Modification of Precipitated Calcium Carbonate Filler for Papermaking with Adsorption of Cationically Derivatized Chitosan and Carboxymethyl Chitosan

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To improve the performance of precipitated calcium carbonate (PCC) as a papermaking filler, the combination of cationically derivatized chitosan and carboxymethyl chitosan was employed as modification agents for PCC. When the dosage ratio of cationic chitosan to carboxymethyl chitosan was 1:2, the two polymers were efficiently deposited onto precipitated calcium carbonate, which showed better retention than the control PCC at the same dosage. The brightness and opacity of handsheets filled with modified precipitated calcium carbonate were markedly improved in comparison to the control. Furthermore, handsheets filled with modified precipitated calcium carbonate reduced the loss of tensile strength compared to the control at the same precipitated calcium carbonate content.

Keywords: Precipitated calcium carbonate; Cationically derivatized chitosan; Carboxymethyl chitosan; Modification; Handsheets

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INTRODUCTION

Mineral fillers are widely used in papermaking. Precipitated calcium carbonate (PCC) is a common filler for paper production. In many paper grades, such as newsprint, writing paper, printing paper, and some functional paper grades, the use of mineral fillers such as PCC is indispensable. It is well known that the cost of PCC is significantly lower than fiber pulp, so as the dosage of PCC increases during paper production, fiber pulp can decrease, which in turn can reduce the cost of paper production (Cheng *et al*. 2011). Also, with higher PCC loading in papersheets, less steam is consumed at the dryer section of the paper machine, which can save energy and improve the efficiency of the paper production (Dong *et al*. 2008). However, the size of PCC particles is much less than that of pulp fiber, so PCC has poor retention in comparison with pulp fibers in the wire section of the paper machine, especially when retention aids are absent during the papermaking process. Furthermore, PCC particles in papersheets can block some hydrogen bonds between pulp fibers, which has a negative impact on some physical properties of papersheets and can result in linting and dusting during printing, especially with higher PCC content in the papersheets (Shen *et al*. 2009).

The modification of PCC is a promising approach to overcome these limitations. The topics have attracted the interests of many researchers, and may include fibrous engineering, nanofiller engineering, and surface modification of mineral fillers (Shen *et al*. 2010a). Inorganic compounds have been used in the modification of PCC filler mainly in order to achieve the better acid-tolerant properties. Such effects have been achieved with calcium-chelating agents, a weak acid, alum salt, phosphoric acid, and sodium silicate, *etc.* (Passaretti 1991; Ain and Laleg 1997; Wu 1997; Pang *et al.* 1998, 2001). Many polymers or their derivatives can be employed to modify mineral fillers for papermaking, for instance starch, alginate, cellulose, and chitosan; such treatments have been found to reduce the negative impact of fillers on the papersheet properties and on the papermaking process (Zhao *et al*. 2005; Shen *et al.* 2009; Cao *et al*. 2011; Fatehi *et al*. 2013a,b; Huang *et al*. 2013). Chitosan is a natural dry strength for paper and an efficient agent to strengthen the wet web of papersheets (Lindström *et al*. 2005). The application of chitosan and its derivatives in papermaking has been an important topic (Niekraszewicz *et al*. 2001; Nada *et al*. 2006; Sun *et al*. 2010; Saeed *et al*. 2011; Chen *et al*. 2013; Hamzeh *et al*. 2013). However, chitosan can only dissolve in some acid solutions, such as hydrochloric acid and acetic acid, and this has limited its application in papermaking and other fields. Cationically derivatized chitosan is an important derivative of chitosan that has more extensive applications than chitosan in papermaking, waste water treatment as a flocculant, and heavy metal chelating agent (Cai *et al*. 2009). Carboxymethyl chitosan is derived from chitosan by carboxymethylation. In comparison with chitosan, the solubility of carboxymethyl chitosan in aqueous solution was improved due to the introduction of the carboxymethyl group, which contributes to a negative ionic charge (Cai *et al*. 2007). Carboxymethyl chitosan could be used in waste water treatment, agriculture, biochemical industry, medicine and health, *etc.* It is well known that the combination of a cationic polymer and an anionic polymer could be used to improve the paper strength (Hubbe 2005; Hubbe *et al*. 2005). As was reported by some researchers, such a combination was applied in the modification of PCC for papermaking (Yang *et al*. 2013). According to the work of Yang *et al.* (2013), modification of PCC by combination of cationic starch and carboxymethyl cellulose resulted in modestly better performance compared to either a cationic starch or carboxymethyl cellulose in filler retention, tensile strength, brightness, and opacity of the filled papersheets.

In this study, the combination of cationic chitosan and carboxymethyl chitosan was employed as modification agents for PCC filler. The particle size and its distribution of modified PCC were analyzed, and the particle aggregation of PCC before and after modification was observed using a scanning electron microscope (SEM). The brightness and opacity of handsheets filled by modified PCC were investigated in comparison with the control PCC. The effect of modified PCC as a papermaking filler on the tensile strength of handsheets compared with the control PCC was also studied by contrast analysis of the handsheets with the same PCC content.

EXPERIMENTAL

Materials

Cationically modified chitosan (2-hydroxypropyltrimethyl ammonium chloride chitosan) and carboxymethyl chitosan were purchased from Nantong LuShen Bioengineering Co. Ltd., China. The average molecular weight and degree of substitution of the cationic chitosan were 300 kDa and 90%, respectively; the average molecular weight and degree of substitution of carboxymethyl chitosan were 200 kDa and 60%, respectively. Papermaking filler grade precipitated calcium carbonate (powder) was supplied by Guangxi Guilin Wuhuan Co. Ltd., China. Bleached softwood kraft pulp imported from Canada was provided by Mudanjiang Hengfeng Paper Co., Ltd., China, and refined in a Valley beater to a beating degree of 40 ^{o}SR before use.

Methods

PCC modification

To understand the modification of PCC with cationically derivatized chitosan and carboxymethyl chitosan, their possible cationic-anionic interaction was investigated using a turbidity analysis test. Three cationic chitosan or carboxymethyl chitosan aqueous solutions, 80, 90, and 95 ppm, were prepared. Then, a set volume of cationic chitosan was added to 100 mL of the same concentration of carboxymethyl chitosan under magnetic stirring at room temperature. The turbidity of these mixtures was tested (Wang *et al.* 2014), and is shown in Fig. 1. When the ratio of cationic solution to anionic solution reached 43 to 45/100, the highest turbidity was achieved for the three mixtures. The turbidity of these mixtures decreased as more cationic solution was added, which potentially was a result of dilution. The above ratio of the cationic solution to anionic solution possibly was the end of the cationic-anionic neutralization interaction. The ratio of cationic chitosan and carboxymethyl chitosan used for modification of PCC was chosen based on their cationic-anionic neutralization interaction.

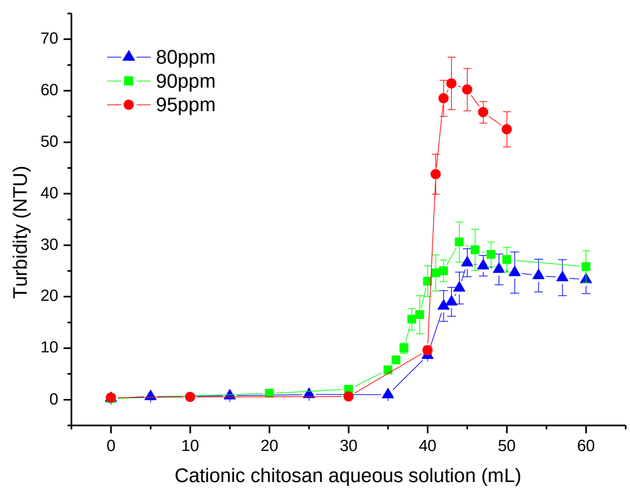

Fig. 1. The turbidity of complex formed between cationic chitosan and carboxymethyl chitosan

An aqueous slurry containing 15 g of PCC (oven dry) and 100 mL of deionized water was prepared. Cationically derivatized chitosan and carboxymethyl chitosan aqueous solutions both with a concentration of 1% were prepared. The cationic chitosan aqueous solution was added into the slurry under stirring at 500 rpm and mixed under stirring at the same speed for 1 min. Then, the carboxymethyl chitosan aqueous solution was added and the slurry was subjected to stirring at 500 rpm for another 9 min. The consistency of the resulting slurry was adjusted to 8.6% by adding extra deionized water, and it was directly used for analysis and handsheet preparation as soon as possible. As a preliminary study, four ratios of cationic/anionic polymer modified PCC were prepared, as shown in Table 1. The particle size and its distribution of modified PCC (0.1% in aqueous medium) were analyzed by a laser particle analyzer LS13-320 (Beckman Coulter, USA). The microscopic morphological characteristics of modified or unmodified PCC particles were observed by a scanning electron microscope (Quanta-200, FEI; Holland) operating at an accelerating voltage of 20 kV. To investigate the deposition efficiency of cationic chitosan and carboxymethyl chitosan during modification of PCC, the supernatant turbidities of the PCC slurry after storing at room temperature for 12 h were tested. The supernatant turbidity experiments were replicated three times for each sample to obtain an average supernatant turbidity.

Table 1. Ratio of Cationic/Anionic Polymer for PCC Modification

Control/modified PCC	Cationic Chitosan (mL)	Carboxymethyl Chitosan (mL)	Water (mL)
0	0	0	75
1	15	60	0
2	15	30	30
3	15	15	45
4	15	7.5	52.5

Preparation of handsheets and determination of PCC retention and paper properties

The handsheets stock containing a certain dosage of PCC based on the oven dry fiber pulp were prepared using a handsheet former (ZQJ1-B-II, Shanxi University of Science and Technology Machinery Factory; China) with a target grammage of 70 g/m^2 and dried with a vacuum dryer under -80 kPa at 90 to 95 °C for 15 min. The amount of modified PCC added into the papersheets was calculated based on the oven dry PCC, and the amount of the modifiers was not considered.

The ash content of the filled handsheets was analyzed according to the TAPPI standard T 211 (TAPPI T 211 om-07 (2007). The retention of PCC in filled handsheets was calculated based on the ash content by the method reported by Shen *et al.* (2010b). Three handsheets were measured for each sample to obtain an average retention of PCC. The tensile indices of filled handsheets were determined using a ZL-300A strength tester (Changchun Small Experimental Machine Factory, China). Brightness and opacity were evaluated by a YQ-Z-48A Brightness and Opacity meter (Hangzhou Qingtong Instrument Development Co., China).

RESULTS AND DISCUSSION

Particle Size and Distribution of Modified PCC

The shape and particle size of papermaking fillers have an important effect on the paper properties (Hubbe and Gill 2004). The particle size and distribution of modified PCC together with its aggregation were analyzed in this study. The volume based equivalent spherical mean particle size of PCC 0 to 4 were 1.299, 1.226, 1.336, 1.183, and 1.283 µm, respectively. When the ratio of the cationic/anionic polymer used in PCC modification was 1:2, the modified PCC achieved slightly higher volume based equivalent spherical mean particle size than the control PCC, *i.e.*, PCC 0, and the other modified PCC.

As shown in Fig. 2, PCC 0 to 4 showed similar distribution of particle size, and PCC 2 had more particles between 1.5 to 2.5 μm and less distribution between 0.6 and 1.2 μm. Scanning electron micrograph images of PCC 0 to 4 are shown in Fig. 3; PCC 2 (Fig. 3c) and 4 (Fig. 3e) showed larger particle aggregation than the control PCC (Fig. 3a).

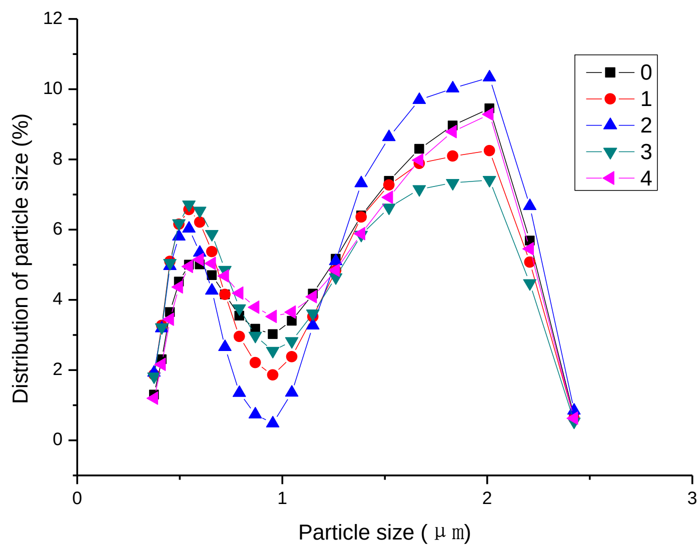

Fig. 2. Particle size distribution of PCC (0 to 4 are the control and modified PCC described in Table 1)

As shown in Fig. 4, the turbidity of PCC 2 supernatant was lower than the control PCC and the other modified PCC. In general, higher deposition efficiency of polymers on PCC during modification results in a clearer supernatant (Shen *et al.* 2010a). Based on the analysis results, modified PCC 2 was chosen as a filler for subsequent handsheet preparations and was named MPCC.

Influence of PCC Modification on Its Retention

It is well known that the complexes of polyelectrolyte and *in-situ* deposition of dual polymers on pulp fiber can reinforce the hydrogen bonds of inter-fiber bonding, resulting in improvement of such properties as tensile strength (Hubbe 2005; Hubbe *et al.* 2005). In this study, PCC modified by the combination of cationic chitosan and carboxymethyl chitosan showed better retention than the control PCC. Due to the weak anionic property on the surface of the PCC with a zeta potential -15.9 mv, the cationic chitosan could be efficiently deposited onto the surface of the PCC. Then, the carboxymethyl chitosan with the weak anion could deposit onto the cationic chitosan anchored on the PCC.

Because the cationic chitosan was able to form ionic bonds and hydrogen bonds with the pulp fibers, and the hydrogen bonds between carboxymethyl chitosan and fibers of pulp, the MPCC had the better joint bonding for pulp fiber due to the polymer deposited on its surface. This interaction was favored by the abundant hydroxyl groups on the fibers, despite their relatively weakly anionic character.

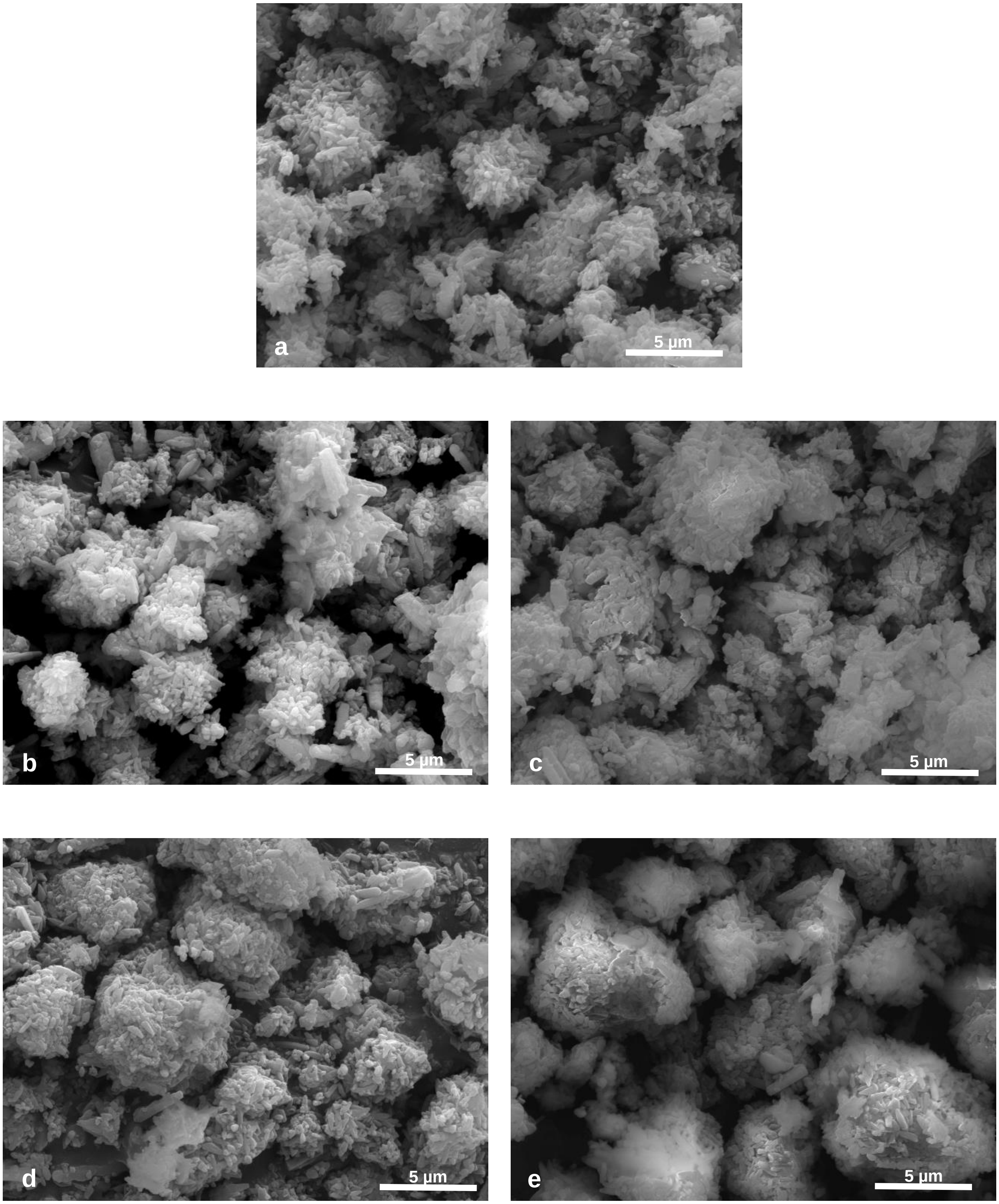

Fig. 3. Scanning electron micrographs images of PCCs. (a) PCC 0, (b) PCC 1, (c) PCC 2, (d) PCC 3, and (e) PCC 4. (0 to 4 are described in Table 1)

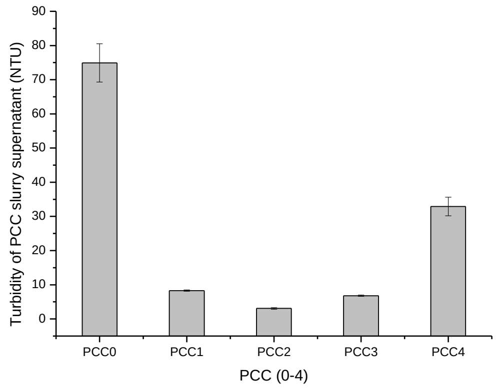

Fig. 4. Turbidity of the PCC slurry supernatants (0 to 4 are the control and modified PCCs described in Table 1). Data are presented as the mean ± standard deviation of three replications.

As shown in Fig. 5, in comparison with the control PCC, the MPCC showed higher retention in various PCC dosages, especially in the case of higher filler dosage. The modification of PCC efficiently improved PCC retention in this lab test.

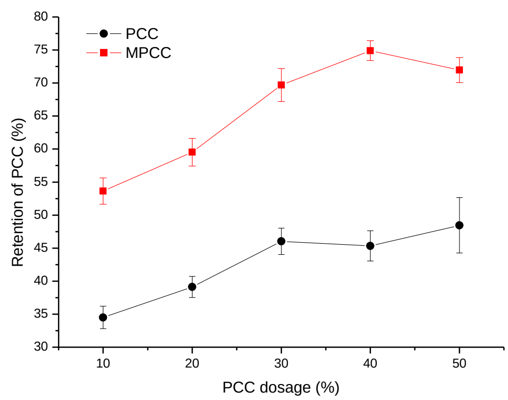

Fig. 5. Effect of filler modification on filler retention. Data presented as the mean ± standard deviation of three replications

Effect of PCC Modification on the Properties of Filled Papersheets

One of the primary aims of using PCC as a filler during papermaking is the improvement of brightness and opacity of the papersheets because the filler has higher brightness and light scattering coefficient than pulp fibers. The MPCC particles were larger than those of the control PCC; therefore, the corresponding specific surface area would be smaller and it would be expected to have less light scattering and opacity for the same amount of filler. However, as shown in Fig. 6a, the filled handsheets with MPCC achieved both higher brightness and opacity than those filled with the control PCC. When higher dosage of PCC and MPCC was used, the handsheets filled with MPCC achieved the higher improvement of brightness and opacity in comparison with the control PCC. The results shown in Fig. 6a could be explained based on the change of PCC retention as shown in Fig. 5. Obviously, the retention of MPCC is quite higher than that of control PCC at the same dosage. The higher retention of MPCC counteracted the negative effect of MPCC larger particles on the brightness and opacity of the filled handsheets. The results shown in Fig. 6a confirmed the positive effect of PCC modification on its retention in handsheets. In general, the papersheet filled with PCC will suffer from some loss of physical properties, such as the tensile strength. However, for handsheets containing the same ash content, *i.e.*, with the same PCC content, the loss of tensile index of the handsheet filled with MPCC was lower than that filled with the control PCC (Fig. 6b). The combination of cationic chitosan and carboxymethyl chitosan used in the modification of PCC may have improved the contribution of hydrogen bonds to inter-fiber bonding. Because hydrogen bonding is one of the most important factors for tensile strength of papersheets, the modification of PCC may be a useful approach to reduce the negative effect on the tensile strength of PCC as a papermaking filler.

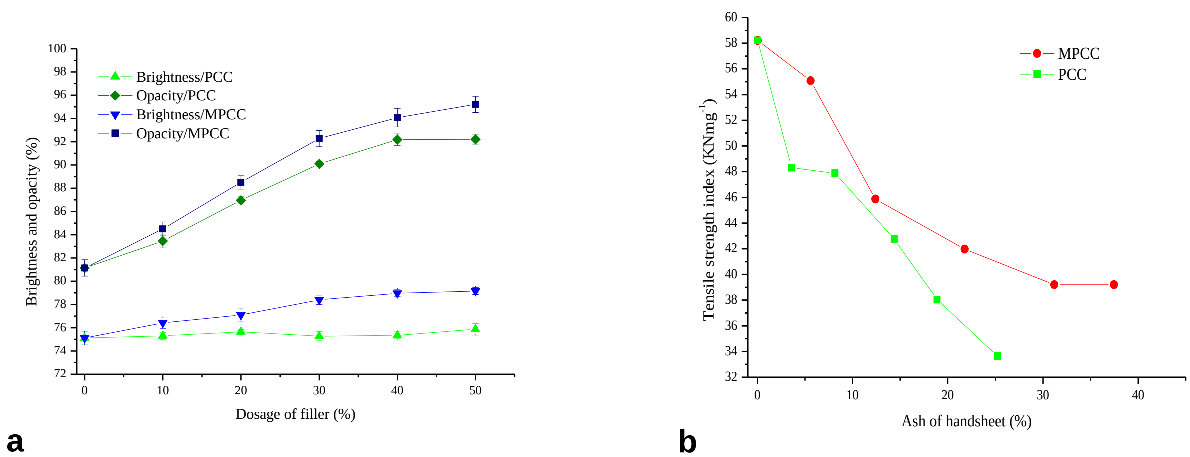

Fig. 6. Effect of PCC modification on the properties of filled handsheets. (a) Paper brightness and opacity as a function of PCC dosage, and (b) paper tensile strength as a function of ash content

CONCLUSIONS

1. In comparison with the control PCC, the particle size and its distribution of PCC modified with a combination of cationically derivatized chitosan and carboxymethyl chitosan did not change too much. Polymers were most efficiently deposited onto the surface of PCC in cases when the cationic chitosan and carboxymethyl chitosan had a dosage ratio of 1:2.
2. The retention in handsheets of PCC modified by the combination of cationic chitosan and carboxymethyl chitosan with a dosage ratio of 1:2 performed better than the control PCC, especially in cases when higher PCC dosage was used in handsheet preparation.
3. The brightness and opacity of the handsheets filled by modified PCC were markedly improved compared to the control PCC. Also, the addition of MPCC to handsheets resulted in a higher tensile index in comparison to those made with the control PCC in cases when the same PCC content was used in the handsheets. The modification of PCC by the combination of cationic chitosan and carboxymethyl chitosan provided an alternative approach for reducing the tensile strength loss of paper filled with PCC.

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