Clay–Starch Composites and Their Application in Papermaking

Se-Young Yoon, Yulin Deng

School of Chemical and Biomolecular Engineering, IPST, Georgia Institute of Technology, N.W. Atlanta, Georgia 30332-0620

ABSTRACT: Clay–starch composites with different aggregate sizes and starch to clay ratios were prepared by a simple precipitation method. The aggregates of the composites were used as fillers to improve the paper properties. The experimental results showed that the paper strengths increased more than 100% for starch-modified clay compared to untreated clay at 20–30% clay loading. The increase in paper strengths of clay–starch composite-filled handsheets was mainly due to two reasons, i.e., the relatively large aggregate size and the improved internal bonding. The optical properties compared at same mechanical strength were also improved. The water solubility of starch in the clay–starch composite was less than 3% at 50°C for 30 min, and it could be further reduced by adding crosslinker. Bonding sites between composite and fiber were investigated by scanning electron microscope. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1032–1038, 2006

Key words: clay; starch; composite; fillers; strength

INTRODUCTION

For many years, the increase in filler content in papers has been driven by the reduction in papermaking cost, the improvement in optical properties, paper formation, printability, and the water removal rate during papermaking. However, as filler loading is increased, the paper strength, bulk, and stiffness are usually decreased. To increase the proportion of filler without sacrificing paper properties, various methods have been explored. Preflocculation method prior to addition to the paper stock have been well studied in the past.[1–3] From pilot plant trials, Marbee reported that flocculation method could provide an ~26% increase in first pass ash retention and 13% increase in the tensile strength when the same amount of filler was used.[4] Lumen loading method that held filler mainly within the lumens of fibers have been studied for many years.[5–7] Filler modification with polymers, such as chemically bonded poly(acrylic acid) and poly(vinyl acetate) to fillers, was also reported.[8] Gill modified precipitated calcium carbonate (PCC) surface by introducing catioinic groups on PCC using epichlorohydrin and polyamino-amide or polyamine.[9] The result showed that the breaking length was improved about 10% at the same brightness (89%) using 1% polymer-treated PCC. Silenius recently reported a method of using PCC and wood fibrils to composites for improving paper properties.[10] They added carboxymethyl cellulose (CMC) to fibrils at high temperature during or after carbonization. It was reported that Scott Bond strength of CMC treated PCC with fibrils was increased to about 40–130% at 10 and 20% filler additions, respectively. They also claimed that the retention of CMC-treated PCC with fibrils was improved about 50% compared to untreated PCC. However, the ratio of filler loading to wood fines is low. Although many approaches have been studied for improving the paper strength at high filler content, except for the preflocculation method, none of these technologies has delivered a practical solution to paper manufactures.

Traditionally, starch has been used in wet-end papermaking applications because of its relatively low price and its ability to improve paper strength. The mechanism of their contribution to improvements in dry tensile strength has been suggested. It is believed that starch adsorbs to cellulosic fibers during wet end processing, thereby enhancing bonding through the formation of hydrogen bonding.[11] Gaspar concluded that improvement in dry strength were due to increase in shear strength per unit bonded area.[12] Although starch can improve the strength of paper, there are some problems related to high starch addition in wet end papermaking process. For example, the retention of neutral starch in a pulp furnish is very poor (less than 40%).[13] To enhance the adsorption of noncharged starch to anionic surfaces of wood fiber, the cationic groups were introduced to starch backbones. How-

ever, many problems are associated with the use of cationic starches. For example, the chemical modification of starch by cationics will significantly increase the cost of papermaking. Although the adsorption of starch can be improved by introducing cationics, the retention of starch on wood fibers is still a problem when anionic trash in the wet-end furnish is high, such as in ground wood pulps and recycled fibers. It is well known that the adsorption of cationic starch on fibers will reach a saturation condition and further increase of the adsorption amount beyond the saturation point is impossible. Therefore, the amount of starch on wood fibers is limited by its maximum adsorption amount. The positively charged starch may also cause fiber flocculate and the system to become overly cationic if the amount of starch is high. The flocculation of the fiber suspension may also cause poor paper formation.[14] If the retention of the starch cannot be well controlled, unretained starch will accumulate in the whitewater and create pitch, slime, and sticky problems.

Recently, we reported a method for the modification of PCC with coated starch gel.[15] The results indicated that the strength of PCC-filled sheets can be significantly improved if the filler surface is coated by starch. However, the starch coating process in our previous study was relatively complicated, and so a simple coating process is needed.

To maximize the efficiency and reduce the papermaking problems using starch-coated fillers in papermaking, the solubility of starch after being coated on filler surface should be very low. If starch is insoluble in water and retained perfectly on wire, a large amount of starch can be used for improving paper strengths and the accumulation of soluble starch in wet water can be prevented.

Insoluble or less soluble starches have been developed for a filling material or ion-exchange resin. It can be mainly divided into two categories. One is the precipitation of cooked starch using organic solvents such as ethanol and acetone or saline salts such as $MgSO_4$ and $(NH_4)_2SO_4$. The other is crosslinking method using aldehyde, vinyl sulfone, or epichlorohydrin. It is known that ammonium sulfate salt is an effective "salting out" material for enzymes, protein, and starch. Hernandez et al. made water-insensitive starch fiber using 10% starch suspension that was extruded from a nozzle into a coagulation bath containing 44% $(NH_4)_2SO_4$.[16] However, the starch itself after cooking has relatively lower light-scattering characteristics than wood fiber. Thus, optical properties such as brightness and opacity will be decreased.

Although the high cost makes their application difficult, various fibrous or needle-like fillers have been developed for improving papermaking process and paper properties.[17−19] For example, fibrous calcium silicate hydrates improved sheet bulk, porosity, and light-scattering properties.[16] These kinds of fibrous or needle-like fillers might also have better retention due to their morphological characteristics. The method we developed in this study shows that the starch-coated clay has a relatively large size with a fibril shape, and so the particles will be easily entrapped by fiber network to give a high total retention.

In this study, the different aggregates from clay–starch composites were prepared and their effects on paper properties were investigated. Compared to our previous approaches, relatively larger starch ratio in clay–starch composites was used because of the low solubility of starch prepared in this study. As a result, the paper properties are further improved.

EXPERIMENTAL

Materials

Dry Branch Kaolin (Dry Branch, GA) provided the calcined kaolin clay. Raw corn starch was used for this experiment. Ammonium sulfate was obtained from Aldrich. Bleached hardwood and softwood pulps were each refined in a Valley beater to a freeness of 400 CSF. Equal proportions of the two pulps were mixed, and the mixture was used as the base pulp furnish for the handsheets. Percol-175 (cationic polyacrylamide retention aid) was obtained from Ciba Specialty Chemicals (Suffolk, VA). Crosslinker, Eka AZC 5800LN (Ammonium zirconium carbonate, 30% solution), was procured from Eka Chemical (Marietta, GA).

Preparation of fibrous clay–starch composites

The 1 : 1 clay to starch ratio of composites was prepared as follows: 5 g of clay was added to 3–4% uncooked raw corn starch suspension that contained 5 g of dry weight starch. The mixture was then stirred and cooked at 95°C for 30 min. Cooked clay–starch mixture was poured into 40% ammonium sulfate solution with 500 rpm stirring speed. After 30 s stirring, fibrous clay–starch composites were precipitated out. The resultant composites were collected on filter paper, washed free of salt, and recollected. The filtrated ammonium sulfate solution could be reused by adding additional ammonium sulfate salt. The precipitates of clay–starch composites from ammonium sulfate salt treatment were redispersed in water by mechanical stirring before handsheet making. The different solid content ratios of clay and starch composites were prepared at 1 : 1, 1 : 0.5, and 1 : 0.25, respectively. To determine the effect of crosslinker on the solubility of clay–starch composites, 3% (based on dry starch weight) crosslinker was added to clay–starch suspension and adjusted to pH 12 after cooking.

Characterization of fibrous clay–starch composites

The morphology of the clay–starch composites was characterized using Leica DMLM optical microscope with digital camera. Scanning electron microscope (SEM) was used for characterizing the details of the composite aggregates.

Swelling and solubility of starch were measured at different temperatures. Wet clay–starch composite (2 g) collected after filtration and washing was agitated in 50 g of distilled water for 30 min. The suspension was cooled to 20°C, poured into preweighed centrifuge tubes, and centrifuged at 3000 rpm for 10 min. For the measurement of solubility of starch in the clay–starch composites, the supernatants were gathered and tested by measuring the total organic content (TOC) using Shimadzu Total Organic Analyzer 5050. Swelling power was obtained by weighing the sediments in centrifuge tubes before and after drying using the following equations:

$$\text{Water solubility } (\%) = \frac{\substack{\text{wt. of initial dry starch} - \\ \text{wt. of dry starch not dissolved}}}{\text{wt. of initial dry starch}} \times 100$$

$$\text{Swelling power} = \frac{\text{wt. of wet starch after centrifuge}}{\text{wt. of starch after drying}}$$

Handsheets preparation and determination of paper properties

The pulp was diluted to 0.5 wt % and various amounts of composite aggregates were added during the handsheet making. After the addition of composites, the slurry was stirred for 20 s at 700 rpm without addition of any retention aids. Handsheets with a target basis weight of 60 g/m^2 were produced, according to TAPPI Test Method T 205 "Forming Handsheets for Physical Tests of Pulp." For comparison, the control handsheets were prepared using pure clay, and Percol-175 was added at 0.05–0.1 wt % based on solid fiber for clay retention. After wet pressing twice, all handsheets were dried at 105°C for 7 min on the dryer (Emerson Speed Dryer, Model 130). Physical properties of the papers were measured according to standard TAPPI methods. The filler content was determined by ashing the paper in a muffler oven according to the standard TAPPI method T211.

RESULTS AND DISCUSSION

Characterization of the clay–starch composites

Figure 1 shows optical microscope and SEM images of clay–starch composites. Kaolin clay from SEM [Fig. 1(a)] shows the plate-like structure and the particle size was less than 3 μm. Clay–starch composites (1 : 1 ratio) from 3 to 4% of starch concentrations show long fibrous structure from the optical microscope [Figs. 1(b) and 1(c)]. It was found that the starch concentration in the cooking mixture plays an important role in composite morphology, i.e., large and thick clay–starch aggregates could be obtained when high starch content solution was used in the preparation of aggregates. The stirring rate, stirring time, and the ammonium sulfate concentration were also important for controlling the aggregate polymorphism. As shearing time or force increased or ammonium sulfate concentration decreased, the size of composite aggregates tended to decrease. At low concentrations of ammonium sulfate, the size of composite was very small.

The detailed characteristics of the composites were observed by SEM. The surface image of clay–starch composite is shown in Figure 1(d), and it is shown that clays are distributed well inside the composite and are perfectly coated by starch. It is expected that this coated starch layer will strongly affect the fiber–fiber bonding, which will be discussed later.

The volume change of coated starch was determined by swelling power. Figure 2 shows the swelling behavior of clay–starch composites in terms of temperatures. It can be seen that as temperature increases, the swelling power increases. At 50°C for 30 min, the weight of composite aggregates was about 13 times that of the dried aggregates. Increased volume of composites by swelling might enhance the possibility of hydrogen bonding with wood fibers.

The solubility of coated starch in water in terms of temperature will also be a critical issue for application. If starch is dissolved in water, the structure of composite will be disrupted and the clays in composite aggregates will be separated into individual particles. Also, if the starch solubility is high, it will cause many operational problems in the paper machine and hence lower the physical properties. Therefore, the solubility of precipitated starch in the composites was studied and the results are given in Figure 2. It was found that less than 3% of starch was dissolved in water after the composites were dispersed in water at 50°C for 30 min. When the starch was exposed to high temperature, the solubility increased to 5%. However, crosslinked starch could reduce the solubility of starch even at high temperature. Even though the solubility of crosslinked starch increased slightly as temperature increased, the result was only 1.25% at 90°C.

The effects of clay–starch composites on paper strength and optical properties

Figures 3–6 show the effects of the clay–starch composites on paper physical properties. These data indicate that clay–starch composites could significantly
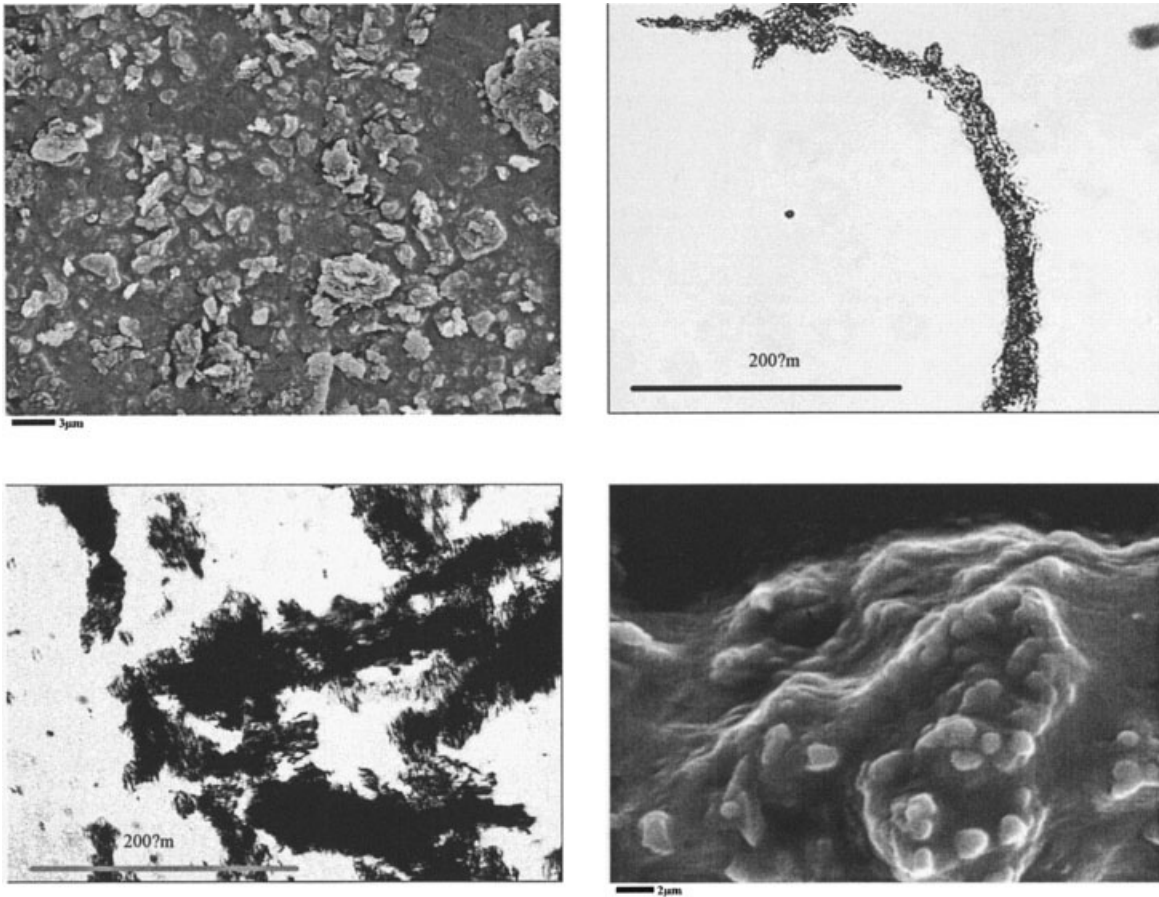
Figure 1 Morphology of clay–starch composite from the optical microscope and SEM. (a) SEM picture of pure clay; (b) and (c) Optical microscope picture of the aggregates prepared at clay to starch ratio of 1 : 1; and (d) SEM picture of clay–starch composite with starch ratio of 1 : 1.

improve paper-strength properties compared to conventional papermaking filler. As the content of pure clay increased, the tensile strength of the handsheet made from unmodified clay decreased significantly as

shown in Figure 3. It is generally accepted that the strength of paper is attributable to the strength and number of interfiber bonds. Clay particles in handsheet interfere the fiber bonding, which reduces the
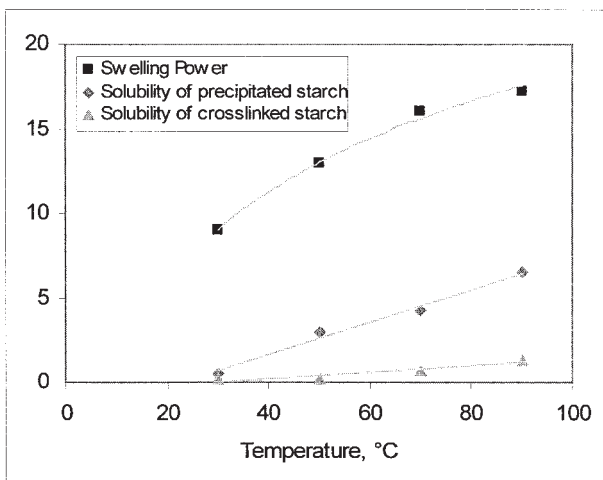
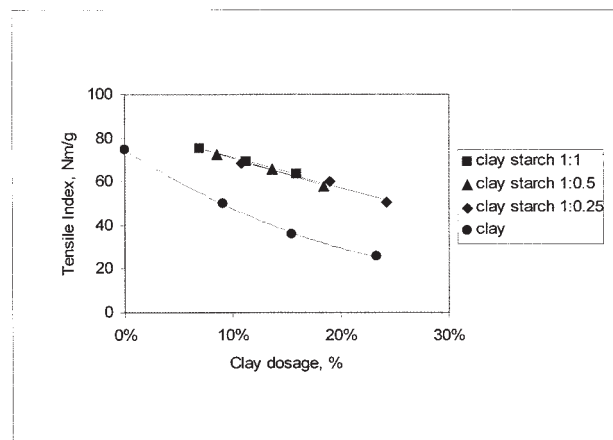**Figure 2** Starch swelling power and solubility at different temperatures.

Figure 3 Tensile strength as a function of filler content for pure clay and the clay–starch composites with different clay to starch ratios.
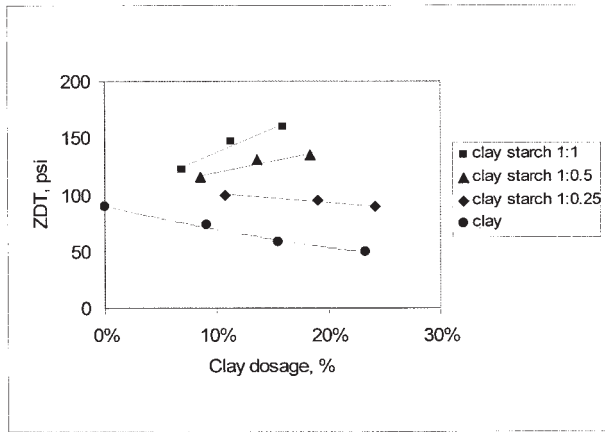
Figure 4 ZDT (Zero Directional Tensile) strength as a function of filler content for pure clay and the clay–starch composites with different clay to starch ratios.
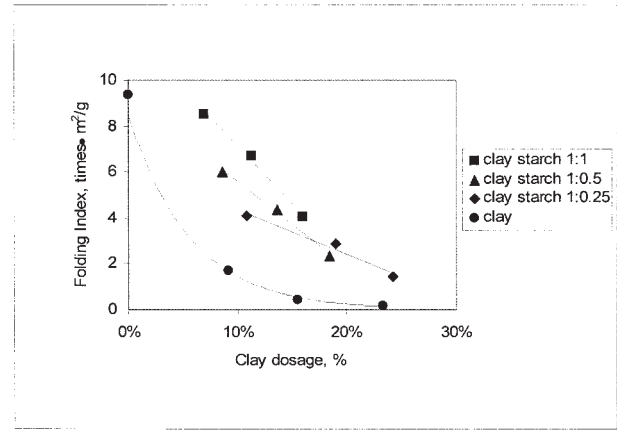

Figure 6 Folding strength as a function of filler content for pure clay and the clay–starch composites with different clay to starch ratios.

strength and number of interfiber bonds. Thus, increased clay content in handsheets caused a greater reduction in tensile strength. Our previous research[15] proposed that the reduced interfiber bonding by the increasing clay content could be compensated through the improvement of the clay–fiber bonding by the starch that was coated on filler. It is reported that the starch-coated PCC could improve the tensile strength up to 30%, compared to the same amount of pure PCC. As shown in Figure 3, the tensile strengths of the handsheets made from three different clay–starch composites increased about 110% compared to original clay at 20 and 30% clay doses. As shown in the Page equation,[20] the tensile strength of paper combines the intrinsic fiber strength, the bonding strength, and the contact area. Since the fiber intrinsic strength was the same for all handsheets, the increase in the paper strength should be contributed from the in-

crease of interfiber bonding and bonding area. It has been proposed that the internal bond strength such as the Scott Bond Energy, the z-direction strength, and peel force in delaminating has the relationship with bonding shear strength.[21] Figure 4 shows the result of z-direction tensile strengths of clay–starch composite filled sheets. For clay–starch composites ratio of 1 : 1 and 1 : 0.5, the Zero directional tensile (ZDT) increases as composite content increases. However, for the pure clay-filled sheets, ZDT decreases as clay content increases. This result means that pure clay interferes with fiber–fiber bonding because there is no clay–fiber bonding, however, clay–starch composites can improve clay–fiber bonding due to starch coating the clay surface. Even though ZDT was increased markedly for clay–starch composites, we saw that the tensile strengths slowly decreased as the composite content increased, as shown in Figure 3. This suggests that the strength of this fibrous composite itself is much
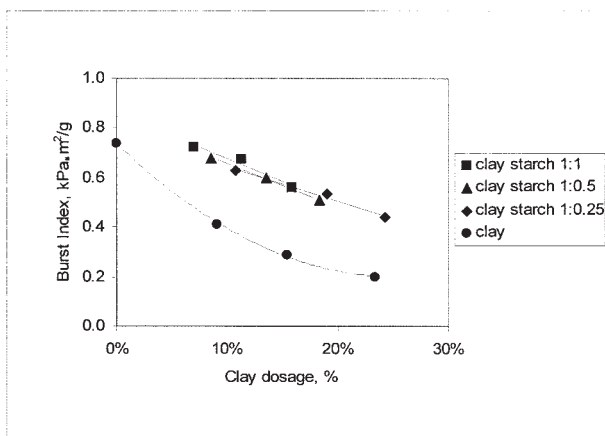

Figure 5 Burst strength as a function of filler content for pure clay and the clay–starch composites with different clay to starch ratios.
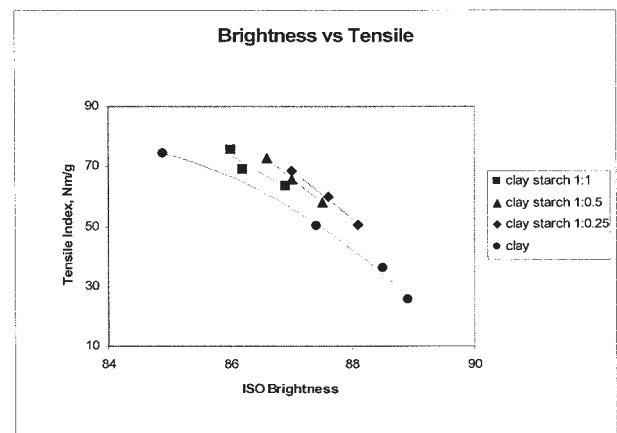

Figure 7 Tensile index versus ISO Brightness as a function of different ratio of clay–starch composites.
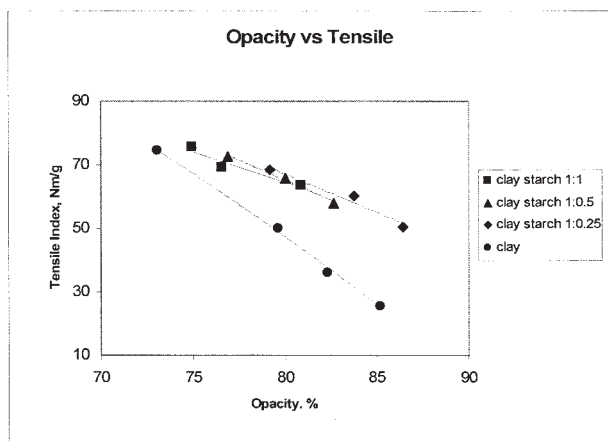
Figure 8 Tensile index versus Tappi opacity as a function of different ratio of clay–starch composites.

weaker than that of wood fiber. However, the bonding strength of this starch-coated composite with wood fiber is much stronger than fiber–fiber bonding.

Figures 5 and 6 show the effect of the clay–starch composite on burst index and folding index. The burst strengths at three different ratios of clay–starch composites increased about 100% compared to pure clay at 20% clay addition. The tendency of burst strength using clay–starch composite is almost the same as that of tensile strength, as shown in Figure 5. Obviously, the increase of burst strength is due to the improved internal bonding of the sheet by the starch. The similar trend was seen for folding strength of the handsheet. i.e., the pure clay reduced folding strength markedly but the clay–starch composites had less reduction on the folding strength. It was also found that the folding strength can be significantly improved when the starch ratio in composites was increased.

Figures 7 and 8 compare the brightness and opacity of handsheets made with pure clay and clay–starch composites. Clearly, the increase of the clay–starch content in sheets can improve paper brightness and opacity, although the improvement degree is less than pure clay. However, the small difference in the optical property improvement between clay–starch composite and pure clay should not be a problem, because it can be compensated by adding more composites to the paper without sacrificing the paper strength. This can be clearly seen by comparing the handsheet optical properties at the same tensile strength, as shown in Figures 7 and 8.

Bonding of clay–starch composites with fiber

From ZDT tests, it was determined that internal bonding was improved by adding clay–starch composite compared to using pure clay. To investigate the bonding between wood fiber and composites, the surface of handsheets filled with clay–starch composites was observed by SEM. Some of the clay–starch composites were stuck on the wood fiber surface and have almost no individual clay particles on fiber surface or between fibers, as shown in Figure 9(a). At higher magnification (b), we could observe the bonding structure between fiber and clay–starch composite in detail. The fibrils from the fiber are strongly bound with the composites so the boundaries of them could not been clearly observed. Appearance of clay–starch composites was also changed during pressing and drying. As can be seen from Figure 9(b) the thermoplasticization makes swollen starch penetrate into fibril network to form a smooth bonding area. Obviously, this will help the bonding of composites with fibrils or fibers.

CONCLUSIONS

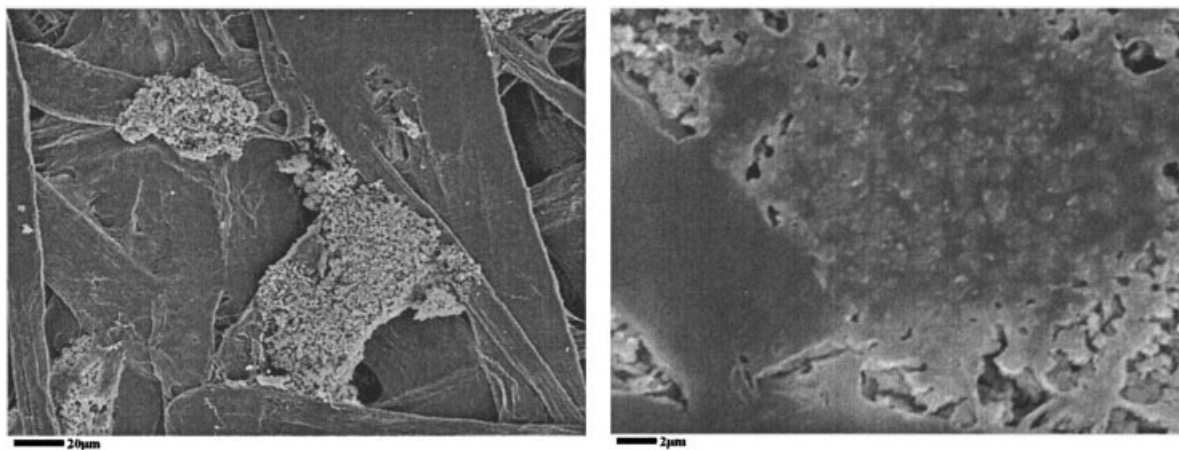This study provided a method of clay–starch composite preparation. The composite such prepared can be

Figure 9 SEM pictures of clay–starch composites filled handsheets (a) Clay : Starch = 1 : 0.25 and (b)1 : 0.5.

used as papermaking filler with much higher paper strength than untreated clay. The method includes steps of mixing, cooking, precipitation, filtration, and washing. From the physical property measurements, clay–starch composites could increase bonding strength markedly as shown in ZDT test, thereby tensile, burst, and folding strength were improved up to more than 100% at 20–30% doses, compared to untreated pure clay. The optical properties increased as the composite amount in sheets increased. At same opacity and brightness, clay–starch composite-filled handsheets have much higher tensile strength than unmodified clay-filled sheets. The bonding of clay–starch composites with fibers was confirmed by SEM. This technology could be very attractive for paper grades needing high filler loading and high physical strength.

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