Improvement of Paper Strength with Starch Modified Clay

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ABSTRACT: In order to improve the strength properties of high filler filled papers, a new technique of coating starch on the clay surface was developed. The stability of the coated starch and its effects on paper properties were studied. It was found that the starch coated on the clay surface swelled in water. This swelled starch film on the filler surface contributes significantly to the filler–filler bonding. The strength properties of handsheets made from starch coated clay, even with unmodified corn starch, could be increased by more than 15% versus those from the traditional method of adding cationic or amphoteric potato starch directly to 50% bleached softwood pulp/50% bleached hardwood pulp. This research suggests that the starch coated filler can be used to make high filler content paper products. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 44–50, 2005

Key words: clay; fillers; modification; strength

INTRODUCTION

The incorporation of mineral fillers to paper stock, prior to the formation of the sheet, has been practiced since the eighth century.[1] This technology has matured rapidly over the past three decades, and it has become an integral part of the papermaking process today. The paper industry utilizes fillers either to reduce paper cost or to provide desired functional end-use properties of paper products. It is estimated that $2.50/ton can be saved for each 1% increase of the filler in paper.[2] These savings come from the reduction of raw materials cost and energy cost. Mineral fillers are much less expensive than wood fibers. Increased fillers will produce sheets that drain and dry more easily on the paper machine, thereby leading to less energy consumption in the driers. Sheet properties normally improved by fillers include opacity, brightness, gloss, smoothness, porosity, and printability. In fact, some of these paper qualities cannot be achieved without the use of fillers.

However, there are disadvantages, such as reduced paper strength and increased size demand, abrasion, and dusting, which are associated with higher filler loading beyond a certain level. Research has been conducted to increase the filler loading without incurring those disadvantages. Many approaches have been used or studied previously, such as preflocculation of the filler, modification of the filler, synthesized fillers with different structures and chemistries, incorporation of polymers in the sheet, lumen loading, and multiple-layer forming.

Filler modification is an active research area with most of the attention directed toward precipitated calcium carbonate or silicates. Kuboshima[3] used acrylic acid or vinyl acetate to chemically bond polymers to fillers. Gill[4] used epichlorohydron and polyamino-amide/or polyamine polymer to modify the filler surface to improve filler–fiber bonding. An international patent application[5] revealed a method to produce fibrous calcium silicate hydrates and their application as a filler in papermaking. It was claimed that the use of this product in paper could increase the sheet bulk, porosity, and light-scattering properties of paper. Another patent application[6] revealed polymers that can bond fillers and fibers together in papermaking. The polymers have phosphonated and sulfonated substituent groups and optional amide substituent groups. These novel polymers are effective at retaining fillers in the sheet, especially when used with starch. Takahashi et al.[7] claimed a method of producing calcium carbonate in the form of spindles or needles with a minimum diameter of 0.1–2.5 μm and a maximum diameter of 0.3–20 μm. The calcium carbonate in various shapes obtained by Takahashi et al.[7] provided better yield and wire abrasion resistance,

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compared to typical calcium carbonate filler. These calcium fillers were also shown to provide fine quality paper and coated paper with firm body and excellent brightness, opacity, smoothness, writing suitability, tactility, printability, and other properties. Although the new filler materials claimed in the above patents may significantly improve papermaking processes and paper properties, the high cost of the new fillers makes it difficult to apply these fillers commercially.

Starch is currently the most widely used dry strength agent in paper because of its low price and high performance.[8] Starch is a glucose polymer in which anhydroglucose units are joined to each other by a 1,4-α-D-glucosidic bond. Glucose chains are either straight chains (amylose) or branched chains (amylopectin). In a normal case, the proportion of amylose in starch is approximately 20–25%. Starch has abundant hydroxyl groups, which are capable of forming hydrogen bonds with wood fiber to improve paper strength. The most common method to use starch as a papermaking wet-end strength additive is to add cooked starch to the pulp furnish with a controlled charge condition. When mixed with fiber and filler, the starch adsorbs on the surface of both filler and fiber. It has been reported that the retention of neutral starch in a pulp furnish is less than 40%.[8] Thus, starches are often modified as cationic charged or amphoteric starches to increase starch retention because pulp furnishes are negatively charged. The starch modification process usually increases the cost of starch by at least $500/ton. Although the cationic starches show improved adsorption on fibers and fillers, achieving a high retention of starch on fibers still poses a problem in the papermaking process. If the retention of starch cannot be well controlled, unretained starch will accumulate in the white-water and create pitch, slime, and stickiness problems. Alternatively, if the starch can be strongly coated to the filler surface, it is expected that the filler–fiber bonding can be significantly improved and strong paper sheets can be obtained. In this study, we developed a new clay filler modification method at very low cost, which can increase the filler loading in paper while maintaining sheet strength.

EXPERIMENTAL

The pulp used for making paper handsheets was a mixture of 50% bleached softwood pulp and 50% bleached hardwood pulp. Both pulps were supplied in dry lap form and were beaten separately to about 400 CSF in a Valley beater. Clay fillers were provided by Imerys (Atlanta, GA) with a surface area of 11 m^2/g and an aspect ratio of 80. Poly(ethylene oxide) (PEO, weight-average molecular weight = 8 million) was purchased from Aldrich. Phenolic formaldehyde resin (PFR) was obtained from Borden Chemicals. Raw corn (28% amylase) and potato (20% amylase) starches were procured from Grain Processing Co. Cationic (0.32% N) and amphoteric starch, which are commonly used as paper dry strength agents, were from Penford Products Co.

The starch was cooked at 95°C for 30 min. Starch coating was conducted by mixing the required cooked starch with clay slurry at a total solid content ranging from 30 to 60%, and the mixture was vacuum dried. The dried solid was then ground with an EKA grinder for 2 min to produce starch modified clay powders. The pulp was diluted to 0.4 wt % and various amounts of filler were added before handsheets were made. After the addition of fibers, filler, and 2 ppm PEO/4 ppm PFR as a retention aid, the slurry was stirred for 20 s at 1000 rpm. A moving belt drainage tester[9] was used to prepare handsheets with a target basis weight of 80 g/m^2. The wet handsheets were pressed at 50 psi, dried at 105°C under 20-psi pressure for 30 min, and then conditioned at 25°C and 50% relative humidity overnight. The physical properties of the paper were measured according to standard TAPPI methods. The filler content was analyzed by ashing the paper in a muffler oven according to standard TAPPI method T211. The electrophoretic mobility (ζ potential) was measured using a Malvern Zetasizer 3000 at a stationary position. The mean size of the particles was determined with a Malvern System 2600 laser particle sizer. A transmission scanning microscopy (TEM) image was obtained with a Jeol 100C TEM microscope operated at 100 kV.

The amount of starch that dissolved in the water from the starch coated clay was measured by a Shimadzu 5050 total organic analyzer after separating the filler particles. The swelling power of the cooked starch was determined by the following procedure: starch was cooked at 95°C for 30 min at 2% consistency. The cooked starch was first air-dried in an aluminum weighing dish and then dried at 105°C for 2 h to form a film with a thickness of about 0.5 mm. The dried starch film was soaked in deionized water for a given time and then removed. Adherent moisture on the film surface was removed rapidly and completely with filter paper. The swollen sample was weighed and dried. The dried sample was weighed again, and the swelling power was obtained by the following formula:

$$\text{swelling power} = \text{weight of wet film}/\text{weight of dried film}$$

RESULTS AND DISCUSSION

Modification and characterization of clay fillers

The starch coating process in the modification of clay is shown in Figure 1. Potato starch, corn starch, and

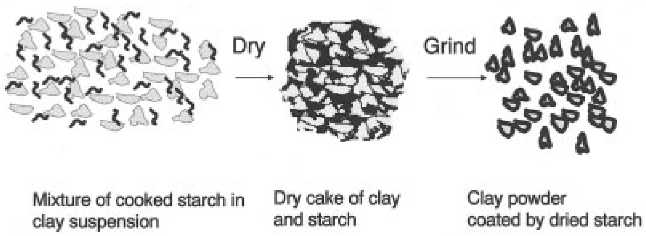

Figure 1 The process for clay filler modification.

cationic potato starch were used for the clay modification. The particle sizes of the clay fillers are shown in Table I, which indicates the apparent particle sizes are almost the same before and after modifications. Therefore, the size effect of the fillers on the paper properties before and after modification should be minimal. The ζ potential of the clay suspension is also shown in Table I. It was found that the original clay filler is negatively charged in water. However, the negative ζ potential of the clay is reduced after modification. This is because the starches used in the coating process are noncharged or positively charged, which shields the charge ions on the clay surface. By contrast, because negatively charged poly(acrylic acid) was added to the clay as a dispersion agent, the effect of the coated starch on the clay surface ζ potential is not significant.

The surface of the modified clay was studied by TEM. Figure 2(a,b) shows the images of original clay and modified clay with 5% coated starch, respectively. Figure 2(c) shows the image of starch coated clay at higher resolution. Note that the edge of the original clay is very sharp. The small crystals on the surface of the clay are clearly visible. For the modified clay, the edge of the clay is smooth. The small crystals on the clay surface are not very clear. The image also shows there are polymeric materials between the modified clay particles. The results indicate that a layer of starch was coated on the modified clay.

Effect of modified filler on paper strength

The effect of clay coated with 5% (based on filler weight) potato starch on the paper strength was studied. Another set of handsheets with 2% (based on total solid weight, including fillers, fines, and fibers) cooked cationic starch (commercial dry strength agent), which was added directly to the pulp furnish, was also made for comparison. This set of samples was termed 2(+)Star + Clay. The results are shown in Figure 3. It was found that the starch coated clay gave much better strength improvement than the traditional addition method (adding cationic starch in the wet end directly). The results in Figure 3 indicate that the handsheet with 25% coated filler had the same tensile strength as the handsheet with 15% unmodified filler made by adding cationic starch directly to the pulp furnish. Generally, paper strength is dependent on the extent to which the fibers are bonded to each other (interfiber bonding) and the distribution of the fibers within the sheet (formation). Bonding comes primarily from the formation of hydrogen bonds between fibers. The bonding strength is dependent on the fiber contact area and the intrinsic strength per unit area of contact. Clay filler cannot directly form hydrogen bonds and other strong bonds with fiber.

The addition of clay in paper reduces the fiber–fiber bonding area and the paper strength is well known. It is expected that the filler–fiber bonding can be significantly improved if the filler surface is coated by starch because starch on the filler surface can form hydrogen bonds with fibers. This concept was proven by the results shown in Figure 3.

The amount of starch coated on clay surfaces is important to note. The effects of clays coated with 2.5, 5, and 10% (based on filler weight) potato starch on the paper strength were compared (Fig. 3). The starch content between 2.5 and 10% clay has no obvious different effect on the paper tensile strength. It is interesting to note that an amount as low as 2.5% starch is able to give very good performance, but extra starch showed no further beneficial effect.

In order to understand the effect of starch coating on the strength of handsheets, the thickness of the starch on the filler surface was calculated. It was established that the specific surface area of the clay used in this study is 11 m^2/g (manufacturer data). When 1 g

TABLE I
Characterization of Clay Fillers

Sample	Abbreviation	Particle size (μm)	ζ Potential (mV)
Clay	Clay	9.53	−40.2
Potato starch (2.5%) coated clay	2.5 potato–clay	9.90	−37.0
Corn starch (2.5%) coated clay	2.5corn–clay	9.76	−36.5
Potato starch (5%) coated clay	5potato–clay	9.72	−34.6
Corn starch (5%) coated clay	5corn–clay	9.74	−32.7
Cationic starch (5%) coated clay	5(+)star–clay	10.97	−30.6
Potato starch (10%) coated clay	10potato–clay	10.10	−31.8

The results are from light scattering measurements.

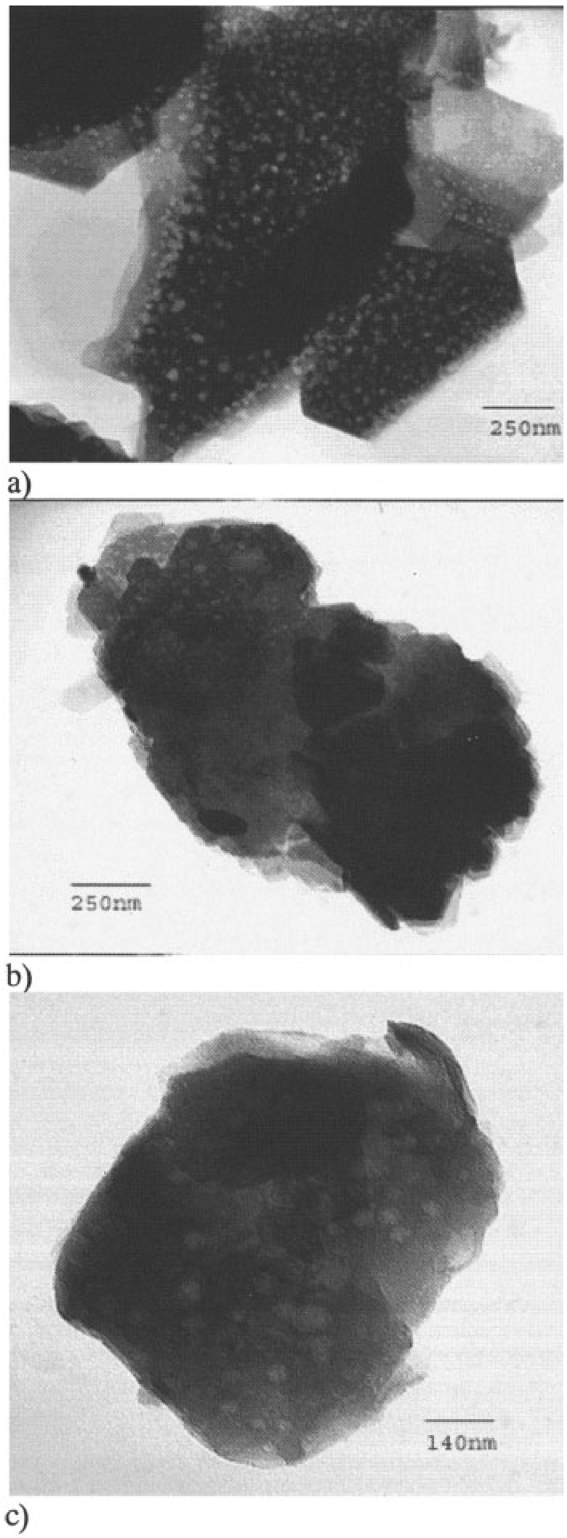

Figure 2 (a) Clay, (b) modified clay with 5% coated starch, and (c) modified clay at higher magnification.

of clay is coated with 2.5% starch, one can have the following:

$$11\ (\text{m}^2/\text{g}) \times h \times \rho_s = 0.025\ (\text{g})$$

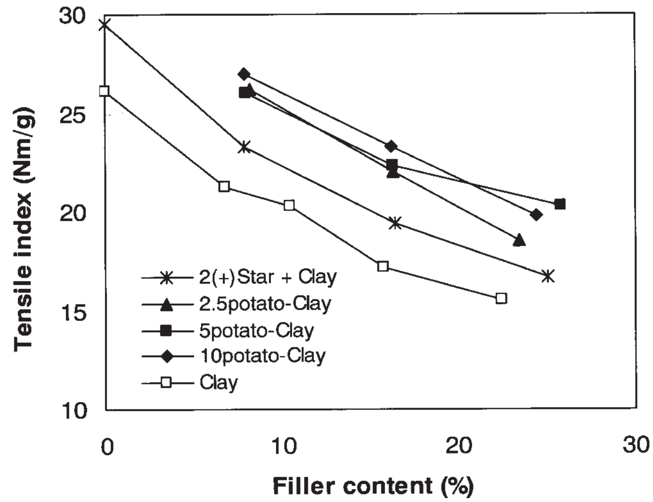

Figure 3 The effect of starch coated clay on the paper tensile strength.

where h is the starch thickness on the clay surface and ρ_s is the density of the dry starch (1.55 g/cm^3 for uncooked starch crystals). Thus, the thickness of the starch layer is 1.47×10^{-9} m (1.47 nm), which would be equal to about 10 carbon–carbon bonds. In reality, the starch may not crystallize well on the clay surface, so the density of these noncrystal starch layers may be lower than 1.55 g/cm^3. The thickness would then be higher than 1.47 nm. The results indicated that this layer is enough to improve the bonding between fillers and fibers.

The improvement in the paper strength using different starches was also studied, and the results are shown in Figure 4. It is well known that potato starch

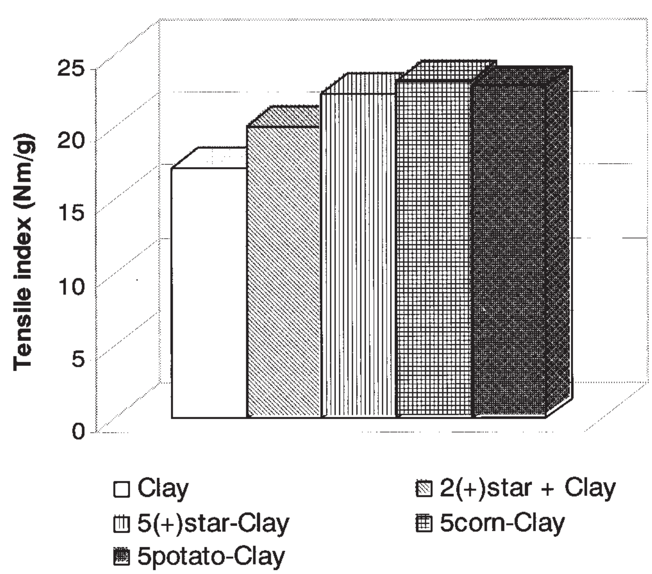

Figure 4 The effects of different coated starches on the paper tensile strength (15% filler content).

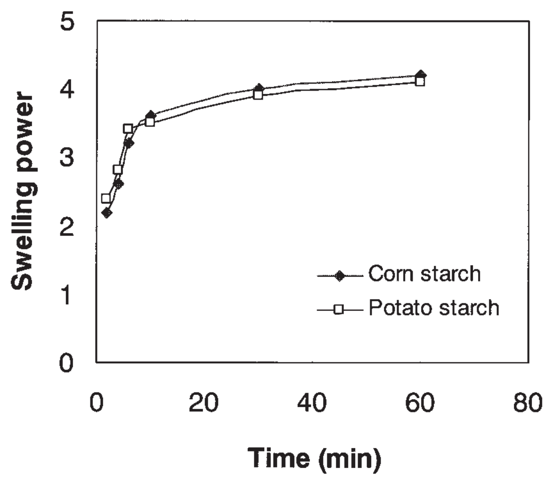

Figure 5 The swelling power of once-cooked starch.

generally performs much better than corn starch when they are used as paper strength additives. Surprisingly, it was found that the different starches have almost the same effect on improving the paper tensile strength when they were coated and dried on clay surfaces. These results suggest that papermakers can use the less expensive unmodified corn starch (~$200/ton) with starch coating technology to achieve much higher paper strength than that of the more costly cationic starch (>$1,000/ton) with current papermaking technology.

Swelling and dissolution behavior of cooked starch

Because the filler–fiber bonding strongly depends on the starch on the filler surface, it is important to know if the coated starch layer, using the method developed in this study, is strong enough in the papermaking process. Although the coated starch on the clay surface is in dry form, it is expected that the dried starch can swell in water when the clay is added to water. In order to study the swelling behavior of the dry starch layer on the clay surface, dry starch films cast from cooked starch were used. Figure 5 shows the swelling behavior of dried corn and potato starch films. It can be seen that the dried starch films swelled quickly in the first few minutes. In about 0.5 h, both the corn and potato starches were swollen to about 4 times their dry weights, which are the saturated state. This indicates that the cooked starch could adsorb 3 times its weight in water. Considering the densities of water as 1 g/cm^3 and starch as 1.55 g/cm^3, the coated starch on the clay surface (1.47 nm thick according to a previous calculation) would swell to about 8.3 nm in water. These swelled starch layers are deformable and provide many hydrogen bonding groups on the filler surface. As a result, they will increase the clay interaction and provide strong bonding with the wood fibers during papermaking.

It is known that dried starch particles will swell in water to form a hydrogel in water. Therefore, it is expected that the dry starch layer on the filler surface will swell but not dissolve under typical papermaking conditions. This hypothesis was studied by measuring the dissolved starch in water after dispersing starch coated clay in water under shear. During the experiments, 0.5 g of the corn starch (2.5%) coated clay (2.5corn–clay) sample was dispersed in 40 mL of distilled water and stirred at 1200 rpm under room temperature. Samples were drawn at certain intervals and centrifuged at 3000 rpm. The total organic content in the supernatant was analyzed to determine the starch content dissolved in water. Figure 6 shows the percentage of starches dissolved from the clay surfaces as a function of time. It can be seen that 15% starch dissolves in water soon after the starch coated clay was added to water. However, the remaining starch was still coated on the clay surface after several hours. The results indicated that most of the starch was retained with the clay filler in the paper during papermaking.

Effect of modified filler on optical properties of paper

It has been found that starch coated filler could be used to achieve high filler content paper while maintaining the paper strength. However, the optical properties are also very important. The effects of different coated starches on paper opacity and brightness are shown in Figures 7 and 8, respectively. Results indicate that different coated starches do not have an apparent effect on paper brightness and opacity. This is not surprising because the starch only formed a very thin layer on the clay surface, and it is colorless. Fur-

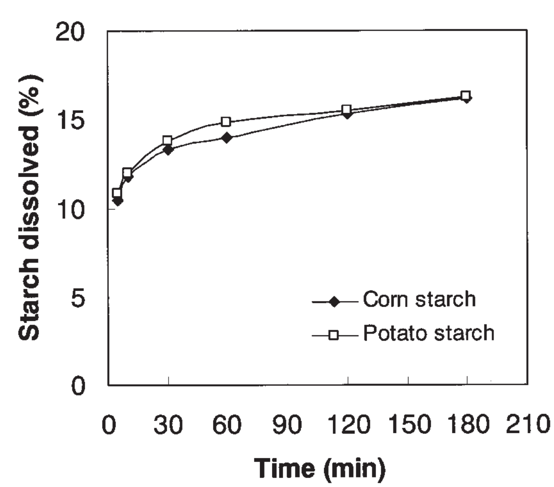

Figure 6 The stability of coated starch on the filler surface.

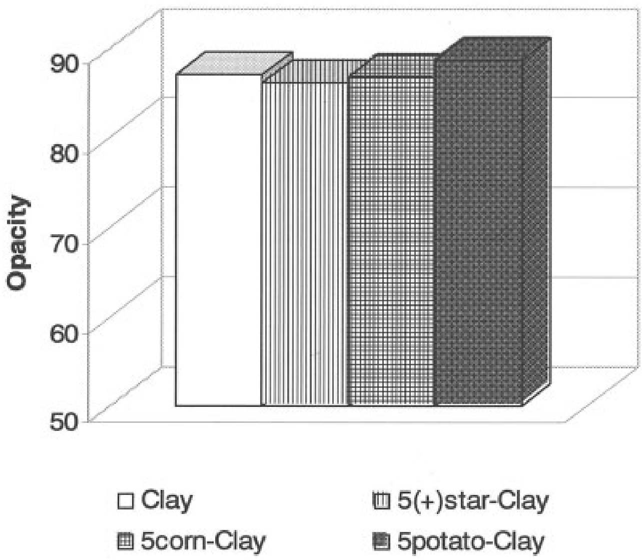

Figure 7 The effect of starch coated filler on the paper opacity (filler content 15%).

thermore, because the size of the fillers before and after starch coating is almost the same, the effect on the paper opacity would be minimal.

Effect of modified filler on filler retention

Clay filler is negatively charged. After modification with starches, the surface charge changed, as shown in Table I, which may affect the filler retention. The retention of the fillers on paper was examined by ashing the handsheets. These results are summarized in Figures 9 and 10. It can be seen that with PEO/PFR as a retention aid, the effect of modified filler on the retention is insignificant. This is not surprising be-

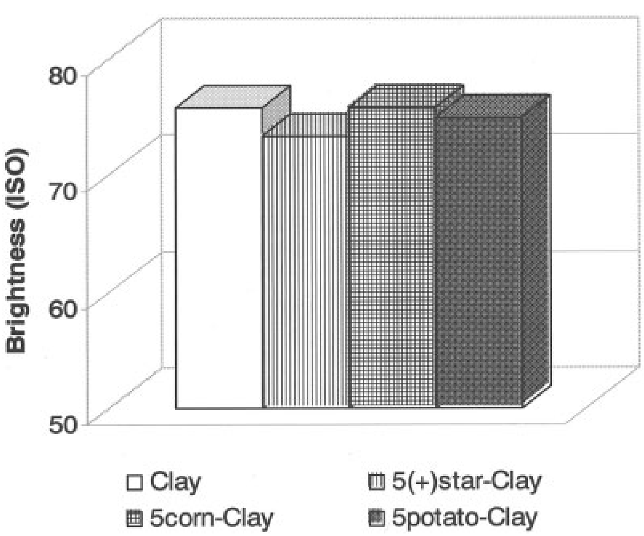

Figure 8 The effect of starch coated filler on the paper brightness (15% filler content).

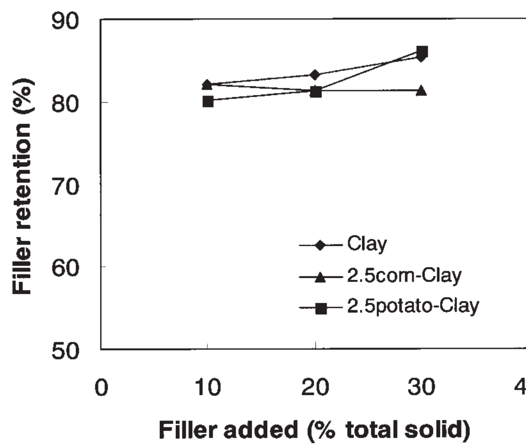

Figure 9 The filler retention with PEO/PFR as a retention aid.

cause PEO/PFR is a nonionic retention system, and it is not sensitive to the charge characteristics of fillers.[10] The effect of starch coating on the clay retention using cationic polyacrylamide was also studied. Surprisingly, the retention efficiency of the modified clay was much higher than that of original clay. The reason may be because the coated starch layer on the filler surface changed the hydrophilic properties and reduced the charge density of the clay fillers. For unmodified clay, a charge neutralizer, such as poly-diallydimethylammonium chloride, was needed in order to obtain the same retention level as starch coated fillers.

CONCLUSIONS

The following conclusions can be drawn from this research work.

- Unmodified starch can be coated to the filler surface. The coated and dried starch layer will swell

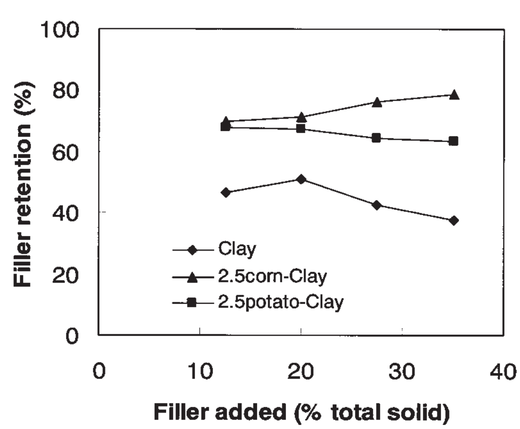

Figure 10 The filler retention with cationic polyacrylamide as a retention aid.

and only dissolve slightly in water during the papermaking process.

- Starch coated clay filler increased the paper strength significantly, with little effect on optical properties, compared with that of unmodified clay.
- Different starches (corn, potato, or cationic) gave similar effects when they were coated and dried on the clay surface. Papermakers can derive significant benefits from using low cost raw corn or potato starches to achieve much higher strength than the cationic and amphoteric starches, using the starch coating technique.
- The starch content can be as low as 2.5% of the clay filler. For paper products with 20% filler, the starch content was about 0.5% of the total weight.
- Modified clay filler is more easily retained in paper with cationic polyacrylamide retention aids.
- The starch content in white-water could be significantly reduced, because most starches are retained on the paper web with the filler or are still attached on the filler surface.
- High filler content paper may be produced from the starch coated filler while maintaining the paper strength.

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