology of modified precipitated calcium carbonate filler was different from that of unmodified precipitated calcium carbonate filler, indicating the role of filler modification in structure change. The modified precipitated calcium carbonate particles appeared to be somewhat "clustered", possibly partly proving its better retention performance in comparison to unmodified precipitated calcium carbonate filler.

SEM images of the unfilled paper-sheet and filled paper-sheets are shown in Fig. 3(c)–(e). When fillers were incorporated, the paper-sheet morphology was changed, and filler particles deposited on the fiber surfaces in the fiber-based matrices. Noticeably, the modified precipitated calcium carbonate filler particles were more firmly and effectively adhered and bonded to the fiber surfaces, in comparison to unmodified precipitated calcium carbonate filler particles. Also, as seen from Fig. 3(c) and (d), the surface encapsulation as a result of filler modification was quite evident. The surface encapsulating effect of the modifiers on precipitated calcium carbonate filler was thought to be favorable to the enhancement of the compatibility and affinity of filler particles to cellulosic pulp fibers.

Based on the XPS analysis and SEM observations, it should be noted that, for filler modification using carboxymethyl cellulose and alum, the encapsulation of filler particles with precipitated carboxymethyl cellulose and the clustering of filler particles might decrease the light scattering ability of the filler. However, strikingly increased filler retention as a result of filler modification contributed significantly to the improvement in optical properties of the paper. Also, the formation of $Al(OH)_3$ precipitates could possibly give certain minor contribution to optical improvement as their refractive index is higher than that of cellulosic pulp fibers.

From the above discussions, the initially presumed filler modification process was confirmed. When carboxymethyl cellulose and alum were used as modifiers, the surface encapsulation of filler was not only feasible, but also beneficial.

4. Conclusions

In the presence of alum, carboxymethyl cellulose was proved to be suitable for use in the encapsulation modification of papermaking grade precipitated calcium carbonate filler, and filler modification was capable of improving the use of filler in papermaking.

When the dosages of carboxymethyl cellulose and alum were 4% and 12% (based on the dry weight of precipitated calcium carbonate), respectively, filler modification improved filler retention by as high as 71.5%, and the optical properties (brightness and opacity) of the filled paper was strikingly enhanced, while the strength properties were practically not negatively influenced. Also, Filler modification increased the air permeability of the paper, and yet the apparent density was generally uninfluenced. XPS analysis and SEM observations of the fillers confirmed the occurring of surface encapsulation during the filler modification process. SEM images of the paper-sheets indicated that the modified precipitated calcium carbonate filler particles were more effectively adhered and bonded to the fibers, in comparison to the unmodified filler particles.

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