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Unmodified Starch Granules for Strengthening Mineral-Filled Cellulosic Fiber Networks Promoted by Starch Pretreatment with a Cationic Polymer Flocculant in Combination with the Use of an Anionic Microparticulate Material

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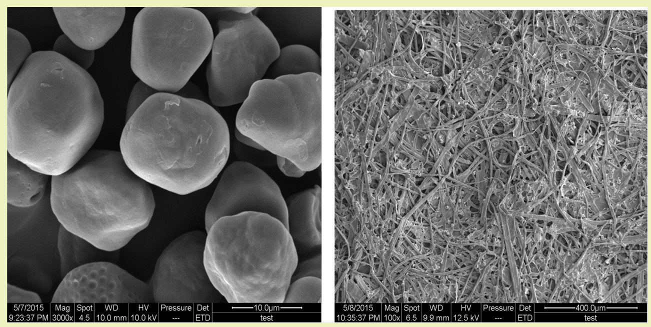
ABSTRACT: The efficient use of renewable resources (e.g., starch) is essential to the green economy. On the basis of commercially available microparticle retention and drainage systems, the process concept of trapping unmodified starch granules in mineral-filled cellulosic fiber networks for strength enhancement by incorporation of cationic polymer flocculant pretreated/bridged starch granules in combination with the use of an anionic microparticulate material was discussed and demonstrated. Specifically, a high molecular weight cationic polyacrylamide and a modified bentonite, which are commercially available in the market, were used as the polymer flocculant and the anionic microparticulate material, respectively. The paper strength loss upon the addition of precipitated calcium carbonate filler particles was significantly mitigated by employing such a concept, which may provide an alternative strategy for improving the strength properties of mineral-filled paper grades.



KEYWORDS: *Unmodified starch granules, Mineral fillers, Cationic polyacrylamide, Bentonite, Papermaking*

■ INTRODUCTION

Starch-bearing plants are the most consumed staple food sources around the world. Commercially, starch is widely used in the manufacture of various products, including food, paper, textiles, building materials, and alcohol for fuel.[1] As a renewable, easily available, and readily biodegradable biopolymer (i.e., a homopolymer of glucose derived from plants), there is a huge potential to make better and more diversified use of starch, which fits well into the green economy concept.[2−9]

Globally, the paper industry is the second biggest consumer of starch, only surpassed by the food industry. In fact, starch, which is chemically similar to cellulose, is the most used biopolymer in the paper industry involving the utilization of cellulosic fibers for the production of various paper-based products. It is widely used for both wet-end and surface applications. In particular, the addition of starch-based chemicals can deliver improvements in paper strength, fines retention, printability/writability, water-resistance, and surface appearance. Starch-based chemicals can also be used as emulsifier in sizing agents, pigment coating binder/cobinder, and anionic trash catcher.[10−12]

Mineral fillers such as calcium carbonate and clay are commercially used in the production of printing/writing paper grades to deliver such significant benefits as cost reduction and printability/writability improvement. However, the addition of filler particles, particularly at high levels, can result in decreased paper strength due to their interference with fiber−fiber bonding.[13,14] This negative impact associated with filler addition can be mitigated by various proposed processes such as surface modification of filler particles with cellulose-bondable polymers or their composites, polymer-induced preflocculation of filler particles, and composite formation between filler particles and cellulosic fines/fibrils, allowing for increasing the filler content while maintaining an acceptable level of paper strength.[15−24]

Differing from previous reports, the process concept of adding unmodified starch granules for strengthening mineral-filled cellulosic fiber networks (i.e., paper) promoted by starch pretreatment with a cationic polymer flocculant in combination with the use of an anionic microparticulate material was discussed and demonstrated in this preliminary study. A microsized precipitated calcium carbonate was used as the mineral filler. A cationic polyacrylamide and a modified bentonite were used as the polymer flocculant and the anionic microparticulate material, respectively. It was hypothesized that

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such a process might be useful for trapping starch granules in the fiber networks, leading to strength enhancement upon drying.

■ MATERIALS AND METHODS

Materials. Unmodified corn starch granules and precipitated calcium carbonate particles (Figure 1a,b) were purchased from Shandong Runyin Biochemical Engineering Co., Ltd., China and Guangxi Guilin Wuhuan Co, Ltd., China, respectively. Hardwood-derived cellulosic fibers (bleached chemical pulp), initially imported from Canada, were supplied by Mudanjiang Hengfeng Paper Co., Ltd., China. Prior to paper sheet preparation, this pulp was treated in a Valley beater to a beating degree of 26° SR. Cationic polyacrylamide (Percol182), a high molecular weight retention polymer, was provided by BASF (China) Co., Ltd. A modified bentonite (Figure 1c), an anionic microparticle retention aid, was obtained from Suzhou Yifan Chemical Co., Ltd., China. Note that the SEM images included in this paper were collected using a scanning electron microscope (SEM, QUANTA 200). Here, the powders of starch, precipitated calcium carbonate filler, and bentonite were used for SEM observations, i.e., no pretreatment was conducted.

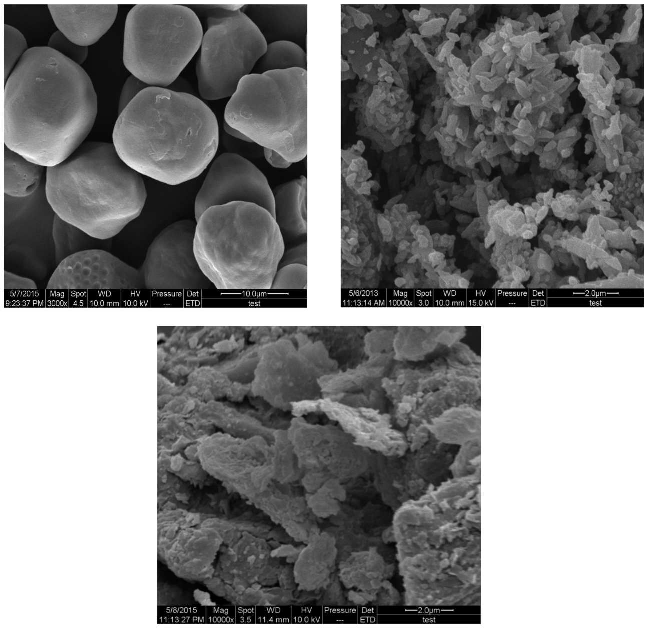

Figure 1. SEM images of unmodified corn starch (top, left), precipitated calcium carbonate (top, right), and bentonite (bottom).

Preparation of Paper Samples. Prior to sheet formation, a papermaking stock (i.e., a slurry) consisting of cellulosic fibers and other components was prepared. In accordance with the concept demonstrated in this study, the process steps involved in stock preparation are as follows: (1) Precipitated calcium carbonate particles were added to fiber slurry, and the mixture was sufficiently mixed. (2) A slurry of cationic polyacrylamide pretreated unmodified corn starch granules (prepared by mixing in an aqueous medium) was added to the slurry containing fibers and filler particles, followed by mixing for 1 min. (3) The as-prepared fiber-containing mixture was sheared for 2 min. (4) A bentonite slurry was added and mixed for 2 min. The filler addition level was 10%, based on the dry weight of papermaking stock. In other sets of experiments, the papermaking stocks were prepared for the formation of other categories of paper sheets: (1) unfilled paper sheets (filler particles were not added; cationic polyacrylamide and bentonite were sequentially added); (2) filled paper sheets with sequential addition of starch granules, cationic polyacrylamide, and bentonite; (3) filled paper sheets with sequential addition of cationic polyacrylamide and the premixture of bentonite and starch granules (i.e., bentonite and starch granules were premixed in in an aqueous medium).[25] Note that for the preparation of papermaking stock, a very common mechanical stirrer produced by a Chinese company (Changzhou Guohua Co., Ltd.) was used for mixing and shearing. For the pretreatment of unmodified starch granules with cationic polyacrylamide or premixing of starch granules with bentonite, a dynamic drainage jar produced from a United States company (Paper Research Materials, Inc.), designed for testing the drainage/retention of papermaking stock, was used. The mixing or stirring was conducted at about 500 rpm, while shearing (2 min) was conducted at about 800 rpm.

Paper sheets with a target basis weight of 90 g/m^2 were prepared using a ZQJ1-B200 mm sheet former (China). The wet sheets were pressed at 0.4 MPa for 5 min, followed by drying at 120 °C for another 5 min. Subsequently, the dried sheets were conditioned in a desiccator (>24 h) prior to tensile strength determination.

Determination of Paper Tensile Strength, Filler Retention, Filler Bondability Factor, and Starch Retention. The tensile strength of paper sheets was tested using a ZL-300A tensile strength tester (China). Filler retention was determined based on the weights of ash and filler particles initially added to the fiber slurry.[26] Filler bondability factor (on the basis of tensile strength) was calculated based on the tensile indices of filled and unfilled paper sheets in combination with filler content:[20]

$$\text{Filler bondability factor} = \frac{\text{Strength of filled paper}}{\text{Strength of unfilled paper}} \times \text{Filler content of filled paper} \times 100$$

Starch retention was determined based on the interaction of dissolved starch with iodine solution (i.e., iodine dissolved in an aqueous medium of potassium iodide), and a UV/vis spectrophotometric method was used.[27] The paper sheets were soaked in water, heated to about 100 °C, and cooked at this temperature for 10 min, allowing for extraction of starch from the sheets. Based on the identified wavelength of 590 nm for maximum absorbance, starch retention was then tested.

■ RESULTS AND DISCUSSION

Process Concept Involving Pretreatment of Unmodified Starch Granules with a Cationic Polymer Flocculant in Combination with the Use of an Anionic Microparticulate Material. In the paper industry, microparticle retention and drainage systems have unique advantages in promoting drainage of water and retention of fine particles (including cellulosic fiber fines and filler particles) during papermaking.[28−36] In contrast to conventional polymer retention systems, microparticle systems tend to give better retention, drainage, and formation.[37] On the basis of typical microparticle systems consisting of a cationic retention polymer and an anionic microparticulate material, the process concept involving pretreatment of unmodified starch granules with a cationic polymer flocculant in combination with the use of an anionic microparticulate material for strengthening mineral-filled cellulosic fiber networks was proposed, which is schematically illustrated in Figure 2. Note that in this study a high molecular weight cationic polyacrylamide and a modified bentonite were used as the polymer flocculant and the anionic microparticulate material, respectively.

In an aqueous medium, unmodified starch granules basically carry a weak negative charge due to the dissociation of hydroxyl groups.[1] Pretreatment with a high molecular weight cationic polyacrylamide would induce the bridging of the granules to the polymer chains, leading to their anchoring/attachment to this cationic polymer flocculant.

Upon the addition of as-formed starch-based composites (i.e., cationic polyacrylamide bridged starch granules) to the

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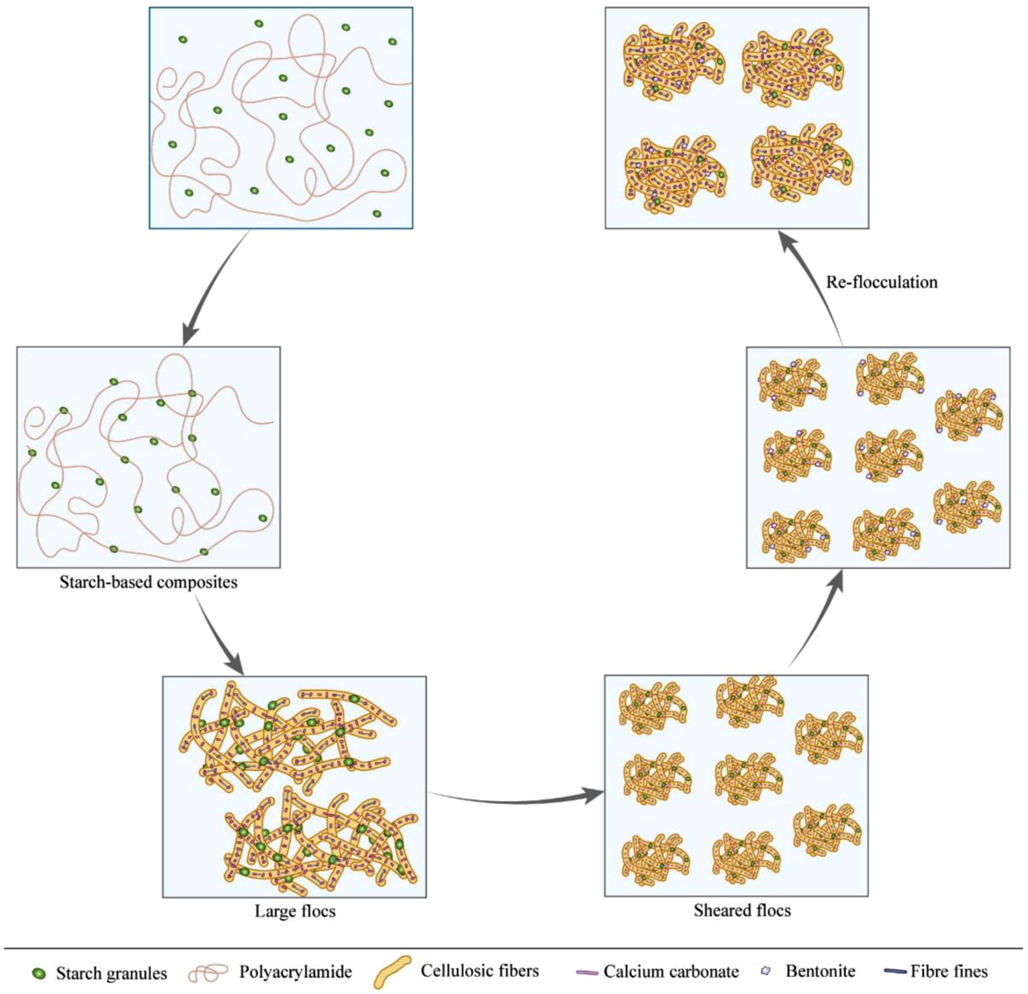

Figure 2. Schematic illustration of the process concept involving pretreatment of unmodified starch granules with a cationic polymer flocculant in combination with the addition of an anionic microparticle for strengthening mineral-filled cellulosic fiber networks. In accordance with this process concept, starch granules are attached to cationic polyacrylamide and then constrained in the fiber networks as a result of interactions among furnish components. Note that in this study, a high molecular weight cationic polyacrylamide and a modified bentonite were used as the polymer flocculant and the microparticle, respectively; also, a microsized precipitated calcium carbonate was used as the filler material. The first "arrow" is related to a certain time interval for attachment of starch granules to the polymer chains. The second "arrow" refers to the introduction of cationic polymer bridged starch granules to a slurry containing cellulosic fibers/fines and filler particles. The third "arrow" refers to the introduction of relatively high shear forces. The fourth "arrow" refers to the introduction of bentonite particles. It is further noteworthy that the shapes of various components shown in this figure are for illustrative purposes only, and they are not indicative of the exact structures.

slurry containing cellulosic fibers (together with a very small amount of fiber fines) and calcium carbonate particles, large flocs can be formed as a result of the polymer bridging action, which enables the binding of calcium carbonate particles and fiber fines to cellulosic fibers. As a high molecular weight polymer flocculant, cationic polyacrylamide can result in very fast formation of the flocs from papermaking stock components consisting of fibers and fine particles.[38] Simultaneously, starch granules, initially anchored/attached to cationic polyacrylamide, are embedded/constrained in the flocs. In this flocculation interaction, in some sense, a higher dosage of cationic polyacrylamide may result in the formation of larger flocs.

The as-formed flocs are then degraded/broken under relatively high shear forces.[39] In this case, the polymer chains may be shortened. Consequently, the presence of cationic polyacrylamide delivers accessible positively charged sites to the sheared flocs.

Subsequently, the introduction of negatively charged bentonite particles results in the reflocculation of the sheared flocs mainly based on the attraction between the anionic moieties of bentonite and the cationic sites of the flocs. In this reflocculation interaction, upon floc breakage, the presence of cationic polyacrylamide provides anchoring spots for bentonite, and bentonite acts as a bridge for other components including cellulosic fibers/fines, precipitated calcium carbonate particles, and starch granules.[40−42] Due to the addition of bentonite, the bound strength of the absorbed polymer layers on the particles suspended in the aqueous medium, including cellulosic fibers/fines, filler particles, and starch granules, can be enhanced.[43] Water can also be effectively eliminated from the flocs during reflocculation, forming tight microaggregates favorable for sheet formation. The flocculation and reflocculation induced by the delicate combination of cationic polyacrylamide with bentonite are essential for the formation of tight microaggregates, facilitating both water removal and fines retention during papermaking.[44] It is noted that the efficiency of retention or drainage is dependent upon the size of bentonite particles or the chaining/agglomeration of these particles in their primary

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state, and a larger size or more chaining/agglomeration is likely shift the benefits more toward retention efficiency and away from an exclusive concentration on drainage and formation.[45] Nevertheless, the trapping of starch granules in the micro-aggregates would facilitate starch retention in the cellulosic fiber networks and hence internal bonding strength development upon drying, due to the cellulose-bondable nature of starch.

Currently, cationic starch is the most used wet-end strength additive in the paper industry, which can readily be adsorbed onto cellulosic fibers as a result of electrostatic attraction. As a low cost biopolymer, cationic starch has a strong affinity with cellulosic fibers mainly due to cationic−anionic interaction and its cellulose-bondable nature.[46,47] However, in general, the maximum amount of cationic starch is limited to about 1.5% (on the basis of the dry weight of paper), and a higher dosage may lead to overcationization and hence decreased paper machine efficiency.[25,48,49] This poses a significant limitation on the strengthening capacity associated with the use of cationic starch. Since unmodified starch is only weakly charged (i.e., a very weak negative charge), its addition at the wet-end section of the paper machine has a much higher strengthening potential in comparison to cationic starch provided that it is effectively retained in the sheet.[25,49,50] The addition of unmodified starch via size press can be another option, but extra energy consumption is needed during the redrying process.[49] Therefore, the process concept shown in Figure 2 might provide a possibility for maximizing the strengthening potential associated with the use of starch, while the uniformity of the paper might be maintained due to the unique advantage of micropartculate retention systems with respect to sheet formation.

Impact of Starch Pretreatment in Combination with Bentonite Addition. The effect of adding unmodified starch granules on paper tensile strength, filler retention, and filler bondability factor is shown in Figure 3. Note that the tensile strength of the unfilled paper was relatively low due to the low intensity of pulp beating/refining (the beating degree of the pulp used in this study was 26° SR). Filler addition resulted in a dramatic decrease in paper strength, due to poor bondability of filler particles with cellulosic fibers.[15,51] For the three processes associated with the addition of unmodified corn starch granules in combination with the microparticle system (consisting of cationic polyacrylamide and bentonite), paper tensile strength and filler bondability factor were simultaneously increased, while the differences in filler retention were not obvious. Interestingly, the process involving pretreatment of starch granules with cationic polyacrylamide followed by bentonite addition gave the highest paper tensile strength and filler bondability factor, which could be due to the favorable intermolecular interactions in the wet end of papermaking.

The impact of cationic polyacrylamide dosage is shown in Figure 4. With the increase in cationic polyacrylamide dosage from 0.02% to 0.08%, filler retention and filler bondability factor were gradually increased possibly due to the enhanced binding action of the polymer in terms of filler-fiber interactions. However, the change in cationic polyacrylamide from 0.08% to 0.1% only exhibited a negligible impact. The tensile strength basically reached a plateau at 0.08% or 0.1%. A relatively high cationic polyacrylamide dosage may provide favorable particle−particle bonding interactions in the aqueous medium, facilitating the aggregation of particulate furnish components. In this case, cationic polyacrylamide can be considered as a "bonding material" or "binder" for particulate components. Efficient adsorption of cationic polyacrylamide on cellulosic fibers, fiber fines, starch granules, and filler particles may also be desired to provide sufficient anchoring points for bentonite.[40] The impact of bentonite dosage is shown in Figure

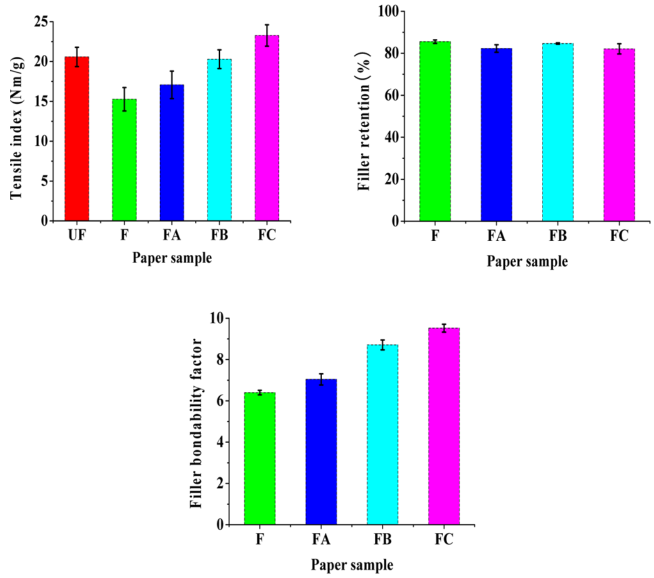

Figure 3. Effect of starch addition on paper tensile strength, filler retention, and filler bondability factor. Note: UF refers to unfilled paper sheets. F refers to filled paper sheets with sequential addition of cationic polyacrylamide and bentonite. FA refers to filled paper sheets with sequential addition of starch granules, cationic polyacrylamide, and bentonite. FB refers to filled paper sheets with sequential addition of cationic polyacrylamide and bentonite pretreated starch granules. FC refers to filled paper sheets with sequential addition of cationic polyacrylamide pretreated starch granules and bentonite. The dosages of starch granules, cationic polyacrylamide, and bentonite were 5%, 0.05%, and 0.5%, respectively, based on the dry weight of papermaking stock.

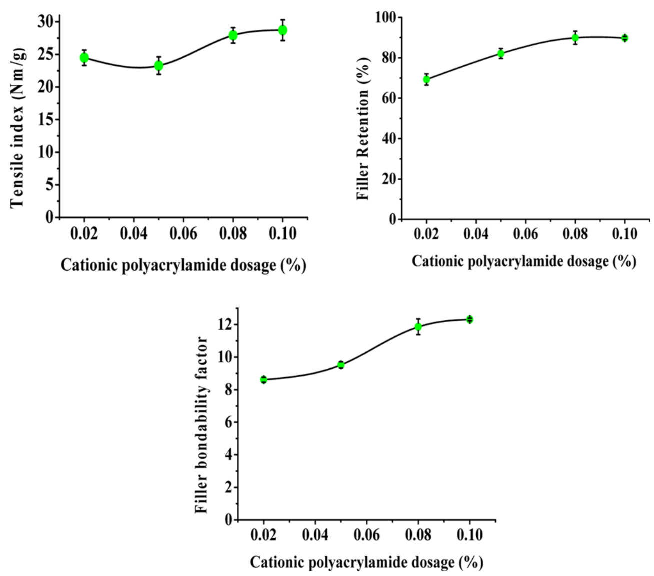

Figure 4. Paper tensile strength, filler retention, and filler bondability factor as a function of cationic polyacrylamide dosage. Note: The paper sheets were prepared based on starch pretreatment with cationic polyacrylamide in combination with bentonite addition. The dosages of starch granules and bentonite were 5% and 0.5%, respectively, based on the dry weight of papermaking stock.

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5. An optimum dosage of 0.5% can be seen as regards paper tensile strength, filler retention and filler bondability factor. On the other hand, the paper strengthening impact of starch granules was highly dependent upon their dosage (Figure 6). It is noteworthy that low retention of uncooked starch granules would be challenging. Particularly, the recirculation of unretained starch in paper machine systems can cause sanitary problems and the increase of chemical oxygen demand (COD) and biological oxygen demand (BOD) of paper mill effluent.[52] For paper tensile strength and filler bondability factor, peak values were reached at 8%. The increase in starch dosage did not result in the reduction in filler retention, which is a promising phenomenon in terms of the potential combined use of filler particles and starch granules in the paper industry. However, the increase in starch dosage led to a reduction in starch retention in the paper web. At a starch dosage of 1%, starch retention was around 70%. As shown from the SEM images (Figure 7), unmodified corn starch granules constrained/trapped in the fiber networks were swelled and partially gelatinized under the conditions studied, which in turn contributed to the consolidation/strengthening of mineral-filled fiber networks.

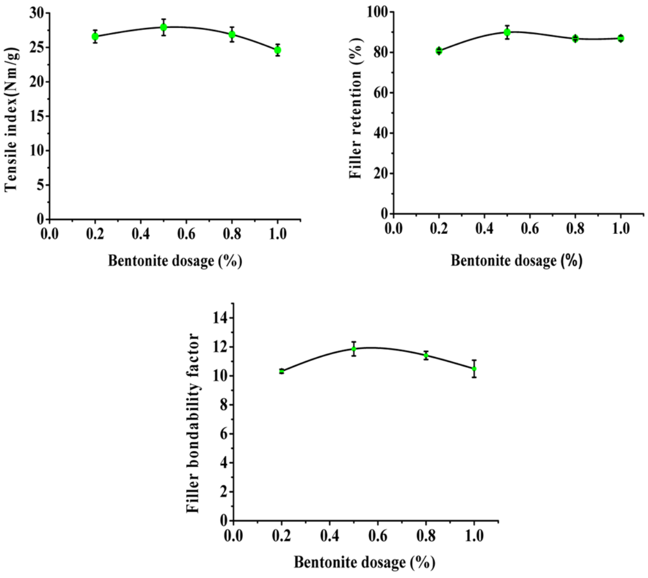

Figure 5. Paper tensile strength, filler retention, and filler bondability factor as a function of bentonite dosage. Note: The paper sheets were prepared based on starch pretreatment with cationic polyacrylamide in combination with bentonite addition. The dosages of starch granules and cationic polyacrylamide were 5% and 0.08%, respectively, based on the dry weight of papermaking stock.

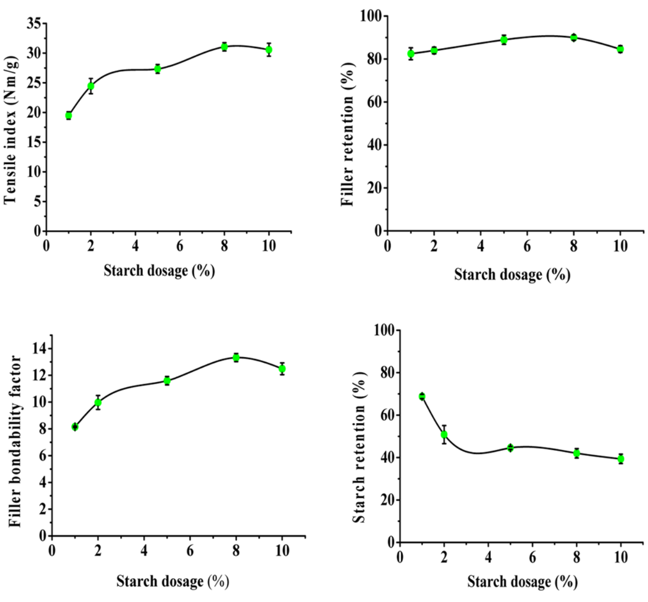

Figure 6. Effect of starch dosage on paper tensile strength, filler retention, filler bondability factor, and starch retention. Note: The paper sheets were prepared based on starch pretreatment with cationic polyacrylamide in combination with bentonite addition. The dosages of cationic polyacrylamide and bentonite were 0.08% and 0.5%, respectively, based on the dry weight of papermaking stock.

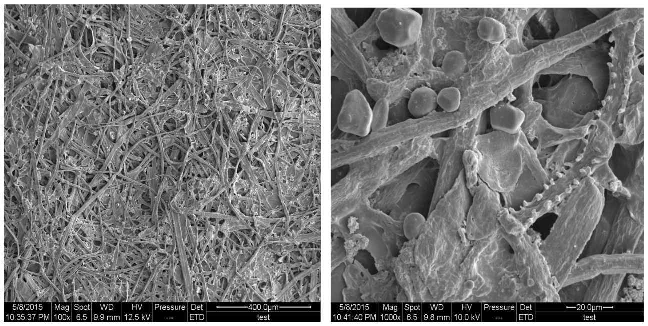

Figure 7. SEM images of a filled paper sample taken at two magnifications. Note: The dosages of starch granules, cationic polyacrylamide, and bentonite were 8%, 0.08%, and 0.05%, respectively, based on the dry weight of papermaking stock.

Despite the fact that the process concept involving the trapping of unmodified starch granules in filler-containing fiber networks as a result of starch pretreatment with a cationic polymer flocculant in combination with the use of a microparticulate material was quite effective, future work related to other critical aspects such as those related to sheet formation is still needed.

■ CONCLUSION

To enhance the strength properties of mineral-filled cellulosic fiber networks (i.e., paper), the process concept of wet-end addition of cationic polymer flocculant bridged starch granules in combination with post-addition of an anionic microparticulate material was discussed and demonstrated. In accordance with this concept, a high molecular weight cationic polyacrylamide and a modified bentonite were used as the flocculant and microparticulate material, respectively. The effectiveness of the process concept was preliminarily identified. The results also showed that at a given filler addition level, i.e., 10%, paper strength enhancement was dependent upon the dosages of cationic polyacrylamide, bentonite, and starch. This concept may provide a possibility to mitigate the negative impact of filler addition through the combination of microparticle systems with unmodified starch granules.

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Notes

The authors declare no competing financial interest.

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