Filler Modification for Papermaking with Cationic Starch and Carboxymethyl Cellulose: A Comparative Study

He Yang, Li Qiu, Xueren Qian, and Jing Shen*

The use of mineral fillers in cellulosic paper products can result in cost/energy savings and improvement of paper properties. However, the increase in filler addition levels is hampered by the negative impact of fillers on paper strength, poor filler retention, *etc.* As an attempt to improve the use of fillers in papermaking, filler modification with the combination of cationic starch and carboxymethyl cellulose was preliminarily explored in this mini-study. This concept was compared with filler modification with either cationic starch or carboxymethyl cellulose. The combination of cationic starch with carboxymethyl cellulose resulted in improved attachment of the starch to the filler, possibly suggesting the *in-situ* formation of polymer complexes with lower solubility than starch. With respect to filler retention, tensile strength, brightness, and opacity of the filled paper, the combined use of cationic starch and carboxymethyl cellulose resulted in a modified filler material with modestly better performance, in comparison to filler modification with either cationic starch or carboxymethyl cellulose. The combined use of a cationic polymer and an anionic polymer to modify fillers may provide an alternative approach to improving the use of mineral fillers in the paper industry.

Keywords: Cationic starch; Carboxymethyl cellulose; Filler modification; Papermaking

*Contact information: Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Material Science and Engineering College, Northeast Forestry University, Harbin 150040, China; *Corresponding author: jingshen.china@hotmail.com*

INTRODUCTION

Cellulosic fibers are the main component of paper products. In addition, various categories of fillers, coating pigments, and chemical additives (either performance chemicals or process chemicals) can be used in paper production. For many paper grades, such as printing/writing and packaging paper grades, the wet-end use of calcium carbonate and other mineral fillers is a well-known practice to reduce papermaking cost, decrease energy consumption, and improve paper properties (*e.g.*, opacity, brightness, and printability) (Cheng *et al.* 2011; Dong *et al.* 2008; Deng *et al.* 2010; Song *et al.* 2012; Zhang *et al.* 2013). Furthermore, the use of some specialty fillers, such as titanium dioxide, can enable the use of traditional cellulosic paper for functional applications (Shen *et al.* 2011; Shen and Qian 2012).

In the area of fillers for papermaking, the development of technologies for cost and energy savings, paper property improvements, process optimization, and increased environmental friendliness is of continuing significance. In this sense, the relevant research topics in this area may include fibrous filler engineering, nanofiller engineering, filler preflocculation, organic filler engineering, and surface modification of mineral fillers (Shen *et al.* 2010a). The successful implementation of filler engineering technologies can in some sense be strategic for further development of the global paper industry. These technologies are expected to mitigate various challenges associated with filler addition in papermaking, which include deteriorated paper strength, poor filler retention, wire abrasion, lowered efficiency of the sizing agents, and "dusting" during printing.

Modification of fillers with various polymers (*e.g.*, starch, cellulose, chitosan, and alginate) or their composites is an interesting concept for enhancing the bondability of fillers (Cao *et al.* 2011; Deng *et al.* 2010; Fatehi *et al.* 2013a,b; Ding and Liu 2012; Huang *et al.* 2013; Nelson and Deng 2008; Shen *et al.* 2008,2009,2010b; Song *et al.* 2009; Yan *et al.* 2005; Yoon and Deng 2006a,b, 2007; Zhao *et al.* 2005). This modification is expected to lead to a reduced negative impact of filler addition on paper strength, allowing for increased filler content of paper products and hence more cost and energy savings. The use of cationic polymers (*e.g.*, cationic starch) in filler modification can result in pre-flocculation/aggregation of filler particles, and the pre-attachment of polymer molecules to several particles is likely to contribute to increased bondability with cellulosic fibers (Chauhan and Bhardwaj 2013; Cheng *et al.* 2011; Sang *et al.* 2012). Bio-based sucrose and molasses (Fahmy 2007a,b; Fahmy and Mobarak 2008a,b, 2009, 2011,2013; Fahmy *et al.* 2006) are also potential candidates for improving the use of fillers by engineering of the cellulosic fiber-based networks.

The combination of a cationic polymer and an anionic polymer is known to provide significant paper strength improvement (Ankerfors *et al.* 2009; Fatehi *et al.* 2009,2010; Hubbe 2005; Hubbe *et al.* 2005; Lofton *et al.* 2005; Gärdlund *et al.* 2005). For such a combination, the interaction of polyelectrolyte complexes with cellulosic fibers (*i.e.*, fiber modification with these complexes) can be critical for efficient paper strength development. These complexes are formed by cationic-anionic interactions between the polymers. Similarly, it might be interesting to investigate the applicability of such a combination to filler modification for papermaking.

In the current study, the concept of filler modification for papermaking with the combination of two typical ionic biopolymer additives widely used in the paper industry, *i.e.*, cationic starch and carboxymethyl cellulose, was preliminarily explored. Using precipitated calcium carbonate as the filler material, comparisons were made on three fiber modification approaches involving the use of the biopolymers. These include the following: 1) filler modification with the combination of cationic starch and carboxymethyl cellulose; 2) filler modification with cationic starch; and 3) filler modification with carboxymethyl cellulose. The effect of filler modification on the use of the filler material in papermaking was also evaluated. The overall objective of this study was to give a preliminary evaluation/demonstration of the simple concept of filler modification for papermaking with the dual biopolymers.

MATERIALS AND METHODS

Materials

Cationic tapioca starch (powder) with the trademark of GELTRON® 24 was supplied by General Starch Limited, Thailand; its degree of substitution (DS) was claimed to be 0.028 to 0.033. It was claimed by the supplier to be suitable for use as a strength/retention additive for papermaking. Carboxymethyl cellulose (powder), a rapidly water-soluble biopolymer tailored for papermaking wet-end applications, was obtained from CP Kelco (a Huber company) (Finnfix® GW); its degree of substitution was claimed to be 0.4 to 0.65. Powdery precipitated calcium carbonate with a brightness of 92.4% ISO was supplied by Guangxi Guilin Wuhuan Co., Ltd., China. Wood-derived bleached kraft pulp imported from Canada was provided by Mudanjiang Hengfeng Paper Co. Ltd., China, and was refined in a Valley beater to a beating degree of 30 ^{o}SR.

Filler Modification

Three approaches were used to prepare modified fillers: 1) cationic starch/ carboxymethyl cellulose modified filler (approach A); 2) cationic starch modified filler (approach B); and 3) carboxymethyl cellulose modified filler (approach C). The latter two were used for comparative investigation into the impact of filler modification by combining cationic starch with carboxymethyl cellulose. Powdery cationic starch was cooked/gelatized at 90 ^{o}C prior to use in filler modification.

Approach A

An aqueous slurry containing 9.42 g of precipitated calcium carbonate was prepared. Under stirring at 500 rpm, a cationic starch solution and carboxymethyl cellulose solution were then sequentially added. The mixture was then mixed under stirring at the same speed for 15 min. The total volume of the mixture was finally adjusted to 250 mL by adding extra water. The resulting slurry was directly used for paper-sheet preparation.

The dosages of cationic starch and carboxymethyl cellulose used for filler modification were chosen based on their possible cationic-anionic interaction in an aqueous medium. In a preliminary investigation, various amounts of 0.01 g/mL cationic starch solutions were added to a 0.005 g/mL carboxymethyl solution, and the mixtures were stored (in a stationary manner, without any stirring) for 24 h; subsequently, photographs of the mixtures were taken (Fig. 1). It was found that when the weight ratio of cationic starch to carboxymethyl cellulose was in the range of 8 to 14 g/g, visually rather similar amounts of clear precipitates were formed, possibly indicating the substantial formation of polyelectrolyte complexes with varied net charges. Further increases in weight ratio resulted in a sharp increase in supernatant turbidity, possibly indicating that suspending of polyelectrolyte complexes in the aqueous medium. As a preliminary attempt to modify precipitated calcium carbonate with cationic starch and carboxymethyl cellulose, the weight ratio of 10 g/g was chosen, and the dosages of cationic starch and carboxymethyl cellulose were 5% and 0.5%, respectively, based on the dry weight of precipitated calcium carbonate. It was expected that such dosages might lead to the *in-situ* deposition of polymer complexes on precipitated calcium carbonate. In a similar work, polydiallyldimethylammonium chloride and carboxymethyl cellulose were sequentially added to a fiber suspension as an approach to modify fibers based on the expected mechanism of *in-situ* formation of polyelectrolyte complexes for paper strength development (Hubbe 2005). Because the solubilities of these complexes can be lower than that of cationic starch or carboxymethyl cellulose, filler modification might result in greater and more irreversible deposition. Compared with filler modification with cationic starch alone (approach B), the use of carboxymethyl cellulose together with cationic starch in the current approach resulted in more efficient polymer deposition on filler particles, as estimated from the supernatants of modified filler slurries after storing at room temperature for 24 h (Fig. 2). In general, the clearer the supernatant is, the better the polymer deposition (Shen *et al.* 2010a).

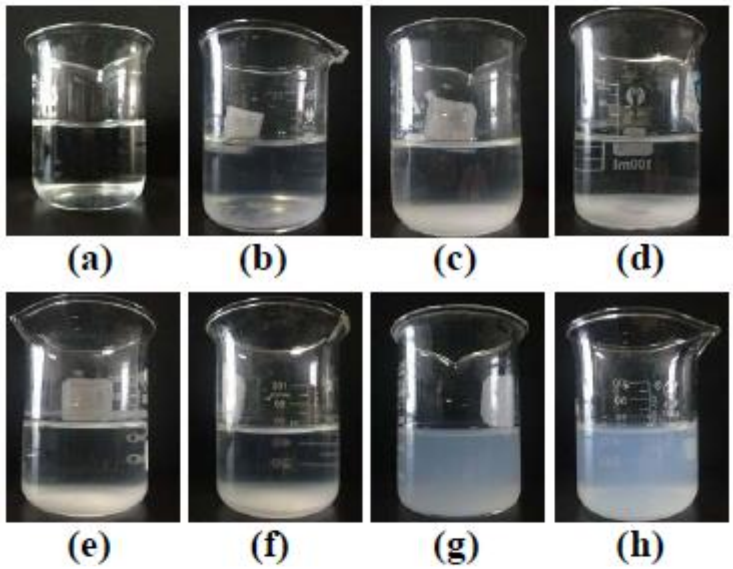


Fig. 1. Photographs of various aqueous systems after storing (in a stationary manner, without any stirring) at room temperature for 24 h: (a) carboxymethyl cellulose solution; (b)-(h) aqueous systems prepared by adding various amounts of cationic starch solutions to carboxymethyl cellulose solution (weight ratios of cationic starch to carboxymethyl cellulose of 6, 8, 10, 12, 14, 16, and 18 g/g, respectively)

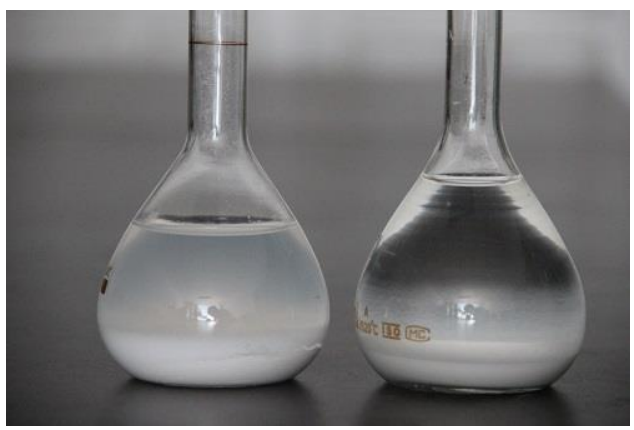


Fig. 2. Photographs of cationic starch modified filler slurry (left) and cationic starch/carboxymethyl cellulose modified filler slurry (right) after storing at room temperature for 24 h

Approach B

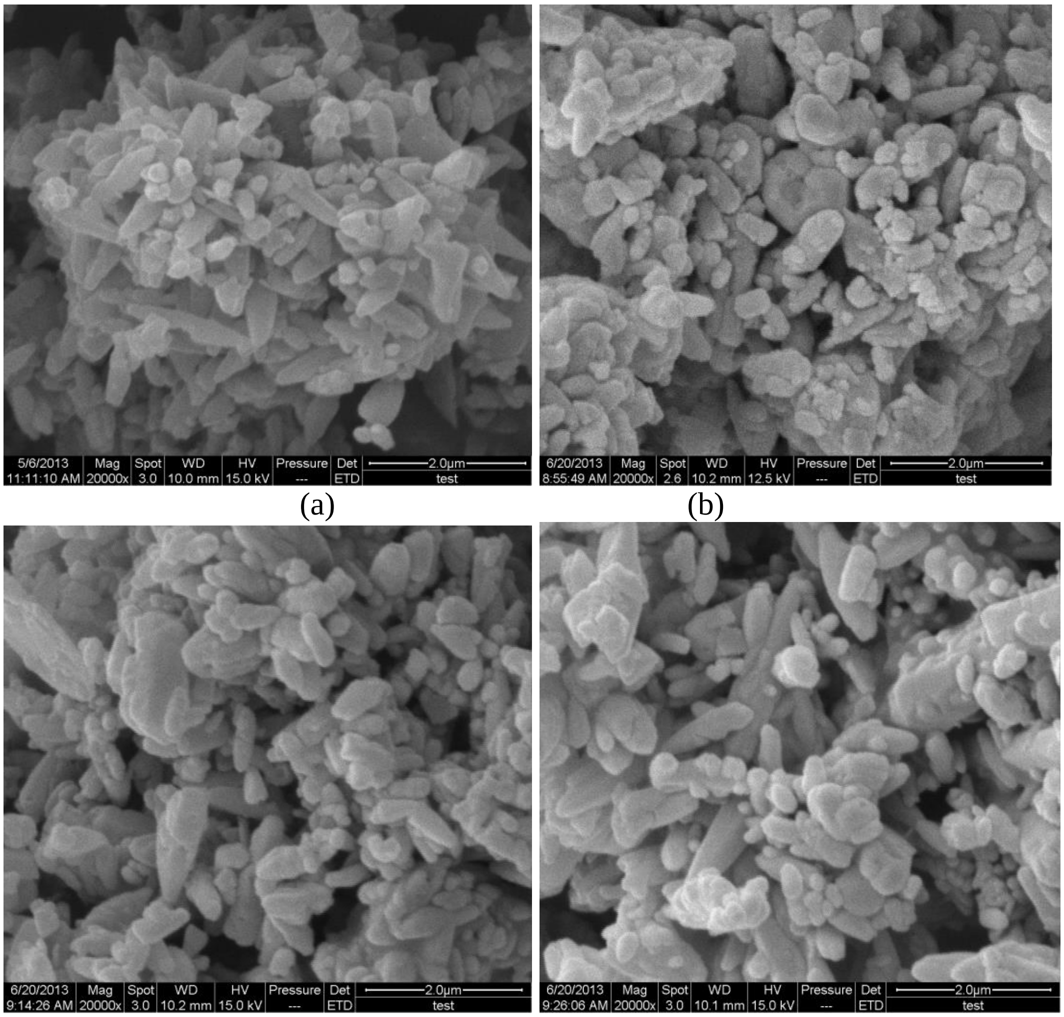
An aqueous slurry containing 9.42 g of precipitated calcium carbonate was prepared, followed by the addition of cationic starch solution. The mixture was mixed under stirring at 500 rpm for 15 min.

The total volume of the mixture was finally adjusted to 250 mL by adding extra water. The resulting slurry was directly used for paper-sheet preparation. Note that the dosage of cationic starch was 5%, based on the dry weight of precipitated calcium carbonate.

Approach C

This approach was generally the same as approach B. The only difference is that instead of cationic starch, carboxymethyl cellulose with a dosage of 0.5% (based on the dry weight of precipitated calcium carbonate) was used in filler modification.

Scanning electron micrographs of modified fillers prepared from approaches A through C as well as the unmodified filler are shown in Fig. 3.



(a) (b) (c) (d)

Fig. 3. Scanning electron micrographs of different fillers: (a) precipitated calcium carbonate (unmodified filler); (b) cationic starch modified filler (approach A); (c) carboxymethyl cellulose modified filler (approach B); (d) cationic starch/carboxymethyl cellulose modified filler (approach C)

Preparation of Paper-sheets and Determination of Filler Retention and Paper Properties

The pulp and filler (either the modified or unmodified filler) were mixed prior to sheet formation. No extra retention agent was added. Paper sheets with a target basis weight of 60 g/m^2 were prepared using a ZQJ1-B-II sheet former (China). The wet sheets were pressed at 0.4 MPa for 5 min and were then dried using a plate dryer for 5 min. The target filler addition level was 20%, based on the target dry weight of paper-sheets. For the use of modified fillers in paper-sheet preparation, the amount of fillers was calculated based on precipitated calcium carbonate, *i.e.*, the organic part (single polymer or dual polymers) of the modified fillers was not considered.

Filler retention was determined by incinerating the paper sheets at 525 ^{o}C for ash content measurement. A calculation was made to convert ash content to filler retention, as reported by Shen *et al.* (2010a). Filler content of the filled paper-sheets was also calculated.

The tensile strength of paper sheets was determined using a ZL-300A strength tester (China) (temperature: 25 ^{o}C; relative humidity: 40%). The brightness and opacity of paper sheets were tested using a YQ-Z-48A brightness & color tester (China) (temperature: 28 ^{o}C; relative humidity: 40%). Paper thickness was tested using a ZUS-4 paper thickness tester (China), and paper density was then calculated (temperature: 28 ^{o}C; relative humidity: 40%).

RESULTS AND DISCUSSION

Concept of Filler Modification with a Cationic Polymer and an Anionic Polymer

The combination of a cationic polymer and an anionic polymer to promote inter-fiber joint bonding and improve paper strength has been widely researched (Ankerfors *et al.* 2009; Fatehi *et al.* 2009, 2010; Hubbe 2005; Hubbe *et al.* 2005; Lofton *et al.* 2005; Gärdlund *et al.* 2005; Sang *et al.* 2010). In this case, the fiber modification concepts based on dual polymers may include the following: 1) pre-formation of polyelectrolyte complexes for subsequent deposition on fibers; and 2) *in-situ* deposition of dual polymer complexes on fibers (Hubbe 2005). It would be interesting to investigate such concepts with respect to filler modification. Similar to fibers, the fine filler particles can potentially be used as carriers for these polymer complexes. The combination of these complexes with filler particles may lead to the development of alternative approaches to fabrication of filler/polymer composites for papermaking applications. As the complexes have high bondability with fibers, the negative impact of filler/polymer composites on paper strength would be lower than that of totally inorganic filler particles. On the other hand, the attachment of polymer complexes to filler particles may also result in improved filler retention due to enhanced filler aggregation induced by the organic complexes (*e.g.* micro- or nano-particles).

Figure 4 is a schematic of a filler modification concept involving the addition of a cationic polymer and an anionic polymer to a filler suspension, where cationic-anionic interactions can be favorable for the deposition of polymers on a filler particle or several filler particles.

Chemicals based on starch and cellulose can be used in the production of various bio-based products for diversified applications (Bénézet *et al.* 2012; Ghanbarzadeh *et al.* 2011; Gilfillan *et al.* 2012; Kaisangsri *et al.* 2012; Maran *et al.* 2013). Cationic starch is the most widely used bio-based additive for papermaking wet-end applications, as a paper strength promoter and/or retention agent. Carboxymethyl cellulose is also commercially used for paper strength improvement. In the current study, by following the concept shown in Fig. 4, these two biopolymers were combined to modify precipitated calcium carbonate filler, and the influence of filler modification on the use of the filler material in papermaking was preliminarily explored.

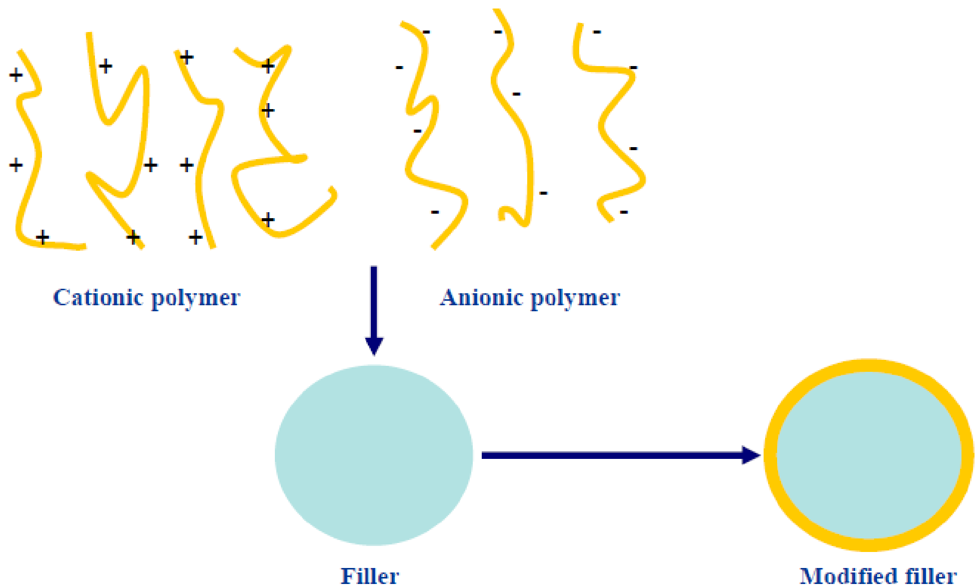


Fig. 4. Schematic of the concept of filler modification with a cationic polymer and an anionic polymer

Influence of Filler Modification on Filler Retention and Paper Properties

The influence of filler modification on filler retention is shown in Fig. 5(a). Filler modification with cationic starch alone resulted in a significant increase in filler retention (above 300%), which is due to pre-flocculation of filler particles based on the flocculating nature of cationic starch (Sang *et al.* 2012) (see Fig. 3(b)). However, filler modification with carboxymethyl cellulose alone resulted in a decrease in filler retention, which can be explained by its role in dispersing the filler particles. It was reported that carboxymethyl cellulose could be used as an effective dispersant for pulp slurries (Giri *et al.* 2000; Rantanen *et al.* 2006). Similarly, once the negatively charged carboxymethyl cellulose is attached to filler particles, the particle-to-particle repulsion is enhanced and filler retention in paper sheets is discouraged. Compared with filler modification with cationic starch, filler modification with the combination of cationic starch and carboxymethyl cellulose resulted in a little bit (almost negligibly) higher filler retention. The impacts of filler modification on filler retention can also be seen in the filler contents of unfilled and filled paper-sheets (see Fig. 5(b)).

The influence of filler modification on the tensile strength of the filled paper is shown in Fig. 5(c). The addition of unmodified precipitated calcium carbonate prior to paper-sheet formation resulted in a significant decrease in tensile strength as a result of the interference of non-bondable filler particles with inter-fiber bonding. Filler modification with cationic starch resulted in a minor decrease in tensile strength; a possible self-explanatory reason is related to significantly increased filler retention as a result of filler modification (see Fig. 5(a)-(b)). Filler modification with carboxymethyl cellulose resulted in an increase in tensile strength, primarily because of decreased filler retention and the possible bondability of carboxymethyl cellulose with cellulosic fibers. In the case of filler modification with the combination of cationic starch and carboxymethyl cellulose, a modest increase in the tensile strength of the filled paper was achieved compared with filler modification with cationic starch. Thus, by considering both filler retention and tensile strength of the filled paper, filler modification with cationic starch and carboxymethyl cellulose is modestly superior to filler modification with cationic starch or carboxymethyl cellulose alone.

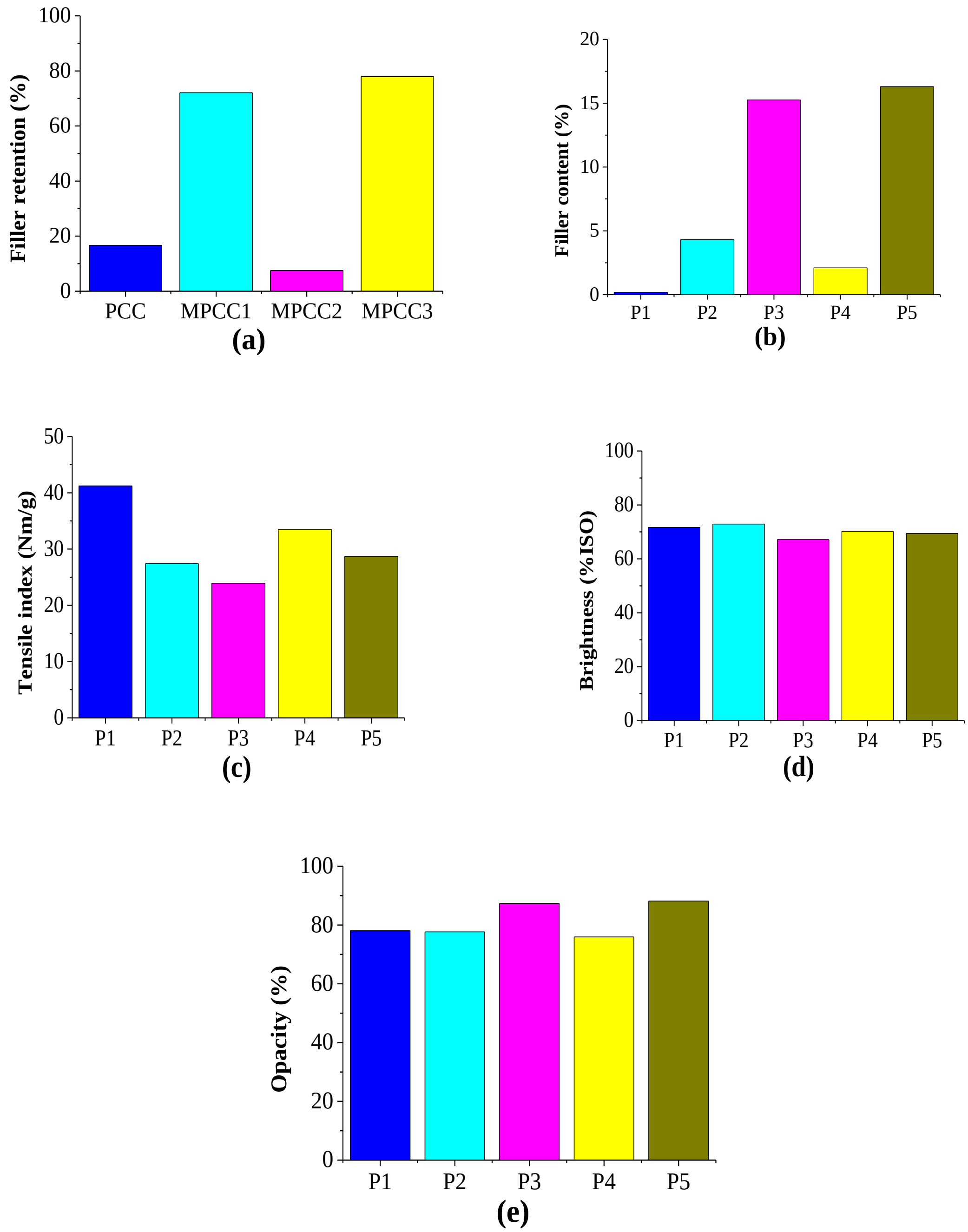


Fig. 5. Effect of filler modification on filler retention and the properties of filled paper-sheets: (a) filler retention; (b) filler content; (c) tensile strength; (d) brightness; (e) opacity
Note: PCC, MPCC1, MPCC2, and MPCC3 refer to precipitated calcium carbonate, cationic starch modified precipitated calcium carbonate, carboxymethyl cellulose modified precipitated calcium carbonate, and cationic starch/carboxymethyl cellulose modified precipitated calcium carbonate, respectively; P1, P2, P3, P4, and P5 refer to unfilled paper, precipitated calcium carbonate filled paper, cationic starch modified precipitated calcium carbonate filled paper, carboxymethyl cellulose modified precipitated calcium carbonate filled paper, and cationic starch/carboxymethyl cellulose modified precipitated calcium carbonate filled paper, respectively.

The influence of filler modification on optical properties (brightness and opacity) of the filled paper is shown in Fig. 5(d)-(e). Compared with filler modification with cationic starch, filler modification with the combination of cationic starch and carboxymethyl cellulose resulted in a slight increase in brightness and almost identical opacity. On the other hand, compared with filler modification with carboxymethyl cellulose, filler modification with the combination of cationic starch and carboxymethyl cellulose resulted in nearly identical brightness and higher opacity. Therefore, in terms of optical properties of the filled paper, the combined use of cationic starch and carboxymethyl cellulose was somewhat superior to the use of either cationic starch or carboxymethyl cellulose.

CONCLUSIONS

1. When precipitated calcium carbonate was used as the filler material, the addition of carboxymethyl cellulose together with cationic starch in the filler modification process resulted in hardened attachment of cationic starch to the filler.
2. Under the conditions studied, compared with filler modification with either cationic starch or carboxymethyl cellulose, at the filler addition level of 20 wt%, based on the dry weight of filler and fibers, the combined use of cationic starch with carboxymethyl cellulose resulted in a modified filler with modestly better performance with respect to filler retention, tensile strength, brightness, and opacity of the filled paper.

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