Tailoring starch-engineered mineral particles towards enhanced interaction with cellulosic fibers

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ABSTRACT

Interaction of unmodified starch with guest molecules or ligands (e.g., fatty acids) as a basis for the formation of starch-encapsulated mineral filler particles is an effective process for mitigating the negative impact of filler addition on the strength properties of cellulosic networks. As unmodified starch is essentially nonionic, the interaction of starch-engineered fillers with negatively charged cellulosic fibers is somehow limited. Here, the concept of substituting unmodified starch with a minor amount of cationic starch in filler engineering with starch inclusion complexes was proposed. It was hypothesized that filler-fiber interaction would be enhanced by cationic-anionic attraction. Encouragingly, the effectiveness of this concept was demonstrated to be very pronounced. For instance, at a cationic starch percentage of 3% (relevant to the weight of total starch), filler retention and filler bondability with cellulosic fibers were significantly improved, leading to further mitigated negative impact of filler addition on tensile strength. Basically, this easily scalable concept may shed light on greener, more efficient use of filler technologies on the basis of starch inclusion complex formation, opening up new possibilities for real commercial applications.

Keywords: Unmodified starch; Cationic starch; Starch inclusion complex; Cellulosic networks; Mineral fillers
1. INTRODUCTION

As a plant-derived macromolecule, starch is widely used in the commercial production of cellulosic paper-based bioproducts. In general, starch-based chemicals are added into the cellulosic stock (i.e., a dilute aqueous slurry mainly containing cellulosic fibers) prior to the construction of cellulosic networks, or used via surface application (i.e., surface engineering of cellulosic networks). Basically, the use of starch-based chemicals can deliver improvements in paper strength, sheet uniformity, fines retention, machine runnability, and liquid barrier properties. In line with the global trend towards a green economy, the more efficient use of chemical additives derived from renewable resources instead of non-renewables is of strategic significance.1-10

As a sustainable biopolymer, starch has lots of commercial uses, and there has been a growing interest to find new capabilities/markets.11-17 Hydrogen bonds tend to be formed between starch and cellulosic fibers during sheet formation or paper surface treatment. The cellulose-bondable nature of starch provides a basis for its interesting role in enhancing the bondability of mineral filler particles with cellulosic fibers, which in turn significantly mitigates the detrimental impact of increased filler addition on paper strength. Due to the much lower cost of mineral fillers in comparison to cellulosic fibers and their role in enhancing some critical properties (e.g., opacity and printability) of the paper, the use of starch and other cellulose-bondable polymers for maximizing the allowable filler addition level is believed to have a strong practical significance.18-23

Surface coating of mineral filler particles with starch inclusion complexes is one of the interesting concepts to deliver enhanced filler bondability with cellulosic fibers.24-32 In this “releasing-combining” concept, starch-derived macromolecules (e.g., amylase and amylopectin) are released from unmodified starch granules upon sufficient cooking/gelatinization, which is subsequently precipitated onto mineral filler particles with the aid of guest molecules and co-additives. The instant change in the water-solubility of the released macromolecules is essential for surface engineering of mineral filler particles.

Unmodified starch is largely nonionic. Consequently, the interaction of the resulting starch inclusion complex modified mineral fillers with negatively charged cellulosic fibers is somehow limited, i.e., cationic-anionic interaction is basically unavailable. Thus, this interaction may need to be improved, so that the performances of the modified fillers can be enhanced, which is indeed desirable, particularly in terms of very efficient real commercial applications. To this end, introducing cationic groups to engineered fillers may be a possible strategy.

Similar to unmodified starch, cationic starch can also interact with guest molecules to form cationic starch inclusion complexes.33,34 Despite the fact that cationic starch alone can be used to modify the surface of mineral particles (e.g., targeted for enhancement of filler bondability with cellulosic fibers),35,36 the use of unmodified starch in filler engineering can have a unique advantage in terms of paper strength development. This advantage is due to the reduction of the molecular weight of unmodified starch during cationic modification. In the paper industry, a reduction in the molecular weight of starch is generally known to result in a loss in its potential for enhancement of paper strength.37 On the other hand, since cationic starch is more hydrophilic than unmodified starch, the inclusion complexes formed between cationic starch and guest molecules (e.g., fatty acids) tend to be less easily precipitated/anchored onto filler surfaces in comparison to the case of complex formation based on unmodified starch.

The intermolecular interaction between unmodified starch and cationic starch tends to allow their co-precipitation during filler modification involving the concept of forming starch inclusion complexes. As such, the combination of unmodified starch with cationic starch in the formation of starch inclusion modified mineral fillers may deliver enhanced interaction with cellulosic fibers on the basis of cationic-anionic attraction (i.e., the interaction between the cationic moieties of surface-engineered mineral particles and the negatively charged groups of cellulosic fibers in an aqueous medium). In the current study, encouragingly, it was found that the combination of unmodified starch with a minor amount of cationic starch (a readily available commercial product) in the formation of starch inclusion complex based hybrids was effective in enhancing their interaction with cellulosic fibers for papermaking applications.

2. MATERIALS AND METHODS

2.1 Materials

Unmodified corn starch was purchased from Shandong Runyin Biochemical Engineering Co., Ltd (China). Cationic tapioca starch was provided by General Starch Ltd (Thailand), and the degree of substitution was claimed by the supplier to be about 0.036. Cellulosic fibers (softwood-derived bleached kraft pulp) were supplied by Mudanjiang Hengfeng Paper Co. Ltd., China. This pulp was processed in a Valley Beater to a beating degree of 31 “SR prior to its use in the construction of cellulosic networks. Mineral particles (micosized precipitated calcium carbonate particles) were purchased from Guangxi Guilin Wuhuan Co. Ltd (China). Cationic polyacrylamide and bentonite, used in combination as a microparticulate retention system prior to sheet formation, were provided by BASF Co., Ltd (China) and Suzhou Yfian Chemical Co., Ltd (China) respectively. The viscosity-average molecular weight (on the basis of intrinsic viscosity measurement) and charge density (on the basis of PCD titration) of cationic polyacrylamide were claimed by the supplier to be about 8 x 10^6 g/mol and 1.2 x 10^-6 eq/g, respectively.38 Sodium oleate
and calcium chloride were analytical reagents purchased from Shanghai Yuanfan Chemical Co. Ltd (China) and Xilong Chemical Co. Ltd (China), respectively.

2.2 Fabrication of starch-engineered mineral particles

To a four-neck round-bottle flask, 3 g of starch (or a combination of two starches) and 97 g of distilled water were added. The flask was then put into a water bath held at 95 °C, and the mixture was stirred at 500 rpm for 1 h to allow sufficient gelatinization. Subsequently, sodium oleate solution was added at an amount of 3% (on the basis of the dry weight of starch). The resulting mixture was stirred at 95 °C for 30 min. After cooling, the mixture was diluted to 500 ml.

To a beaker, 6 g of precipitated calcium carbonate and 200 mL of 0.02 mol/L calcium chloride solution were added. Upon sufficient mixing, 200 mL of the as-prepared aqueous mixture containing cooked starch and sodium oleate was added, and stirring was continued for 30 min (500 rpm). Finally, the resulting mixture was washed three times by centrifugation (3000 rpm, 5 min). This suspension containing starch inclusion complex modified mineral particles was sufficiently mixed prior to its addition to cellulosic slurry for sheet formation.

2.3 Determination of deposition efficiency

The starch inclusion complex based hybrids were incinerated at 525 °C for 4 h to remove the organics. Accordingly, the deposition efficiency of starch inclusion complexes during filler modification process was estimated according to equation (1):

\[
DE \, (\%) = \frac{M_1-M_2}{M_4} \times 100
\]

where \(M_1\) is the dry weight of the hybrids, \(M_2\) is the dry weight of incinerated hybrids, and \(M_4\) is the total dry weight of starch (or a combination of two starches) and oleic acid.

2.4 Construction of cellulosic networks

Mineral filler particles or starch inclusion complex based hybrids were added into the cellulosic slurry, followed by stirring at 700 rpm for 2 min. Cationic polyacrylamide solution was added, and the mixture was stirred at 700 rpm for 1 min. Upon increasing the stirring speed to 1200 rpm, the mixture was sheared for 2 min. The stirring speed was then lowered to 700 rpm, and bentonite dispersion was added. Mixing was continued at 700 rpm for another 2 min.

After the preparation of cellulosic stock, cellulosic networks (paper sheets) with a target basis weight of 60 g/m² were formed with a ZQJ1-B200mm paper sheet former (China). Filler addition level (on the basis of precipitated calcium carbonate) was 20%, relative to the total dry weight of cellulosic stock. The wet sheets were pressed at 0.4 MPa for 5 min, and dried at 105 °C for 5 min.

2.5 Determination of tensile strength, filler retention, starch retention, filler bondability factor, and optical properties

The cellulosic networks were sufficiently conditioned in a glass desiccator, and tensile strength was tested with a ZL-300A strength tester (China). Brightness and opacity were tested with a YQ-Z-48A brightness & color tester (China). Filler retention (FR) and filler bondability factor (FBF) (calculated on the basis of tensile strength and filler content) were determined by the following two equations:

\[
FR \, (\%) = \frac{A_1-A_2}{A} \times 100
\]

where \(A_1\) is the dry weight of ash in the cellulosic networks, \(A_2\) is the dry weight of ash derived from cellulosic fibers, and \(A\) is the dry weight of precipitated calcium carbonate added into the cellulosic slurry.

\[
FBF = \frac{S_{\text{filled}}}{S_{\text{unfilled}}} \times FC \times 100
\]

where \(S_{\text{filled}}\) is the strength of the filled cellulosic networks, \(S_{\text{unfilled}}\) is the strength of the unfilled cellulosic networks, and FC is the filler content of the filled cellulosic networks.

For the determination of starch retention (the retained starch in the cellulosic networks relative to the starch added into the cellulosic slurry) in the cellulosic networks, the white water collected from the sheet formation process was cooked at 100 °C for 40 min to allow thorough release of starch-derived macromolecules, followed by UV-vis spectrophotometric measurement at 590 nm and subsequent calculations.

2.6 SEM/TEM observations

SEM/TEM observations of the samples were conducted with a QUANTA 200 scanning electron microscope and a JEOL JEM-2100 high-performance transmission electron microscope.

3. RESULTS AND DISCUSSION

The use of mineral additives in the production of cellulosic paper-based bioproducts is a well-established commercial practice. Key benefits associated with these wet-end additives include reduction in cost and energy consumption, improvement of brightness, opacity, and printability/writability, enhancement of smoothness and uniformity, etc. The enhancement of filler-fiber interaction is essential for increasing the allowable filler addition level, while maintaining the critical properties relevant to commercial end-use applications. In this regard, in accordance with the so-called “filler engineering” strategy, the use of various polymers or their composites/complexes capable of forming hydrogen bonds...
with cellulosic fibers is an interesting topic, which has been widely concerned. On the basis of the easily scalable filler engineering strategy related to surface encapsulation of filler particles with starch inclusion complexes, the concept of combining unmodified starch with a minor amount of cationic starch in filler modification for enhanced interaction of the modified fillers with cellulosic fibers was proposed in this work, which is schematically illustrated in Fig. 1.

![Figure 1](image-url)

**Figure 1.** Schematic illustration of the process concept pertaining to the engineering of mineral filler particles with starch inclusion complexes on the basis of the combination of unmodified starch with a minor amount of cationic starch.

**Note:** (a) the SEM image shows the surface morphology of cellulosic networks filled with starch inclusion complex based hybrids prepared in accordance with the concept (percentage of cationic starch relative to total starch: 1%); (b) the shapes of starch granules and other components as well as the interactions were for illustration purposes only.

The formation of host-guest inclusion complexes is now a well-known area. As two categories of starch, amylose and amylopectin can form inclusion complexes with certain guest molecules or ligands, although the generation of amylose inclusion complexes tends to be much easier. Both unmodified starch and modified starch (e.g., cationic starch) are capable of forming inclusion complexes. Thus, the combination of unmodified starch with a minor amount of cationic starch in interaction with guest molecules can lead to the generation of two classes of inclusion complexes: (a) unmodified starch inclusion complexes and (b) cationic starch inclusion complexes. Due to structural/chemical similarities, the intermolecular attraction between unmodified starch and cationic starch may allow the cogeneration of these different classes of inclusion complexes. In the presence of mineral filler particles, these complexes can be anchored onto filler particles via precipitation (e.g., with the aid of certain cofactors), forming starch inclusion complex based hybrids. In the case of the use of fatty acid salts (e.g., sodium salt of fatty acids) as guest molecules, the hydrophilic carboxylic moieties are distributed in the outer regions, while the tails are extended into the hydrophobic cavities as a result of hydrophobic interaction. The interaction of the hydrophilic carboxylic “heads” with calcium ions can lead to the precipitation of starch inclusion complexes onto filler particles, leading to surface bondability enhancement.

A pronounced feature of the proposed concept is that the combined use of unmodified starch and a minor amount of cationic starch provides a simple approach to the engineering of charge characteristics of the modified fillers, allowing for efficient filler-fiber interaction. The cationic-anionic interaction as a result of the newly added cationic groups is also expected to be favorable for the retention of starch in cellulosic networks. As such, at a minimum, the concept illustrated in Fig. 1 may shed light on the real commercial use of starch inclusion complex
modified fillers in the production of various paper-based products.

In the presence of mineral particles, the deposition efficiency of starch inclusion complexes was dependent upon the amount of cationic starch (see Fig. 2). As shown in Fig. 2, the use of a minor amount of cationic starch, i.e., less than 5% relative to the amount of total starch, resulted in somewhat negligible change in deposition efficiency. However, an amount of 8% (i.e., the percentage of cationic starch in total starch was 8%) led to a noticeable reduction in deposition efficiency. It is noted that the gelatinization temperature of cationic starch is lower than that of unmodified starch, basically due to the hydrophilic nature of cationic groups and the reduction in molecular weight during the cationization of starch. Consequently, cationic starch may have a lower deposition tendency in comparison to unmodified starch, which is in consistency with the data shown in Fig. 2. In general, the deposition efficiency was around 90% in the range of 0 to 5% (percentage of cationic starch relative to total starch), and the supernatants of the slurries containing modified filler particles were found to be quite clear (see Fig. 2).

**Figure 2.** Deposition efficiency of starch inclusion complexes & SEM images of mineral filler particles before and after modification: (a) deposition efficiency as a function of the percentage of cationic starch relative to total starch (top, left); (b) TEM image of unmodified filler particles (top, right); (c) TEM image of starch inclusion complex modified filler particles (cationic starch was not used) (bottom, left); (d) TEM image of starch inclusion complex modified filler particles (percentage of cationic starch relative to total starch: 1%) (bottom, right).

Note: (a) “total starch” refers to the combination of unmodified starch and cationic starch; (b) the photographic images refer to the slurries containing modified filler particles that were allowed to stand at room temperature for 24 h.

The impact of the proposed process concept is shown in Fig. 3. Quite interestingly, the process concept was particularly effective as regards the enhancement of filler retention, filler bondability factor, and starch retention. For instance, very significant impact was achieved at a cationic starch percentage of 3%. This indicates that the combination of unmodified starch with a minor amount of cationic starch resulted in pronounced improvement in filler-fiber interaction, largely due to the electrostatic attraction between the starch inclusion complex based hybrids with cationic characteristics and the negatively charged cellulosic fibers. On the other hand, the impact of the process concept on tensile strength, brightness, and opacity of cellulosic networks was not very noticeable.

Indeed, the engineering of mineral additives with starch inclusion complexes provides an effective strategy for mitigating the negative impact of increased filler addition on paper strength, which is particularly critical for
maximizing the competitiveness of cellulosic paper-based bioproducts for printing/writing applications. The interesting findings related to the combination of unmodified starch with a minor amount of cationic starch for improved filler/starch retention and enhanced filler bondability with cellulosic fibers may facilitate the commercialization of starch inclusion complex based filler technologies towards greener, more efficient papermaking wet-end operations. In this regard, promising commercial impacts relevant to the production of mineral-filled printing/writing paper grades may be expected.

Figure 3. Impact of combination of unmodified starch with a minor amount of cationic starch in formation of inclusion complex based hybrids.

Note: the figure shows the impact of the proposed concept in terms of tensile strength of cellulosic networks, filler retention, filler bondability factor, brightness and opacity of cellulosic networks, and starch retention.
4. CONCLUSION

The process concept of combining unmodified starch with cationic starch in the fabrication of starch-engineered mineral particles (on the basis of the formation of starch inclusion complexes) was proposed. This easily scalable concept delivered significant enhancement of filler/starch retention and filler bondability with cellulose fibers. Noticeably, a weight percentage of cationic starch (relative to the weight of total starch) of 3% was demonstrated to be highly favorable for filler-fiber interaction. The findings from this preliminary study would provide a useful basis for promoting the commercialization of greener, more efficient filler technologies in the paper industry.

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