

MODIFICATION OF PRECIPITATED CALCIUM CARBONATE FILLER USING SODIUM SILICATE/ZINC CHLORIDE BASED MODIFIERS TO IMPROVE ACID-RESISTANCE AND USE OF THE MODIFIED FILLER IN PAPERMAKING

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In order to improve the acid-resistant property of papermaking grade precipitated calcium carbonate filler and to obtain modified filler in powder form, sodium silicate/zinc chloride based modifiers were used in filler modification, and the use of modified filler in papermaking of deinked pulp derived from recycled newspaper was also preliminarily investigated. Under the preliminarily optimized experimental conditions, when sodium silicate, zinc chloride, sodium hexametaphosphate, and phosphoric acid with dosages of 10 wt%, 3 wt%, 1 wt% and 0.2 wt%, respectively, were used as modifiers, and when the temperature, aging time, and PCC concentration during the filler modification process was 70 °C, 7 h and 9.1 wt%, respectively, the acid-resistant property of filler was significantly improved after modification, as evaluated using alum consumption and pH methods. The use of modified precipitated calcium carbonate filler prepared under the optimized conditions provided considerably more brightness and light scattering improvement in comparison to unmodified filler, and filler modification was found to have only negligible influence on tensile and burst strength of the paper, air permeability of the paper, and retention performance of the filler. Surface analysis of the modified filler using XPS and SEM confirmed the occurring of surface encapsulation and modification of precipitated calcium carbonate filler when the relevant modifiers were used in filler modification. The encapsulating effect of modifiers on filler was thought to be favorable to improvement in acid-resistant property, and optical properties of the filled paper.

Keywords: Sodium silicate/zinc chloride based modifiers; Filler modification; Papermaking; Precipitated calcium carbonate filler; Acid-resistant property; Deinked pulp; Optical properties; Surface encapsulation; XPS; SEM

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INTRODUCTION

Fillers are widely used in papermaking to reduce manufacturing costs and to improve critical properties (such as brightness) of paper products. Depending on the pH

range of the wet end system, the specific industrial papermaking operations can be implemented under acid, pseudo-neutral, neutral, or alkaline conditions. In acid and pseudo-neutral papermaking, or even under certain conditions in neutral papermaking, a filler material that is stable and resistant to attack by acid under weakly acidic to acidic conditions is required (Drummond 2001, 2006).

It is widely accepted that the use of calcium carbonate fillers in acid and pseudo-neutral papermaking has many limitations due to their alkaline nature and poor acid-resistant properties, usually making them not quite suitable for use in wood-containing paper or rosin-sized paper. Although titanium dioxide, calcined clay, and talc can be effectively used in acid and pseudo-neutral papermaking under certain controlled conditions, conventional low-cost and high-performance calcium carbonate fillers have certain advantages (associated with papermaking costs or product quality) over these fillers (Shen et al. 2009a). Therefore, improving the acid-tolerant properties of calcium carbonate fillers and enabling their use in acid or pseudo-neutral papermaking has been a hot issue in the field of papermaking wet end chemistry. The relevant strategies regarding the acid-stabilization of calcium carbonate fillers can include the separate addition of calcium carbonate and dissolution inhibitor or weak acid to furnish (Pakarinen and Leino 2001; Laurila-Lumme et al. 2003; Leino 2003), and filler modification (Shen et al. 2009a).

Similar to fiber modification (engineering), filler modification (engineering) is an active research area in papermaking industry, and countless benefits can potentially be provided by efficient utilization of the relevant technologies. For filler modification to improve acid-resistant properties of calcium carbonate fillers, the available methods can generally be classified into two categories (Shen et al. 2009b). One category of methods is only suitable for use in the production of modified calcium carbonate fillers in slurry form, and the corresponding modifiers can include aluminum salt (Wu 1997a), calcium-chelating agent/weak acid (Passaretti 1991; Evans and Slozer 2003), weak base/weak acid (Wu 1997b), calcium-salt-based modifiers (Drummond 2001,2006), phosphoric acid (Pang et al. 1998, 2001, 2003; Pang and Englezos 2003), sodium aluminate/weak acid (Rodriguez and Fortier 1999), and sodium silicate/weak acid (Snowden et al. 2000). These methods are usually simple, their industrial application can possibly be easily achieved, and the filler modification processes can be carried out on-site at the paper mill. Another category of methods is capable of producing modified calcium carbonate fillers in powder form, and the corresponding filler products can easily be stored or conveyed, which might facilitate its use at the paper mill. Tokarz et al. (1991) proposed that, by employing a filler modification process comprising simultaneous addition of a solution of a zinc compound and a solution of a silica-containing substance to calcium carbonate filler slurries at a preferred temperature of 90 °C with preferred system pH maintained at 9.2 to 9.4, modified fillers in powder form with good acid-resistant properties could be obtained. Chapnerkar et al. (1992) proposed that modified calcium carbonate fillers in powder form with good acid-resistant properties could be obtained by applying a process comprising the separate addition of sodium silicate, gaseous carbon dioxide, and zinc chloride to calcium carbonate filler slurries under controlled conditions, followed by further processing.

The filler modification methods capable of producing modified calcium carbonate filler products in powder form may possibly have the disadvantage of relatively high costs. However, in comparison to the methods only capable of producing modified fillers in slurry form, and the methods based on the separate addition of calcium carbonate and dissolution inhibitor or weak acid, the benefits of these methods can include lower calcium ion build-up, as well as more convenient storage and conveyance of the acid-tolerant filler products. Also, the encapsulation of acid-stable coatings on the calcium carbonate filler surfaces surely increases the weight of filler products, which can possibly offset the negative effect of filler modification on costs to a certain degree. Therefore, the filler modification methods capable of producing modified filler products in powder form might still have room for further improvement and development, and the relevant research work is possibly of certain potential significance. For this category of methods, there is still a need to further clarify the effects of sodium silicate/zinc chloride based modifiers on the improvement of acid-resistance of calcium carbonate fillers, and the properties of the filled paper.

In the past few years, many research reports concerning the use of acid-tolerant calcium carbonate fillers in papermaking have emerged (Tokarz et al. 1990; Mathur and Lasmarias 1991; Ain and Laleg 1997; Jaakkola and Mannu 2001, 2003; Pang and Englezos 2003; Pang 2003; Shen et al. 2009b). Also, the industrial applications of acid-tolerant calcium carbonate fillers have already been practiced and commercialized to a certain degree in the papermaking industry. However, the use of acid-tolerant calcium carbonate fillers still has certain drawbacks such as free calcium ion build-up in white water, or relatively high cost. Therefore, further work regarding the acid-tolerant calcium carbonate fillers is still needed.

In this work, in order to improve the acid-resistance of papermaking grade precipitated calcium carbonate filler, filler modification using sodium silicate/zinc chloride based modifiers including sodium silicate/zinc chloride, sodium silicate/zinc chloride/sodium hexametaphosphate, sodium silicate/zinc chloride/sodium hexametaphosphate/phosphoric acid and sodium silicate/zinc chloride/phosphoric acid was preliminarily optimized, and the use of modified filler in papermaking was also explored.

EXPERIMENTAL

Materials

Papermaking grade precipitated calcium carbonate filler was obtained from Guangxi Guilin Wuhuan Co., Ltd., China. Sodium silicate, zinc chloride, sodium hexametaphosphate, phosphoric acid, and alum were all analytical reagents produced in China. Deinked pulp derived from recycled newspaper was supplied by Jilin Chenming Paper Co., Ltd., China, and was slightly refined to a beating degree of 57.0 °SR using a ZQS2 valley beater made in China. Cationic polyacrylamide with the trademark of Percol® 47 used as retention aid was obtained from Ciba Specialty Chemicals Co., Ltd., Germany.

Preparation of Modified Filler

20 g precipitated calcium carbonate filler and 100 mL distilled water were added into the 500 mL flask, and the mixture was stirred and heated to a temperature of 60 °C to 90 °C. The modifiers were then added, and the slurry was further aged at constant temperature until the modification process was completed. The resulting slurry was subsequently filtered, washed and dried at a temperature of 100 °C for 12 h.

Evaluation of Acid-resistance

Alum consumption method and pH method were used for the evaluation of acid-resistant property of modified precipitated calcium carbonate filler, as partly described in the literature (Jaakkola and Mannu 2001). For the alum consumption method, a 3 wt% alum solution was freshly prepared and added to a 50 g sample of 4 wt% modified precipitated calcium carbonate filler slurry prepared using distilled water at a pace that maintained pH at certain values, and the consumption of alum solution was measured. For the pH method, alum solution with concentration of 3 wt% was added to a 50 g sample of 4% modified precipitated calcium carbonate filler slurry to adjust the system pH to 5.50 (the time for pH-adjusting was strictly controlled to be 1 min), and the development of slurry pH as a function of time was measured, and the pH of modified precipitated calcium carbonate filler slurry prepared using distilled water was also measured.

Evaluation of the Use of Modified Filler in Papermaking

The influence of modified filler on static furnish drainage, strength and optical properties, air permeability, and ash content of the paper was evaluated based on the previously published experimental procedures (Shen et al. 2009b).

Static furnish drainage

The pulp with dry weight of 2 g was mixed with 0.5 g filler to form a 1000 mL suspension, and the freeness (°SR) was measured to evaluate the static drainage property of the filler-containing furnish. The apparatus used was a ZDJ-100 beating degree tester made in China.

Preparation of handsheets and measurement of strength properties, optical properties, air permeability, and ash content of the handsheets

The mixture of pulp and filler was diluted to 0.5 wt%, and the target filler loading level was controlled to be 15 wt%. Cationic polyacrylamide solution was added, and the slurry was stirred for 1 min. Diluted alum solution was then added dropwise to adjust the slurry pH to 6.50, and the pH-adjusting time was controlled to be 1 min. Handsheets with target basis weight of 60 g/m² were then prepared using the sheet former (ZQJ1-B200mm) produced in China. The handsheets were further pressed and flattened for 24 h using the apparatus equipped with the sheet former. The conditions for handsheets preparation were kept consistent for all of the samples.

The tensile index values of handsheets were measured using an L&W CE062 tensile strength tester made in Sweden. The burst index values of handsheets were measured using ZDNP-1 burst strength tester made in China. The brightness, opacity and

light scattering coefficient of handsheets were measured using YQ-Z-48A brightness & color tester made in China. The air permeability values of handsheets were measured using YG461E permeability tester made in China.

The handsheets were dried at 105 °C for 6 h, and the dry weight values of handsheets were measured. The dried handsheets were then incinerated at 575 °C for 6 h, the ash weight values were measured, and the ash content values of handsheets (%) were calculated.

XPS Analysis and SEM Observation of the Modified Filler

X-ray photoelectron spectroscopy (XPS) analysis was performed with a Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, UK); Alka X-ray was used as the X-ray source (1486.6 eV, 15kV, 10mA). SEM analysis was performed with a scanning electron microscopy (SEM, QUANTA 200).

RESULTS AND DISCUSSION

Influence of Preparation Conditions of Sodium Silicate/Zinc Chloride Modified Filler on Acid-resistance

When sodium silicate and zinc chloride were used as modifiers in the filler modification process, the influence of filler modification conditions on the acid-resistant property of modified filler was first considered relative to parameters such as the dosage of modifiers, temperature, aging time, and PCC concentration.

As shown in Fig. 1, when the dosage of sodium silicate was 20 wt% (based on the dry weight of precipitated calcium carbonate filler), and when the aging time and temperature were 5 h and 90 °C, respectively, the alum consumption of modified filler corresponding with zinc chloride dosage of 6 wt% was lower as compared with that of other dosages, showing comparatively better acid-resistant property. Therefore, for the zinc chloride dosages in the range of 5 wt% to 12 wt%, the dosage of 6 wt% was selected for further investigations.

When sodium silicate dosage, zinc chloride dosage, aging time, and temperature were 20 wt%, 6 wt%, 5 h, and 90 °C, respectively, the change of temperature influenced the acid-resistant property of filler to a certain degree (see Fig. 2), and the temperature values of 70 °C and 90 °C gave quite similar alum consumption curves, and these two values were superior to 60 °C and 80 °C, taking the acid-resistant property of modified filler into consideration. Considering the filler modification cost, the temperature value of 70 °C was selected as the optimum temperature.

When sodium silicate dosage, zinc chloride dosage, aging time, and temperature were 20 wt%, 6 wt%, 5 h, and 70 °C, respectively, PCC concentration of 9.1 wt% was the optimum value (see Fig. 3), taking the acid-resistant property of modified filler into consideration. For different PCC concentration values (2.5 wt%, 5 wt%, 9.1 wt%, 15 wt%, and 20 wt%) explored in our work, PCC concentration of 9.1 wt% might possibly be the most efficient for the encapsulation of acid-stable coatings on the filler surfaces.

When sodium silicate dosage, zinc chloride dosage, aging time, temperature, and PCC concentration were 20 wt%, 6 wt%, 5 h, 70 °C, and 9.1 wt%, respectively, and when the weight ratio of sodium silicate to zinc chloride was fixed at 10 to 3, the change of sodium silicate dosage affected the acid-resistant property of modified filler, and there were only slight or even negligible differences between the alum consumption curves of modified filler prepared with sodium silicate dosages of 10 wt% and 20 wt% (see Fig. 4). Therefore, the dosage of 10 wt% was preferred, taking the cost of filler modification into consideration. The change in sodium silicate dosage possibly influenced many parameters concerning the filler modification process, such as interactions between modifiers and filler surfaces, and system pH. However, further investigations are still needed to elucidate the underlying mechanisms.

It was also found that the aging time during the preparation process of modified filler also influenced the acid-resistant property, and the optimum aging time was 7 h under the controlled experimental conditions (see Fig. 5).

It should be noted that, these preliminarily optimized parameters were kept constant in the following sections.

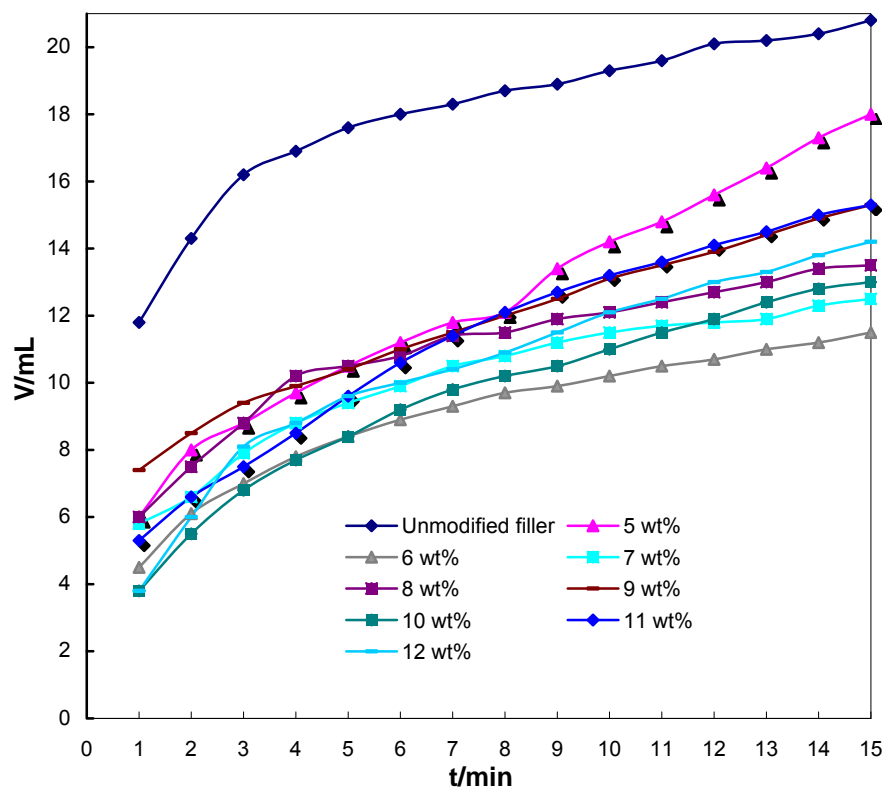


Fig. 1. Alum consumption of sodium silicate/zinc chloride modified filler slurry (sodium silicate dosage: 20 wt%) with pH maintained at 6.00 — Influence of zinc chloride dosage

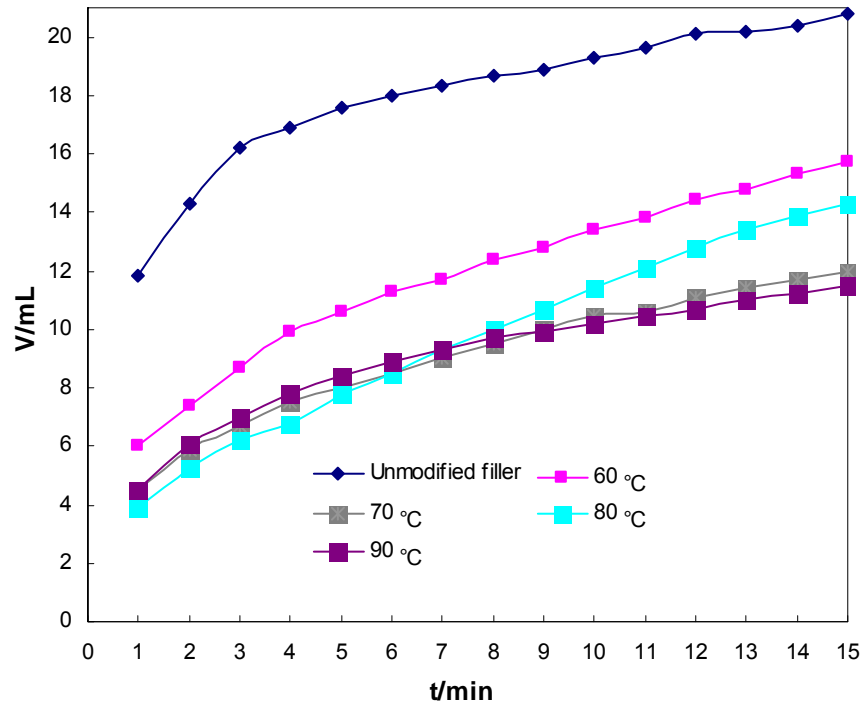


Fig. 2. Alum consumption of sodium silicate/zinc chloride modified filler slurry (sodium silicate dosage: 20 wt%) with pH maintained at 6.00 – Influence of temperature

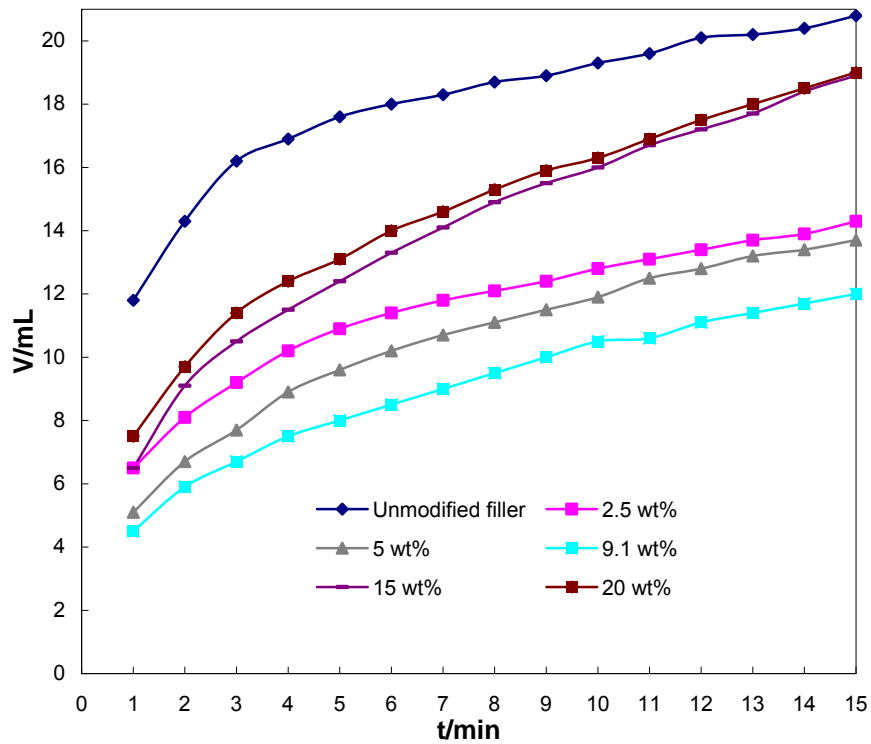


Fig. 3. Alum consumption of sodium silicate/zinc chloride modified filler slurry (sodium silicate dosage: 20 wt%) with pH maintained at 6.00 – Influence of precipitated calcium carbonate concentration

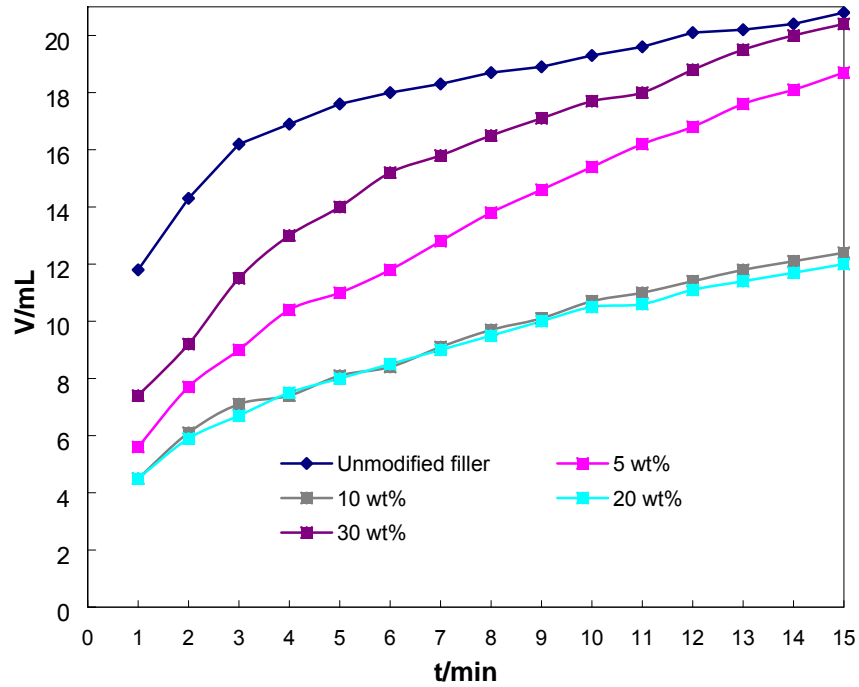


Fig. 4. Alum consumption of sodium silicate/zinc chloride modified filler slurry (weight ratio of sodium silicate to zinc chloride: 10 to 3) with pH maintained at 6.00 – Influence of sodium silicate dosage

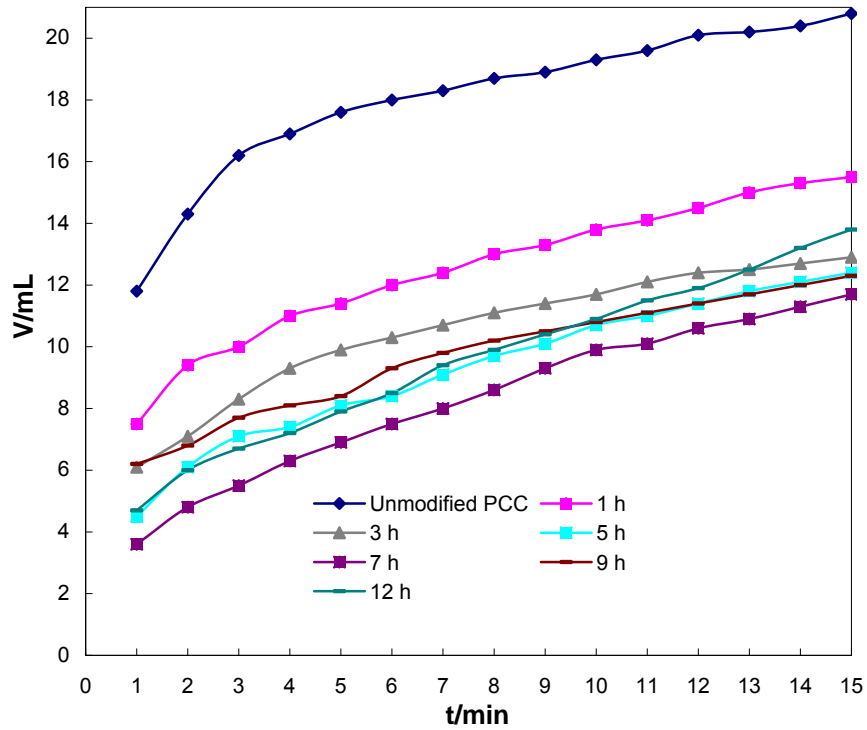


Fig. 5. Alum consumption of sodium silicate/zinc chloride modified filler slurry (sodium silicate 10 wt%; zinc chloride 3 wt%) with pH maintained at 6.00 – Influence of aging time

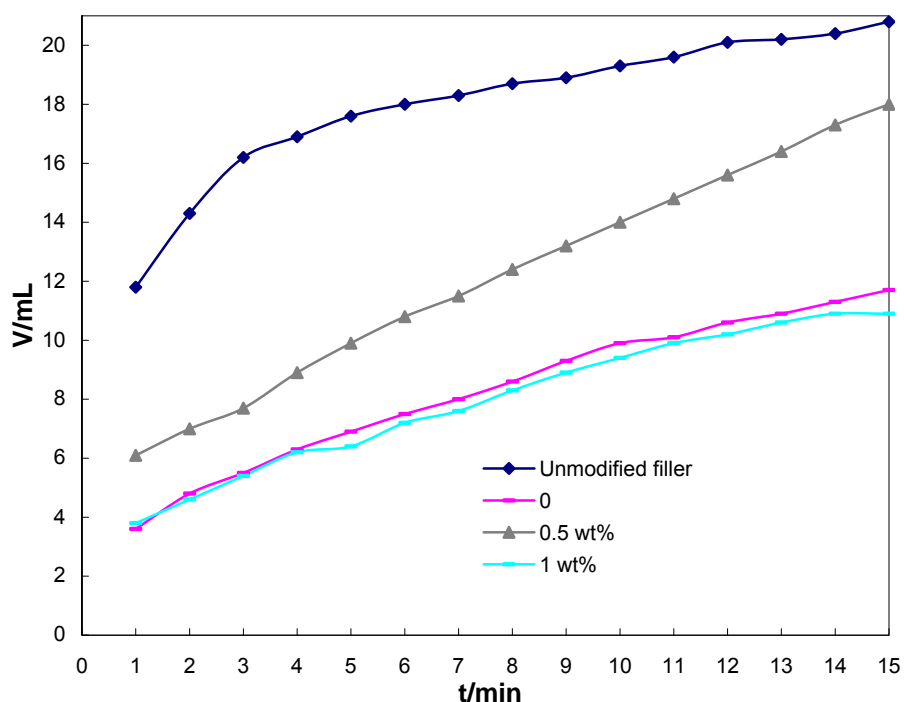


Fig. 6. Alum consumption of modified filler slurry (sodium silicate 10 wt%; zinc chloride 3 wt%) with pH maintained at 6.00 — Influence of the addition of sodium hexametaphosphate

Acid-resistance of Sodium silicate/zinc chloride/sodium hexametaphosphate Modified Filler

When sodium silicate and zinc chloride with dosages of 10 wt% and 3 wt%, respectively, were used as modifiers, the use of sodium hexametaphosphate with dosage of 1 wt% as an additional modifier was found to have a slightly positive effect on the acid-resistant property of modified filler, as shown in Fig. 6. This can possibly be explained by the dispersing effect of sodium hexametaphosphate on filler particles suspended in the slurry, which may enhance the acid-resistant property of modified filler due to the improved formation of acid-stable coatings on the filler surfaces. It should be noted that the addition of sodium hexametaphosphate can give only limited increase in acid-resistance under the controlled experimental conditions, as seen from the alum consumption curves.

Acid-resistance of Sodium silicate/zinc chloride/sodium hexametaphosphate/phosphoric acid Modified Filler

When sodium silicate, zinc chloride, and sodium hexametaphosphate with dosages of 10 wt%, 3 wt%, and 1 wt%, respectively, were used as modifiers, the use of phosphoric acid as an additional modifier could improve the acid-resistant property of modified filler, and its suitable dosage was found to be 0.2 wt%, as shown in Fig. 7. The positive effect of phosphoric acid on acid-resistant property might be due to the pH-buffering effect. It was further found in our work that, as compared with modified filler prepared using sodium silicate, zinc chloride, sodium hexametaphosphate, and phosphoric acid with dosages of 10 wt%, 3 wt%, 1 wt%, and 0.2 wt%, respectively, the

alum consumption of modified filler using sodium silicate, zinc chloride, and phosphoric acid with dosages of 10 wt%, 3 wt%, and 0.2 wt%, respectively, was relatively higher, showing a little weaker acid-resistant property. Similar to sodium hexametaphosphate, the effect of phosphoric acid was also only limited to a certain degree.

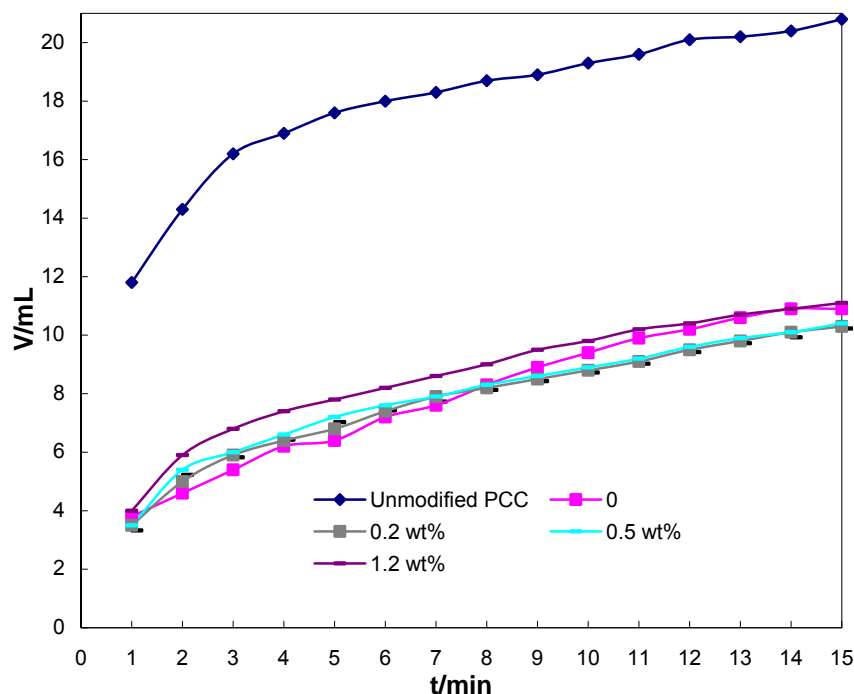


Fig. 7. Alum consumption of modified PCC slurry (sodium silicate 10%; zinc chloride 3%; sodium hexametaphosphate 1%) with pH maintained at 6.00 — Influence of the addition of phosphoric acid

Further Investigations into the Acid-resistance of Modified Filler

From the above discussion, when sodium silicate, zinc chloride, sodium hexametaphosphate, and phosphoric acid with dosages of 10 wt%, 3 wt%, 1 wt%, and 0.2 wt%, respectively, were used as modifiers, the modified filler exhibited high acid-resistance, and the consumption of alum solution for modified filler slurry with pH maintained at 6.00 was less than half of unmodified filler. Similarly, as seen from Fig. 8 to Fig. 10, the alum consumption values for modified filler slurry with pH maintained at 5.50, 6.50, and 7.00 were also much lower in comparison to the unmodified filler. It should be mentioned that, as the maintained system pH changed from 5.50 to 7.00, the stabilities of both modified filler and unmodified filler increased simultaneously, indicating the enhancing effects of pH-decreasing on filler dissolution.

Table 1 shows the pH values of modified filler slurries at different concentrations. With the decreasing concentration of filler slurry, the pH of modified filler slurry increased gradually; however, its value at a specific filler concentration was a little lower than that of unmodified filler. Thus, it can be considered that, after modification, the filler alkalinity possibly decreased to a certain degree, and the surface behavior presumably changed when the relevant modifiers were used.

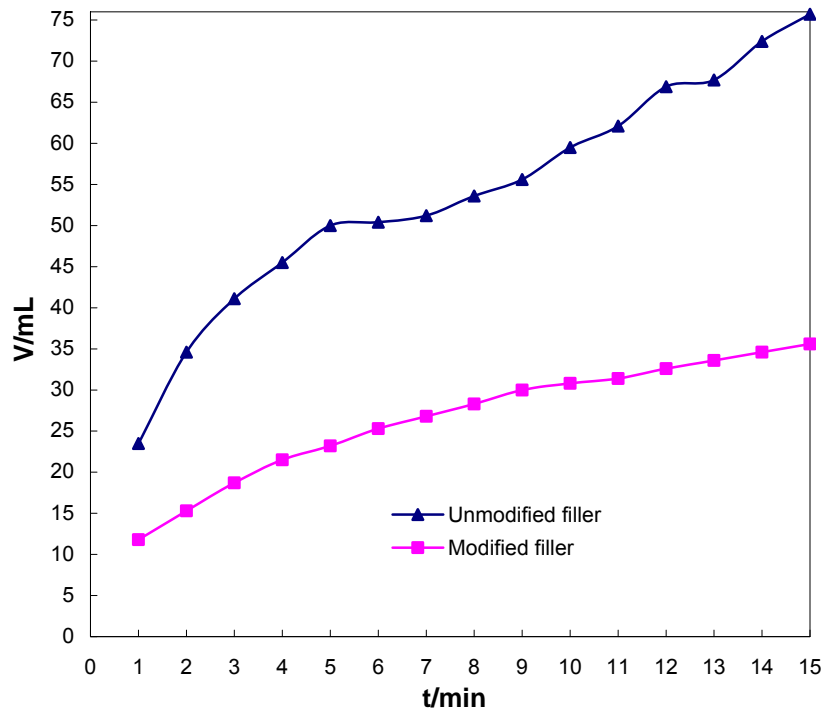


Fig. 8. Alum consumption of modified filler slurry with pH maintained at 5.50

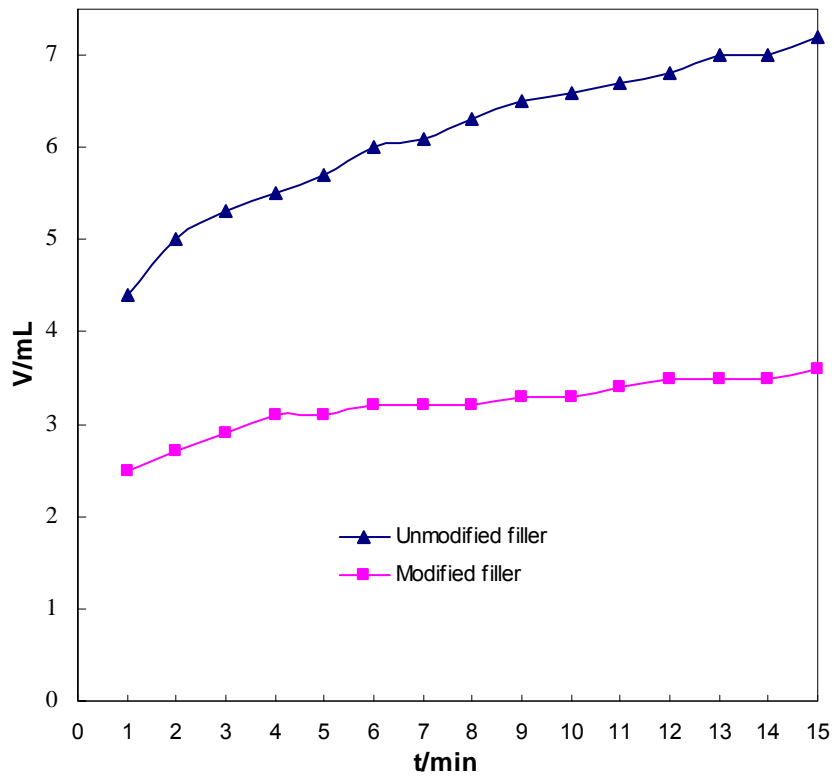


Fig. 9. Alum consumption of modified PCC slurry with pH maintained at 6.50

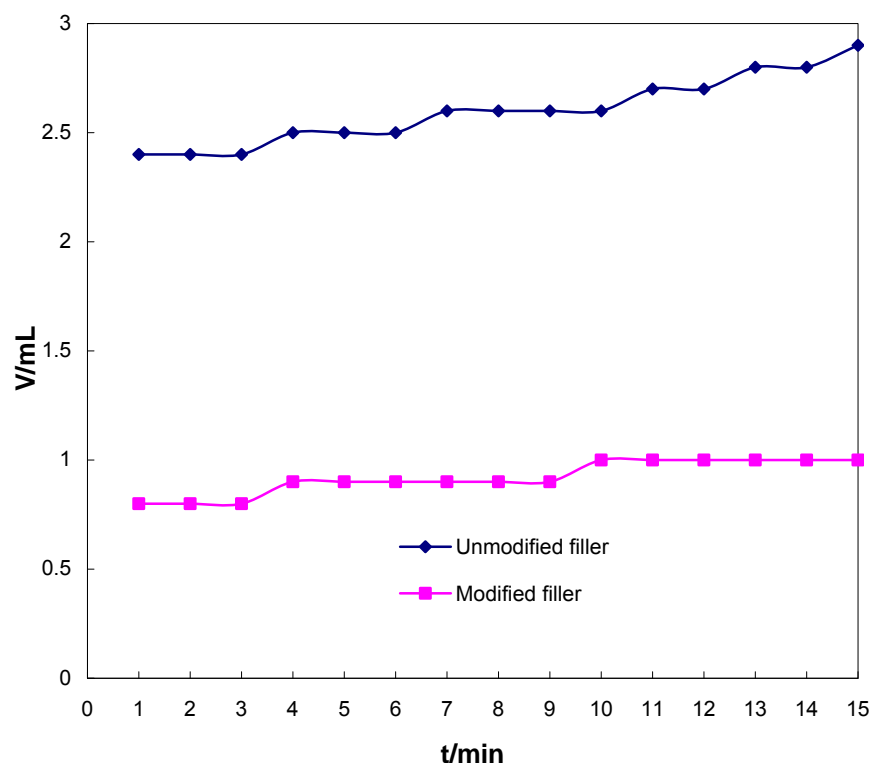


Fig. 10. Alum consumption of modified filler slurry with pH maintained at 7.00

Table 1 The pH Values of Modified Filler Slurries at Different Concentrations

Concentration of filler slurry (%)	Slurry pH	
	Unmodified filler	Modified filler
4	10.07	9.31
0.4	9.83	9.18
0.04	9.66	9.16
0.004	9.18	9.02

Figure 11 shows the development of pH as a function of time of modified PCC slurry after adjustment to pH 5.50 with alum. For unmodified filler, the slurry pH developed rapidly in 30 min, and the value reached above 7 at 30 min, however, for modified PCC, the slurry pH increased relatively slowly in 30 min, and the value of approximately 6.5, much lower than that of unmodified filler, could be reached at 30 min. It should be noted that the consumption of alum solution of modified filler slurry after adjustment to pH 5.50 in 1 min was only 11.8 mL, much lower than that of unmodified filler slurry (23.5 mL). Thus, compared with unmodified filler, even when alum consumption was much lower, the slurry pH of modified filler still developed relatively slowly, indicating the substantial improvement of acid-resistance after filler modification.

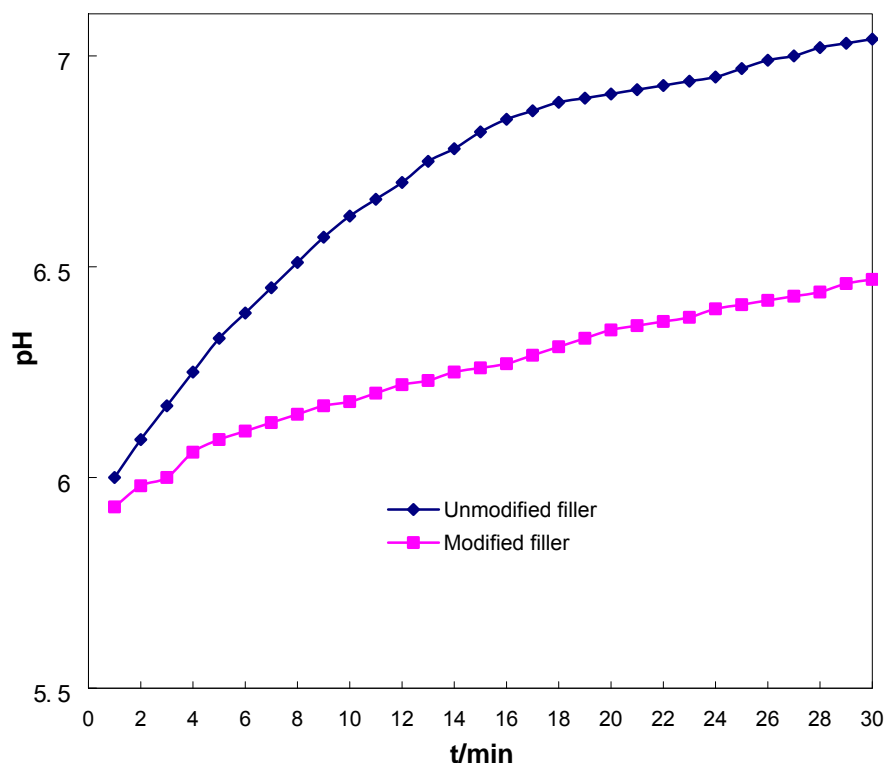


Fig. 11. Development of pH as a function of time of modified PCC slurry after adjustment to pH 5.50 with alum

Influence of Modified Filler on the Static Furnish Drainage

Table 2 shows the influence of addition of modified filler prepared under the preliminarily optimized condition on the static furnish drainage. The addition of either the modified filler or unmodified filler to furnish decreased the furnish freeness to a certain degree, showing the positive effect of filler addition on static furnish drainage. Compared with the furnish containing unmodified filler, the freeness value of furnish containing modified filler was higher. Thus, after modification, the contribution of precipitated calcium carbonate filler to improvement in furnish static drainage was decreased to a certain degree.

Table 2. Freeness Values of the Furnishes

Sample	Freeness (°SR)
Furnish with no filler added	57.0
Furnish containing unmodified filler	48.2
Furnish containing modified filler	53.0

Ash Content of the Paper Filled with Modified Filler

For the use of fillers in papermaking, ash content of the paper products can be used to evaluate the retention performance of fillers. Table 2 shows the ash content values of unfilled handsheets and filled handsheets.

The ash content value of unfilled handsheets was 4.0 wt%, indicating the presence of a certain amount of inorganic pigments in the deinked pulp derived from recycled newspaper. The ash content value of handsheets filled with modified filler was generally equivalent to that of unmodified filler, showing the negligible change in retention performance of precipitated calcium carbonate filler after modification.

Table 3. Ash Content Values of the Filled Handsheets

Sample	Ash content (wt%)
Unfilled handsheets	4.0
Handsheets filled with unmodified filler	16.0
Handsheets filled with modified filler	15.7

Table 4. Optical Properties, Strength Properties, and Air Permeability of the Filled Handsheets

Sample	Brightness (%ISO)	Opacity (%)	Light scattering coefficient ($\text{m}^2 \cdot \text{kg}^{-1}$)	Tensile index ($\text{N} \cdot \text{m} \cdot \text{g}^{-1}$)	Burst index ($\text{KPa} \cdot \text{m}^2 \cdot \text{g}^{-1}$)	Air permeability ($\text{L} \cdot \text{m}^2 \cdot \text{s}^{-1}$)
Unfilled handsheets	61.7	97.3	52.7	17.02	1.22	18.5
Handsheets filled with unmodified filler	67.8	96.4	69.0	11.14	0.66	28.5
Handsheets filled with modified filler	69.1	95.6	76.8	11.17	0.64	30.2

Optical Properties, Strength Properties, and Air Permeability of the paper filled with modified filler

Table 4 shows the optical properties, strength properties, and air permeability of the unfilled and filled handsheets.

The use of unmodified filler and modified filler all strikingly improved the brightness and light scattering coefficient of handsheets. The brightness and light scattering coefficient of handsheets filled with modified filler were much higher as compared with the handsheets filled with unmodified filler. Since the ash content of handsheets filled with modified filler was generally equivalent to that of handsheets filled with unmodified filler, the improvement in brightness and light scattering coefficient after filler modification may presumably be caused by alleviated pulp darkening achieved by improved acid-resistance. Paper opacity was not found to be improved by the use of unmodified filler and modified filler, and this phenomenon may possibly be caused by many factors such as the high-opacity pulp used in this work; further work is still necessary to elucidate the underlying mechanisms.

The use of modified filler and unmodified filler was found to have strikingly negative effects on the tensile and burst indices of handsheets. The tensile and burst indices of handsheets filled with the modified filler were generally equivalent to that of

handsheets filled with the unmodified filler, possibly showing the negligible effect of filler modification on paper strength.

For air permeability of the handsheets, the use of unmodified filler and modified filler provided certain improvements, and the improving effect of unmodified filler was very close to that of modified filler. Thus, filler modification only had negligible influence on air permeability of the paper.

Surface Analysis of the Modified Filler

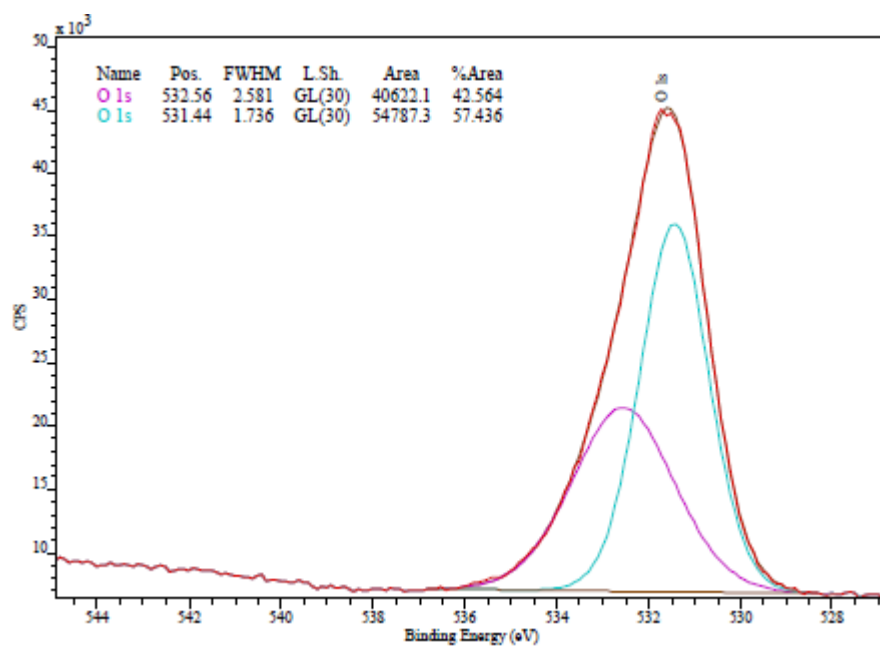
Based on the above discussion, the modified filler prepared under the preliminarily optimized conditions exhibited relatively high acid-resistance, and its use in deinked pulp derived from recycled newspaper provided considerably more improvement in brightness and light scattering coefficient of the filled paper, in comparison with the unmodified filler. The improvement in acid-resistant property after modification was initially assumed to be surface encapsulation, which inhibited its dissolution in acidic medium. In order to confirm this consumption, surface analysis was conducted by XPS and SEM.

X-ray photoelectron O1s spectra of unmodified filler and modified filler are shown in Fig. 12. As shown, for unmodified filler there was a striking peak at 531.35 eV associated with CaCO_3 (Briggs and Seah 1990), and the relatively weak peak at 532.87 eV might possibly be associated with C-OH located on filler surfaces. After modification, the peak at 531.44 eV associated with CaCO_3 became weaker, possibly indicating the encapsulation of filler when the relevant modifiers were used.

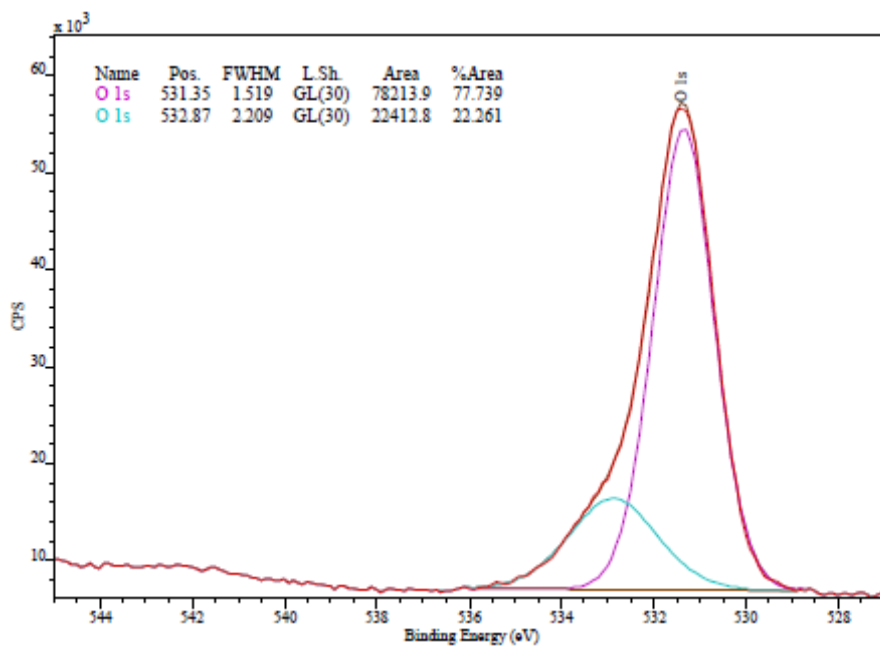
Figure 13 shows the X-ray photoelectron Si 2p spectrum of modified filler. There was a striking peak at 102.46 eV associated with SiO_2 (Barr 1978), which presumably confirmed the precipitation and encapsulation of acid-stable SiO_2 on precipitated calcium carboante surfaces. The weak peak at 101.88 eV, possibly characteristic of $\text{CaO}\cdot\text{SiO}_2$ mixed oxide (Kaneko and Suginoara 1978), could also be observed.

Figure 14 shows the X-ray photoelectron Zn2p spectrum of modified filler, and the peaks at 1021.78 eV (Briggs and Seah 1990) and 1044.88 eV (Haemers et al. 1984) are possibly characteristic of ZnO. It should be noted that, although phosphorus-containing substances were used in the filler modification process, the phosphorus element was not detected when XPS analysis was conducted, probably showing its inability to coat the filler surfaces in any form. Also, it was found in this work that, for the unmodified filler, the silicon element and zinc element were not detected by XPS.

Based on the XPS results, it might be considered that when sodium silicate, zinc chloride, sodium hexametaphosphate, and phosphoric acid with dosages of 10 wt%, 3 wt%, 1 wt%, and 0.2 wt%, respectively, were used as modifiers, the change in surface characteristic occurred, and the improvement in acid-resistant property of filler after modification was possibly predominately achieved by the precipitation of acid-stable SiO_2 on filler surfaces, which might act as barriers and block the dissolution sites. Also, it can possibly be considered that the $\text{CaO}\cdot\text{SiO}_2$ mixed oxide and ZnO coated on filler surfaces might have certain surface-blocking effect upon contact with acid, possibly postponing and suppressing the dissolution of CaCO_3 components of modified filler in acidic or weakly acidic medium.



(a)



(b)

Fig. 12. X-ray photoelectron O1s spectra of fillers: (a) modified filler, and (b) unmodified filler

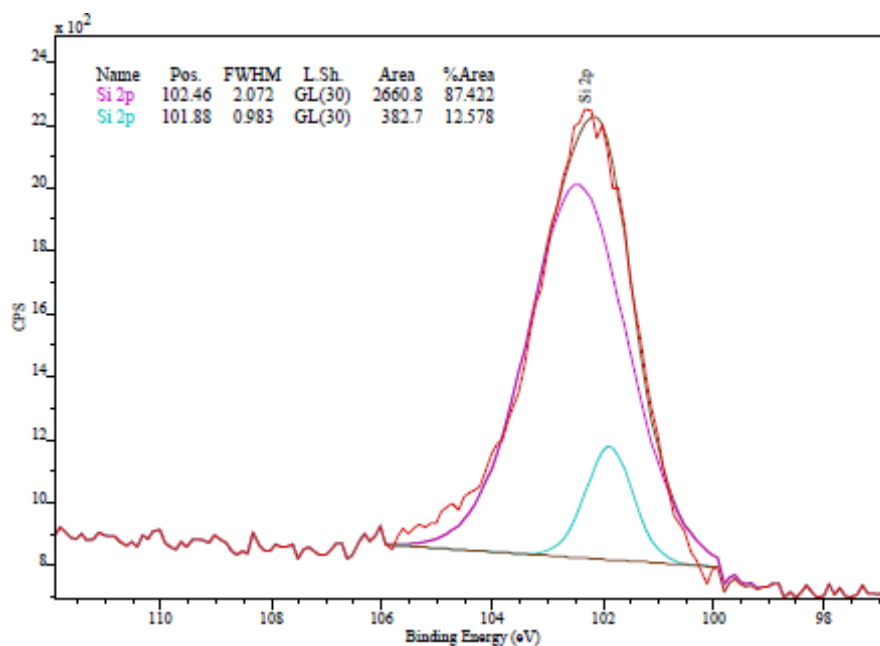


Fig. 13. X-ray photoelectron Si 2p spectrum of modified filler

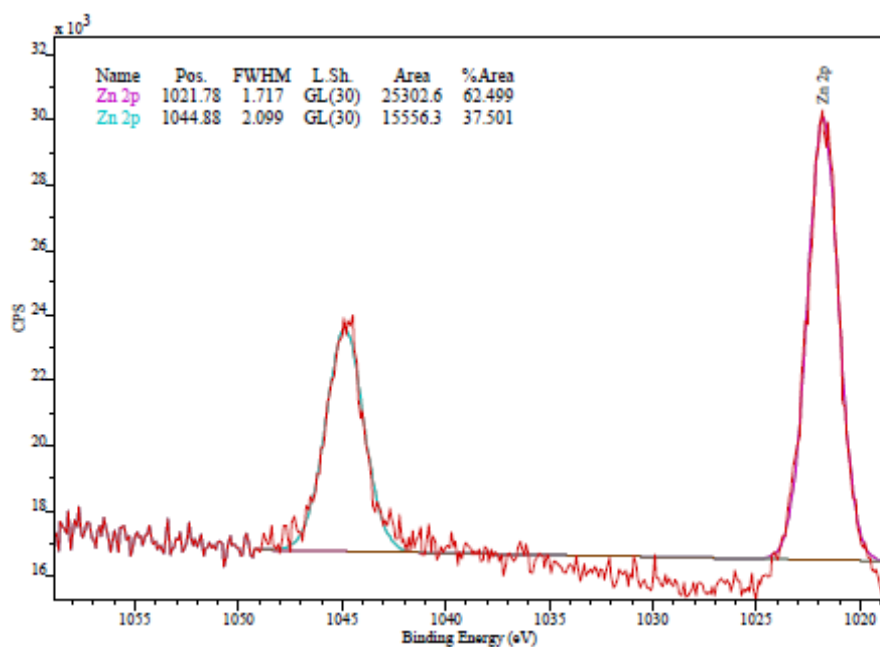
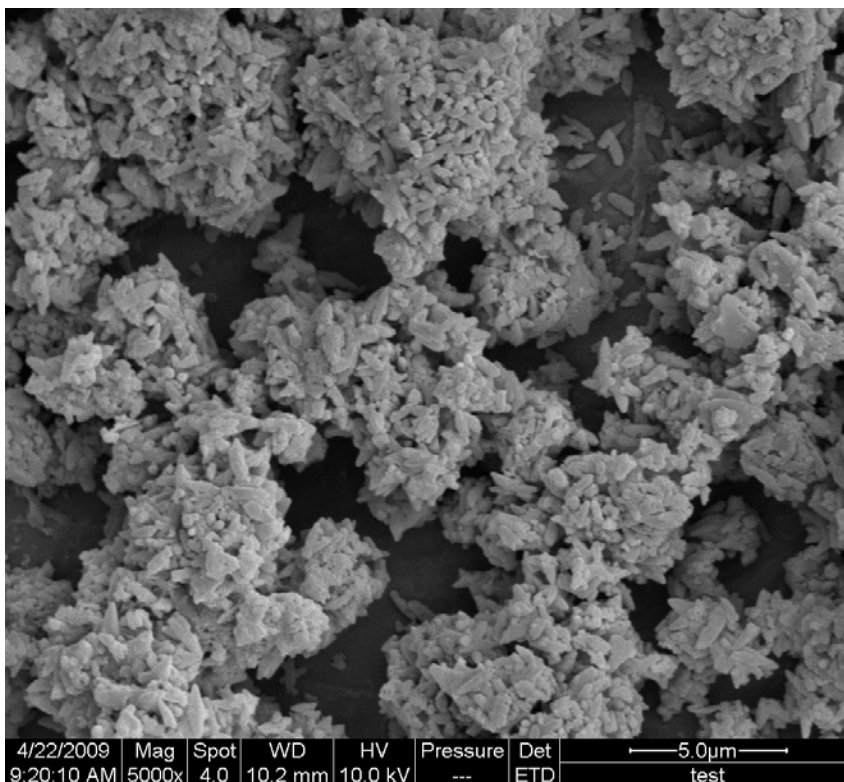


Fig. 14. X-ray photoelectron Zn 2p spectrum of modified filler

Scanning Electron Microscopy (SEM) pictures of unmodified filler and modified filler are shown in Fig. 15. It was found that the surface morphology of modified filler was different from that of unmodified filler, presumably further confirming the occurring of surface encapsulation during the modification process.

Therefore, according to XPS and SEM results, during the modification process of papermaking grade precipitated calcium carbonate filler capable of obtaining modified filler in powder form using sodium silicate, zinc chloride, sodium hexametaphosphate, and phosphoric acid with dosages of 10 wt%, 3 wt%, 1 wt%, and 0.2 wt%, respectively, the occurring of surface encapsulation and modification of precipitated calcium carbonate filler was tentatively confirmed, and the surface characteristic of modified filler was different from the unmodified filler. The change in surface characteristic of filler might be helpful to understanding the relevant results obtained in this work such as the improving effect of filler modification on acid-resistant property and optical properties of the filled paper. It can be considered that, the surface encapsulating effect of modifiers is favorable to the improvement in acid-resistance property, and optical properties of the paper. However, for better understanding of the filler modification process, and further improvement of the property of modified filler product, further work involving more complete characterization might be of extra significance.



(a)

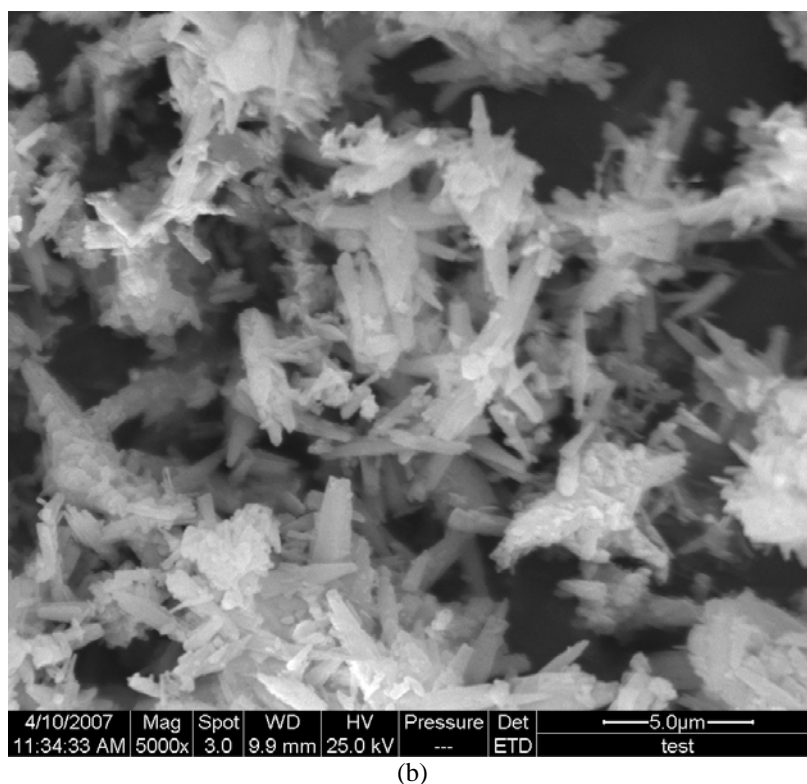


Fig. 15. SEM pictures of fillers: (a) modified filler, and (b) unmodified filler

CONCLUSIONS

1. Under the preliminarily optimized conditions, when sodium silicate, zinc chloride, sodium hexametaphosphate, and phosphoric acid with dosages of 10 wt%, 3 wt%, 1 wt%, and 0.2 wt%, respectively, were used as modifiers, modification of paper-making grade precipitated calcium carbonate filler strikingly improved its acid-resistant property, as evaluated using alum consumption and pH methods. The temperature, aging time, and PCC concentration during the filler modification process was found to be 70 °C, 7 h, and 9.1 wt%, respectively.
2. The use of modified filler prepared under the preliminarily optimized conditions provided considerably more brightness and light scattering improvement as compared with unmodified filler, and filler modification was found to have negligible influence on tensile and burst strength of the paper, air permeability of the paper, and retention performance of the filler.
3. XPS and SEM results preliminarily confirmed the occurrence of surface encapsulation and modification when the relevant modifiers were used to improve the acid-resistance of papermaking grade precipitated calcium carbonate filler. The surface encapsulating effect of modifiers was thought to be favorable to the improvement in acid-resistance and optical properties of the paper.

4. Research work regarding use of other parameters such as the nature of papermaking process waters to evaluate acid-resistance of various fillers, more complete experimental statistics, better understanding of the effects of different filler modification conditions on alum consumption, further optimization of the filler modification process, further comparison of the relevant modifiers, more complete characterization of the modified filler, and systematic evaluation of the economics of the relevant filler modification technology, is still necessary in the future.

ACKNOWLEDGEMENTS

Support from the Foundation (No.0802) of Key Laboratory of Paper Science & Technology of Ministry of Education (Shandong Institute of Light Industry), and Foundation (No.200910) of Tianjin Key Laboratory of Pulp & Paper (Tianjin University of Science and Technology), P. R. China, is gratefully acknowledged. The authors wish to express their thanks for a grant (No.07007) from Northeast Forestry University, P. R. China, which has provided vital support. The authors also wish to thank K. C. Wang, an undergraduate student who started his higher education in 2005 in Material Science and Engineering College, Northeast Forestry University, China, for conducting the experimental work concerning handsheet preparation and measurement of handsheet properties.

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Article submitted: August, 9, 2009; Peer review completed: Sept. 21, 2009; Revised version received and accepted: Sept. 23, 2009; Published: Sept. 23, 2009.