FILLER LOADING IN THE LUMEN OR/AND CELL WALL OF FIBERS – A LITERATURE REVIEW

Pradeep Kumar, Yuvraj Singh Negi, and Surendra Pal Singh*

A review of the literature reveals potential advantages that papermakers can achieve by placing minerals in the lumens or cell walls of fibers before the pulp is formed into paper. Loading of filler into the fiber lumen by mechanical deposition or within the cell wall by in-situ precipitation has been reported to generally result in a moderate reduction in light scattering coefficient and increased strength properties of laboratory handsheets, as well as in paper manufactured with pilot plant equipment, when compared to conventional addition of filler. However, there are some exceptions to this general observation, where the fiber loading is reported to decrease the tensile strength of paper. Some related effects can be achieved by either precipitating mineral onto fiber surfaces or co-flocculating mineral particles with cellulosic fines. Challenges remain with respect to the implementation of fiber-loading concepts at a commercial scale. Also, there is a need for further research aimed at establishing high-end applications in which it may be an advantage to load cellulosic fiber cell walls or lumens with minerals or other substances.

Keywords: Fiber loading; In-situ precipitation; Bagasse pulp; Filler; Light scattering coefficient

*Contact information: Department of Paper Technology, Indian Institute of Technology Roorkee, Saharanpur Campus, Saharanpur-247001, India; * Corresponding author: spsptfpt@iitr.ernet.in*

INTRODUCTION

Mineral fillers are widely used in the manufacture of paper to improve many structural, optical, and printing properties. The filler can be incorporated in a paper sheet in different ways. In conventional loading the filler particles are added directly into the fiber stock suspension and the mineral is retained in the paper either by mechanical filtration or by use of retention-promoting chemicals. Alternatively, mineral particles can be placed in the lumens in the centers of cellulosic fibers. Technologies also exist whereby minerals can be chemically precipitated within the mesopore spaces of fiber cell walls. Such strategies also can be compared to procedures in which mineral particles are precipitated mainly on the outside surfaces of fibers or where mineral particles are co-flocculated with cellulosic fines. The present review article considers published work related to each of these approaches.

Conventional loading of filler with fibers is the most frequently used technique by paper mills, but at high filler levels, problems of fines retention and weakening of the paper sheet assume increasing importance. The retention of fine mineral particles is reduced, resulting in white waters with high solids content. The chemicals used to aid in the retention of fillers also cause flocculation and agglomeration of filler particles and pulp fines, thereby tending to impair the paper formation uniformity, which often limits the effective use of retention aids. Thus, retention is normally compromised with the

quality of the formation of the sheet. Very fine filler particles interfere with the fiber bonding and result in lower sheet strength.

Loading of filler in the fiber lumen or cell wall may offer new avenues to improve retention without affecting the formation adversely, since filler retention may be decreasingly dependent upon chemical retention, flocculation, and agglomeration. Further, this type of loading may be utilized to modify certain fiber characteristics, such as its flexibility, and consequently, the sheet properties.

Several potential advantages of putting filler inside the fiber over conventional filler loading have been suggested, and they can be listed as follows (Allan 1995):

1. Easier white water management due to improved retention
2. Reduction in the dosages of expensive polymeric retention aids
3. Easier drying of paper, due to a higher mineral content at a given level of strength
4. Lower apparent density of the paper in cases where the treatment may inhibit the collapse of fiber voids during drying
5. Less abrasion damage to the forming fabric because the filler is inside the fiber
6. Less two-sidedness because the filler is retained within fibers during sheet formation
7. Less dusty paper than the conventionally filled paper, because the fine filler particles are firmly held inside the fiber

Despite the foregoing potential advantages of fiber loading concepts, none of the technologies considered in the present review article has achieved widespread commercial success. Some of the inherent challenges that any fiber-loading technology needs to overcome in order to become widely adopted may include the following:

1. Difficulties associated with placing the mineral (or other) particles inside the cell walls or lumens of cellulosic fibers
2. Difficulties in avoiding or minimizing the deposition of a substantial proportion of the added material on the outsides of the fibers or in the bulk aqueous solution in which the fibers are suspended
3. Difficulties and/or expenses associated with removal of excess added materials that may have ended up on the fiber surfaces or suspended in the water phase during treatment
4. Competition from alternative technologies that may be able to achieve some of the purported benefits of fiber-loading technologies, while bypassing some of the inherent challenges

LOADING OF FILLER WITHIN THE FIBER LUMEN OR CELL WALL BY MECHANICAL DISPERSION

Cellulosic fibers consist of a porous wall surrounding a central cavity (lumen). In addition, the size and distribution of smaller pores within the fiber has been extensively studied. The volume of pores in fibers has been estimated to be close to 1.5 cm^3/g of fiber material (Li et al. 1995). The volume of the lumen is approximately 0.2 to 0.4 cm^3/g of

fiber (Satyanarayana and Wypych 2007). The average size of the pores in the cell wall is about 0.08 µm and that of the lumen is about 8 µm (Park et al. 2006). The various dimensions suggest that by mechanical dispersion the filler loading will be mainly into the fiber lumen and limited by the lumen volume.

From a conceptual standpoint, the simplest way to load plant-derived cellulosic fibers with inorganic particulate material involves mechanical agitation, followed by a physical separation step. Such approaches take advantage of the fact that the fibers (or tracheids) of many wood species have pit openings large enough to allow access of suitably small particles into the fiber's central cavity, the lumen (Carlquist 2001). The size of a typical pit opening in a softwood tracheid is 2 to 5 µm (Zakaria et al. 2004). Application of vigorous hydrodynamic shear with well-chosen proportions of the fiber, particulate material, water, as well as electrolytes can result in gradual diffusion of small particles into the lumen spaces. Subsequent filtration of the material can be used to rinse away particles that may happen to remain external to the fibers, leaving behind mainly the particles that remain within the lumens. The following subsections provide some examples in which mechanical lumen-loading procedures were demonstrated.

Haslam and Steele (1936) were apparently the first to confirm that suitably fine mineral particles can be placed into the lumens of fibers. They observed that after agitating fibers in the presence of a mineral slurry, not all of the mineral could be washed away, even after multiple rinsing steps. The mineral content that remained after such multiple washing treatments could be increased by vigorously beating the fibers in the presence of the suspended mineral particles. The researchers were also able to observe scattered light from unattached particles suspended in solution within the lumens of fibers; the location within the lumen was demonstrated by the fact that the motion of such particles was often opposite to the prevailing flow surrounding the fibers.

Loading of Titanium Dioxide (TiO_2)

Important early studies of lumen loading were carried out with TiO_2 particles. Such particles would seem to be particularly well suited for mechanical loading strategies, since the particles are very small, typically about 0.2 to 0.3 µm in diameter. Green *et al*. (1982) and Middleton and Scallan (1985) studied the lumen loading of paper pulp with titanium dioxide by mechanical diffusion. They stirred softwood kraft pulp fibers with titanium dioxide slurry and observed that the fine particles were able to diffuse into the fiber lumens through the pit apertures in the cell wall of the softwood fibers. Loaded pulp fibers were washed until the effluent was visibly clear of pigment. Optical microscopy was used to check that the external surfaces of the fibers were essentially free of pigment and to give a qualitative estimate of the degree of lumen loading. Pulp or paper samples were dried at 105 ^{o}C, and ash contents were determined after ignition at 900 ^{o}C, confirming that the lumen-loading process had been successful.

Miller and Paliwal (1985) used southern pine kraft pulp fibers, both dried and never-dried, bleached and unbleached, as well as beaten and unbeaten. They noted that the mechanical diffusion technique allowed only very small roundish shape particles to be loaded inside the fiber lumen. TiO_2 particles could be loaded in the lumen of fiber to a much greater extent than clay particles. The plate-like shape of clay particles contributes to a higher resistance to lumen loading. Bleaching the fibers tended to reduce the lumen-

loading capacity of the fibers, particularly when used with PEI as retention aid. Presumably, the bleaching affected the ionic nature of the fiber or destroyed the crevices in the heavily lignified primary wall and middle lamella. On the other hand, beating tended to increase the lumen-loading capacity of the fibers, as a small amount of mechanical work on the fiber would remove the pit membranes, which obstruct filler entry into the lumen. Two basic steps were involved in this technique of lumen loading. In the first step, filler was impregnated into the lumen by vigorously agitating fiber and filler. Secondly, the external filler was removed from the fiber by continuous washing with water. A Baur-McNett classifier was used for washing purposes. Many other investigators have used the same technique using precipitated calcium carbonate (PCC) in place of titanium dioxide (Middleton *et al*. 2003; Petlicki and Van De Ven 1994).

The loading of fiber by mechanical dispersion is limited to processes in which the diameter of filler particles is smaller than the diameter of pit apertures. Green *et al.* (1982) found that the kinetics of lumen loading is dependent on the stirring rate. They proposed that the chaotic motion of water flexes the fibers and thus causes flow through the lumen. This mechanism helps to explain why the lumen-loading rate was enhanced with increases in the stirring rate. Petlicki and Van De Ven (1994) proposed that fillers can diffuse into the lumen. In their model, the rate of lumen loading was limited by the transport of fillers through the pit apertures in the fiber walls. The model was also validated using the data from Middleton and Scallan (1989) and Alince *et al.* (1991). A later report by Petlicki et al. (1994) also proposed that the filler particles simply diffused into the lumen.

In an attempt to elucidate the mechanisms involved, Scallan and Middleton (1985) showed that the kinetic aspects of lumen loading could be well described by a simplified model. The authors assumed that (a) equilibration of the concentration of mineral particles occurs sufficiently rapidly so that the volumetric concentration of particles suspended in water in the lumen remains the same as the bulk concentration in the suspension outside of the fibers, (b) that the maximum possible deposition is equivalent to the formation of a monolayer of particles on the lumen surfaces, (c) that the rate of collisions of particles with fiber surface (and hence the rate of deposition) is proportional to the concentration in solution, and (d) there is a finite rate of detachment, which depends on the level of hydrodynamic shear. A model based on these assumptions achieved good fits with the data.

Loading of PCC ($CaCO_3$)

Middleton et al. (2003) loaded precipitated calcium carbonate (PCC) filler in softwood bleached kraft pulp fibers. The black spruce fibers were treated by mechanical agitation with the optional addition of cationic polyacrylamide retention aid or sodium polyacrylate (Dixpex N-40) as a dispersant. The pulp was disintegrated at 300 rpm, and the pulp was pretreated and impregnated with polymer in a disintegrator at 100 rpm. In this procedure, never-dried pulp was diluted with additional water and disintegrated for 5 min. Polymer was then added to this fiber suspension at 0.5% w/w on pulp, and adsorption onto the pulp was allowed to occur during 10 min stirring. Finally, the filler (300 g of 20% suspension) and sufficient water to raise the total water 1500 g were added, and the complete mixture was stirred for the specified time with periodic heating.

Following impregnation, the fiber/filler mixture was washed in a single unit of a Bauer-McNett classifier with a 100 mesh screen until the fiber was free of external filler. Filler content was found by ashing at 900 ^{o}C and using a factor of 0.56 to account for the decomposition to calcium oxide. No control of pH was used for any stage of the process. However, pulp disintegration and polymer adsorption were carried out at pH 6 and, when added, calcium carbonate maintained the pH close to 9. The level of PCC filler in the lumen of softwood pulp fiber was found to increase with the addition of cationic polyacrylamide when filler to fiber ratio was 3:1, the pulp consistency at 2%, and temperature at 25 °C. However, lumen loading of filler was reduced with increased temperature, as the ionic interaction became unfavorable. The extent of lumen loading also increased when a higher pulp consistency, and a lower filler to fiber ratio, 1:1, was used.

Loading of Magnetite (Fe_3O_4)

Zakaria *et al*. (2005) used magnetite powder (Fe_3O_4) and loaded such particles into the lumens of unbleached, never-dried kenaf pulp. Magnetic pulp is valued for specialty uses such as information storage, security paper, paper handling, paper sensing, and reprographic applications, including magneto graphic printing and electromagnetic shielding. The filler powder and the pulp fibers were mixed in a laboratory stirrer for 30 to 60 min in the presence of aluminum sulfate (alum). The mixture was then treated with polyethyleneimine (PEI) at various concentrations for 18 hours. After this duration, the pulp suspension was washed with water to remove filler on the surface over a 45-µm filter screen for 30 to 60 min. The use of PEI as a retention aid improved the deposition of filler in lumen tremendously. A PEI dose of 2% of fiber resulted in about 35% filler loading in the fiber. Without the use of PEI, most of the filler was removed during the washing process.

Zakaria *et al*. (2005) confirmed from scanning electron microscope (SEM) examination of cross sections of the fibers that the filler was actually loaded inside the lumen. They observed that all of the mechanical properties of paper such as tensile strength, burst strength, tearing, and folding endurance decreased as the amount of filler in the fiber increased. They assumed that the deposition of pigment in the lumen created stiffness in the fiber, resulting in stiffer paper and reduced interfiber bonding. Any filler remaining on the fiber surface after the washing process also reduces hydrogen bonding. The magnetic properties such as magnetization at saturation and remanent magnetization of the paper were increased as the filler in the fiber was increased.

Role of Retention Aid in Mechanical Loading of Fibers

Though issues related to the sizes of the mineral particles and the sizes of pit openings in the fibers are important, there has been inadequate attention paid in the literature to the role of electrostatic attractions and polymer-induced attachment between the cellulosic surfaces and mineral particles in the course of lumen loading. Some of the most important insights, which have been rarely considered in the course of more recent work, were those reported by Green *et al.* (1982) and by Middleton and Scallan (2003). Green *et al.* (1982) demonstrated that effective deposition of TiO_2 particles within the lumens of unbleached kraft spruce fibers could be achieved only in the presence of

aluminum sulfate (alum), and that the concentration of alum had to be optimized. Figure 1 depicts the kind of lumen loading results achieved by these researchers, showing substantial deposition of TiO_2 particles within the lumens of fibers, but relatively few particles adhering to the outsides of the fibers after rinsing. Two kinds of questions that can arise from such results are (a) what are the forces that cause particles to deposit on the fiber surface within the lumen, and (b) assuming that the composition of cellulosic material is similar throughout the fiber material, why was the relative amount of deposited filler so much higher within the relatively inaccessible surfaces of the lumen?

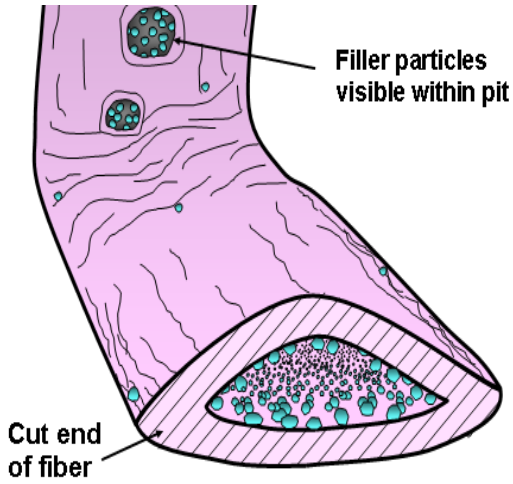

Fig. 1. Illustration describing a lumen-loaded spruce kraft fiber, in which positively charged TiO_2 particles (due to interactions with aluminum sulfate at the optimum pH adjustment) are attracted to the net-negative surfaces of fibers, except that those filler particles landing on the outer wall of the fibers are continually resuspended as a result of hydrodynamic shear in the agitated suspension

Middleton and Scallan (2003) showed that the results obtained by Green et al. (1982) could be explained by opposite net charges of the fiber surfaces (negative) and the mineral (positive) under the optimum conditions of treatment. A high affinity between cationic aluminum ionic species and the mineral surfaces gave them a positive net charge under conditions where the fiber surfaces were still negative. Equivalent results could be achieved if a specially selected TiO_2 product having a positive surface charge was substituted in place of the typical negatively charged TiO_2. The electrostatic mechanism was confirmed by the results of tests in which either a surfactant or increased pH was used to influence the surface forces. A mechanism was proposed in which the electrostatic attractions were sufficient to hold mineral particles onto the fiber surfaces within the lumen, but where hydrodynamic forces during agitation of the suspension were sufficient to repeatedly detach any particles that happened to come into contact with the outer surfaces of the fibers.

Miller and Paliwal (1985), Middleton and Scallan (1989), and Middleton et al. (2003) showed that retention aid polymers can enhance the fiber loading of pigment particles. The best lumen-loading results were achieved when the pigment particles were first loaded in the fibers by agitation in the presence of a filler slurry and then cationic

polymers such as polyethyleneimine (PEI) were used to destabilize the minerals. Post-treatment of the slurry of lumen-loaded fibers with cationic polyacrylamide was shown to be effective for keeping the mineral from coming back out of the fiber lumens during subsequent processing (Middleton and Scallan 1989; Rioux et al. 1992). If the order of addition was reversed and the retention aid was used before lumen loading, the particles tended to become flocculated together and the size of pigment particle agglomerates tended to increase, resulting in reduced lumen loading. Flocculation can result in loss of light-scattering efficiency, and in some cases also paper strength (Miller and Paliwal 1985). Several retention aid systems have been used for lumen loading by in-situ precipitation to increase the loading. Klungness et al. (1996, 2000) used cationic polyacrylamide (C-PAM) followed by an anionic flocculating agent for direct loading and fiber loading. Sivén et al. (2003) found that retention of filler particles in fiber lumens could be increased by adding PEI. Subramanian et al. (2005, 2006, 2007, 2008) used some dual retention aids such as C-PAM along with bentonite, which increased the fiber loading by in-situ precipitation.

LOADING OF FILLER WITHIN THE FIBER LUMEN OR CELL WALL BY CHEMICAL PRECIPITATION

Another basic approach to fiber loading involves in-situ chemical precipitation of the inorganic material. Allan *et al*. (1992b) and Silenius (1996) reviewed several studies on cell wall loading by *in-situ* precipitation of a filler pigment. In principle this can be achieved by a two-step process. In the first step the fibers are immersed in a suitably concentrated solution containing selected inorganic ions. After an optimal filtration or rinsing step to get rid of the excess solution from the outside of the fibers, a second solution is added to the mixture. The materials are selected such that an insoluble compound can be formed between one of the ions in the first solution (now mainly inside the fibers) and the other solution, now able to diffuse into the fibers' spaces. Filler particles are precipitated in situ within the mesoporous spaces of the fiber cell wall by a chemical precipitation reaction. The precipitated pulp fiber is washed with water to remove the excess precipitated filler particles from the external surface of the pulp. Several techniques have been used by different authors, as described in the following subsections.

When one considers the size difference between a fiber lumen and the spaces within the cell wall of a typical kraft (or other) pulp fiber, it is clear that the end result is likely to be different for each of these situations. The lumens of softwood kraft fibers can have widths as great as about 20 µm (depending on how flattened the fiber has become as a result of refining, drying, etc.), whereas the mesopore spaces within a cell wall lie in a range of about 1 to 100 nm, depending on such operations as pulping, bleaching, and drying. Figure 2 provides a conceptual drawing of what it would mean to completely fill the mesopore spaces within a section of cell wall with precipitated mineral (note contrast in the size range in comparison to lumen loading, as depicted in Fig. 1).

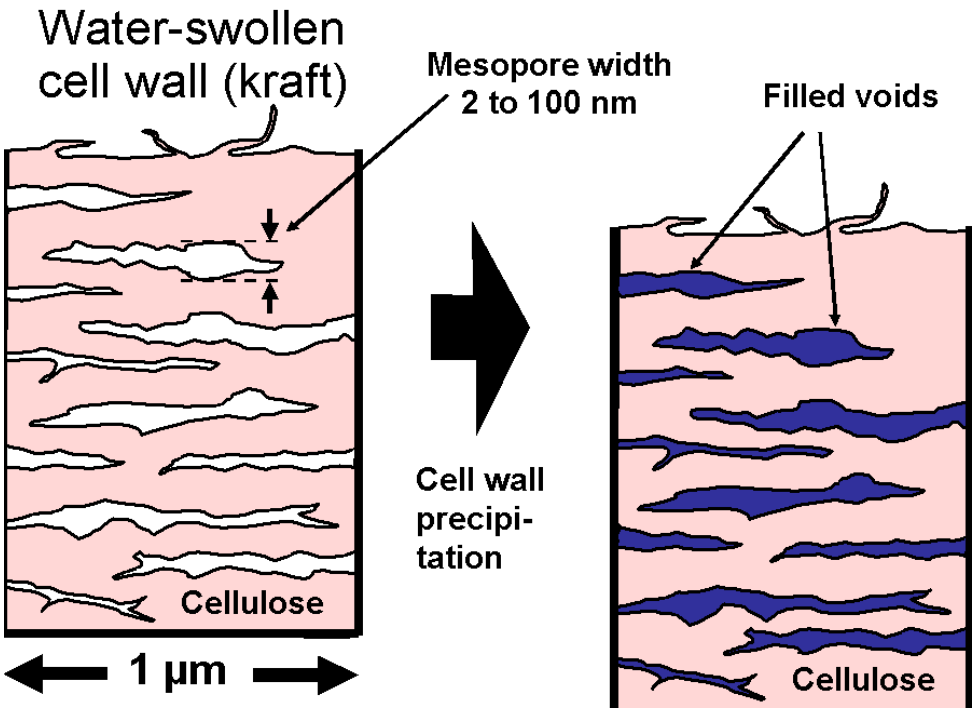

Fig. 2. Illustration of cell-wall filling, based on an assumption that the fiber is water-swollen as a result of such operations as kraft pulping, optional bleaching, and refining, followed by saturation with a first solution, rinsing, then exposure to a second solution, resulting in in-situ precipitation

Precipitation of Nickel Carbonate

For the purpose of study, Allan *et al.* (1992a) used nickel chloride and sodium carbonate solutions to precipitate nickel carbonate. They suggested that the filler particle could be incorporated within the cell wall voids (which can account for as much as 1.5 mL/g of pulp) by in-situ precipitation of insoluble inorganic materials. For determination of the location of the filler, a never-dried alpha-cellulose fully bleached pulp beaten to a 450 mL CSF was soaked in a nickel chloride solution (43% by mass). The excess solution was filtered off under reduced pressure, and the pulp was disintegrated in a saturated solution of sodium carbonate at 100 °C. Nickel carbonate was precipitated. The pulp was collected by filtration and was washed repetitively with hot water to remove the excess of precipitate and soluble salts. The fibers were dried after solvent exchange (from water, then methanol, then anhydrous ether, then hexane) in order to avoid their complete collapse. They were then imbedded in an epoxy resin and were microtomed into slices about 5 µm thick for analysis by energy-dispersive X-ray spectroscopy. It was observed that most of the nickel carbonate precipitated during the process was present within the cell wall pores of never-dried fiber.

Precipitation of Silica Compounds

A Swedish patent (Eriksson 1991) describes a method to create fibers loaded with aluminum silicate by chemical precipitation. In the first step, the pulp is impregnated

with sodium silicate for a certain time and then dewatered. The second step involves the impregnation of the pulp with poly-aluminum sulfate to precipitate aluminum silicate. It was believed that a part of the inorganic matter became deposited either within the cell wall spaces or in the fiber lumens.

Sivén and Manner (2003) used fiber loading of a mechanical pulp by in-situ precipitation of aluminum silicate, based on the method described by Eriksson (1991) but reversing the order of chemical addition. Alum (aluminum sulfate) solution was added to a mechanical pulp at a stock concentration of 15% and mixed for about 10 minutes. To this mixture an alkaline mixture of sodium silicate (42% solid) and sodium hydroxide (10% solid) was then added slowly into the mixing vessel over 15 minutes, increasing the pH from about 4 to over 8.0, thereby precipitating aluminum compound in the fibers.

Although most strategies involving increased mineral contents of paper have tended to increase the scattering of light (tending to increase both opacity and brightness of the paper), Sivén and Manner (2003) found the opposite. Such findings can be explained if one considers the likely effect of filling mesopore spaces. The deposited aluminum silicate can be expected to have a refractive index similar to that of the cellulosic material. For this reason, no significant contribution to light scattering by the mineral is expected when the mineral is loaded into the cell wall. An exception to this rule might be considered, however, if the cell-wall loading greatly reduced the conformability of the fiber, resulting in a bulkier, less bonded sheet of paper.

Chauhan *et al*. (2007) compared the effect of sodium aluminosilicate (SAS) filler on the properties of handsheets of hardwood pulp used in two different ways, fiber loading by in-situ precipitation and by conventional loading. The SAS was precipitated by adding sodium silicate to the aluminum sulfate solution. Handsheets were prepared first by precipitating SAS in the presence of pulp fibers and second by adding SAS particles to the pulp after precipitating them without the pulp. In-situ precipitated fibers were loaded with SAS up to an ash content of about 7.5%. They found that tensile and burst strength properties were on the higher side for sheets loaded by in-situ precipitation than sheets with direct filler loading. Chauhan et al. (2007) found that tear index increased with an increase in ash content when fiber was loaded with SAS by in-situ precipitation.

Precipitation of Calcium Carbonate

Given the predominant role of calcium carbonate filling in today's pulp and paper industry, it is worth considering whether technology based on in-situ precipitation loading can achieve advantages relative to conventional filling of commodity paper grades with the same mineral. Therefore, fiber loading with calcium carbonate using in-situ precipitation technique has attracted the greatest attention of researchers, in comparison with other options reviewed by Allen *et al.* (1992b). The pulp suspension may be first exposed to a solution of calcium chloride, and then subsequently treated with sodium carbonate.

Many different forms of calcium carbonate can be used as paper filler. Natural calcium carbonate is widely available in two mined forms, limestone and chalk. Limestone is ground to a desired particle size and used as filler. Calcium carbonate may be

prepared chemically (PCC). Although natural calcium carbonate can exist in any of three crystalline forms, calcite, aragonite, and vaterite, calcite is thermodynamically the most stable form, and it is by far the most commonly used in papermaking applications. Natural calcite belongs to trigonal (rhombohedral lattice system) crystal system under ambient conditions. Calcite can also be prepared by precipitation (PCC) in numerous morphologies such as scalenohedral ("rosette"), rhombohedral, and the rhomboscalenohedral forms to suit specific applications. For example, scalenohedral calcite improves the brightness, opacity, and smoothness of white paper. However, rhombohedral calcite with an optimal size between 0.2 and 0.4 μm has a high light scattering ability (due to inefficient packing), and it can be used advantageously in certain paper grades (Carmona et al. 2002). The particle size and shape of PCC depends on reaction conditions such as reaction temperature, reaction time, concentrations of reactant, and type of agitation.

A patent by Craig (1952) describes a process for producing a pigmented cellulosic pulp in which calcium chloride was used to saturate the fibers. Subsequently, sodium carbonate solution was added to precipitate calcium carbonate *in-situ*. Thomsen (1962) describes a method in which the fibers were saturated with a 10% solution of calcium chloride. The slurry was then compressed to remove the excess solute to about 50% dryness. Finally the mixture was sprayed with ammonium carbonate solution to precipitate calcium carbonate. The soluble by-product ammonium chloride was then flushed out with water. The washed pulp contained approximately 10% of loading material. Opacity of the cellulose fibers was increased with such internal loading.

A Japanese patent (Yoshida *et al*. 1987) describes a method of fiber wall loading that yields no by-products other than water. In this method, calcium carbonate is precipitated by bubbling carbon dioxide gas through a slurry of calcium hydroxide and pulp. Klungness *et al*. (1993, 1996, 1999, and 2000) used the same approach in their experiments. Calcium hydroxide slurry in water was thoroughly mixed with pulp fibers. This mixture was then passed through a pressured high consistency refiner in the presence of carbon dioxide gas to precipitate the calcium carbonate. The duration of the pressured reaction was about 15 minutes under carbon dioxide pressure of about 35 kPa to 410 kPa.

Klungness et al. (2000) compared properties of handsheets made from fiber-loaded pulp by in-situ precipitation of calcium carbonate with those of handsheets made using conventional loading. They used precipitated calcium carbonate (PCC) of different shapes and sizes as well as ground calcium carbonate (GCC). Fiber loading resulted in the greatest tear index for both eucalyptus and pine kraft pulps. Differences between fiber loading and direct loading were small. Tear index depends to a great extent on the fiber length of the pulps. Because the addition of filler does not change fiber length, no great differences were noted between the types of pulp loading. In the case of direct filler loading, the tear index of paper handsheets decreased with addition of filler.

Klungness *et al*. (1995, 1996, and 1999) conducted fiber loading experiments on industrial-scale equipment using an atmospheric high consistency refiner to mix the calcium hydroxide, followed by high consistency pressurized refining in the presence of carbon dioxide. To incorporate calcium carbonate, pulp was mixed with varying amounts of calcium reactant and water for 15 min at low speed. Alternately, the pulp, water, and calcium blend were passed through the refiner under atmospheric conditions using the

refining plates to mix and refine at the same time. High consistency pulp containing calcium reactant was loaded into the refiner feed tank. Carbon dioxide was injected into the feed tank to react with the calcium hydroxide in the pulp. The fiber-loaded pulp was processed on a pilot-scale paper machine by using industrial-scale equipment for pulp preparation and paper machine evaluation, along with a conventional, direct-loaded calcium carbonate control. By this means the calcium ions were able to diffuse into the fiber wall and subsequently react with carbon dioxide, depositing PCC on the internal and external surfaces of the pulp.

Kumar et al. (2009 and 2011) studied in-situ precipitation of $CaCO_3$ in bleached chemical bagasse and hardwood pulp fibers. Beaten pulp was impregnated with sodium carbonate solution in a beaker with a laboratory agitator operating at 1200 to 1500 rpm. After about 20 minutes of mixing, saturated $Ca(OH)_2$ solution (1.46 g/L) was added to the pulp, which was washed thoroughly to remove the precipitate from the external surfaces of the fibers. Ciobanu et al. (2010) used a new method involving generation of $Ca(OH)_2$ in-situ with the pulp fibers through reaction of NaOH before carbonation to precipitate $CaCO_3$.

EFFECT OF FIBER LOADING ON PULP PROPERTIES

Water Retention Value (WRV) and Pulp Freeness

Klungness *et al*. (2000) studied the effect of fiber loading on the water retention value (WRV) of the pulp. As shown in Fig. 3, fiber loading increased the WRV for both never-dried and once-dried pulp. As expected, the values of WRV for never-dried sheets were greater than those for the once-dried sheets. They also observed that the freeness of pulp (CSF) increased with the fiber loading for both never-dried and once-dried pulps, in contrast with the general observation that CSF decreases when WRV is increased.

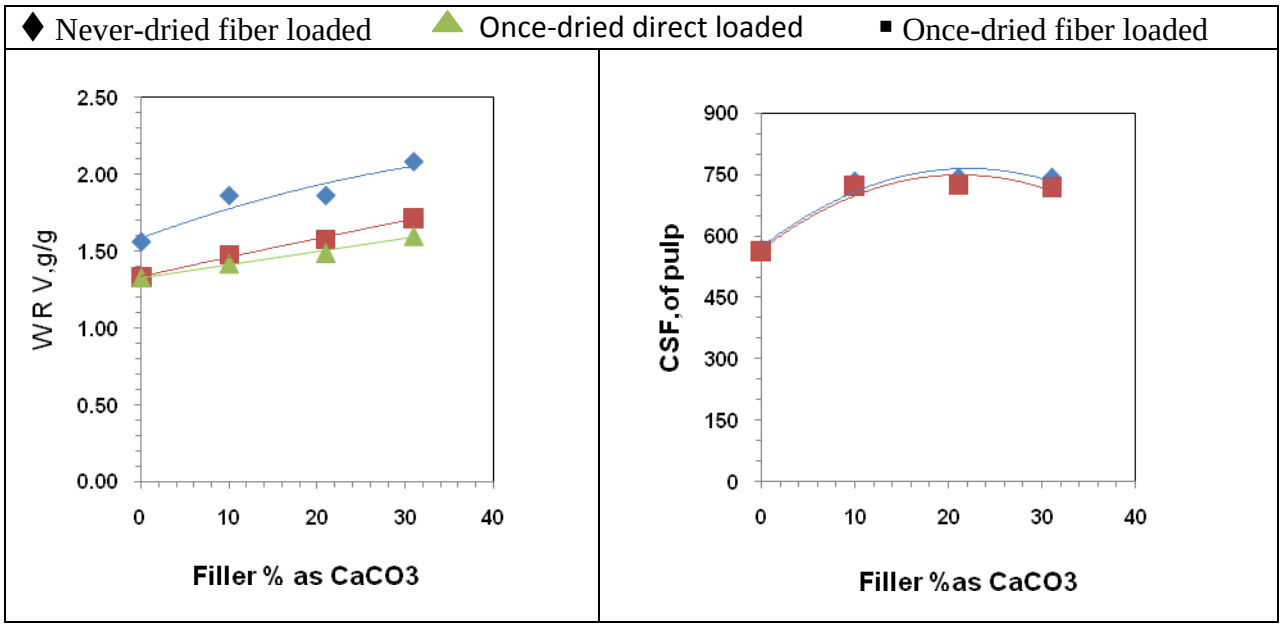

Fig. 3. Effect of drying of fiber-loaded, fiber-loading without drying, and drying of direct-loaded pulp on water retention value and CSF (freeness) of pulp (From data of Klungness *et al*. 2000)

Strength Properties

When loaded mineral content is precipitated within the cell wall of a cellulosic fiber, it is reasonable to expect such filling to affect the conformability of the fibers, thus affecting their ability to bond together upon drying. On the other hand, there is a possibility that fiber bonding is hurt due to mineral content that remains external to the fibers when the paper is made. For these reasons there has been continuing interest in the strength of paper formed from cell-wall-filled fibers.

Several investigators have demonstrated that fiber-loading technology can achieve greater paper strength in comparison with conventional loading at a given filler content. Green *et al*. (1982) using unbleached soft wood pulp and Miller and Paliwal (1985) using bleached soft wood pulp fiber observed that lumen loading of TiO_2 filler in mechanical dispersion resulted in paper sheets having greater tensile strength compared to conventionally filled paper at equal filler content. Increasing the filler content caused a reduction in tensile strength for both lumen-loaded sheets and conventionally loaded sheets; however, the loss due to conventional loading was greater. At a loading of 10% TiO_2, the lumen-loaded sheet was found to lose only 14% of its tensile strength, whereas the conventionally loaded sheet lost 56% of its strength (Miller and Paliwal 1985). Similarly, the loss in tear strength was also less in lumen-loaded sheets. The tensile index was reduced in both lumen-loaded and conventionally loaded pulp sheets for PCC filler, but more so in the case of conventionally loaded sheets. Middleton *et al*. (2003) loaded PCC filler using the technique of mechanical dispersion, and the tensile strength fell off significantly faster in the case of conventionally loaded pulp sheets.

Klungness *et al*. (1993, 1994, 1996, 1999, and 2000) observed that the tensile strength of handsheets made from filler-loaded pulps was higher due to greater internal bonding strength of paper than those of handsheets made from similar direct-loaded pulps at the same calcium carbonate levels as a result of the carbonate being present within the fiber wall and lumen. These results were expected because the mineral content within the fiber cell wall is not expected to interfere as much with fiber-to-fiber bonding as when it is present on the external surface of the fibers.

Klungness *et al*. (2000) observed that at equal filler level, tear strength and bending stiffness of fiber-loaded pulps were not much different from direct-loaded pulps with calcium carbonate particles of different shapes and sizes. However, the tensile index and Scott bond values of fiber-loaded sheets were greater than the direct-loaded sheets, suggesting greater fiber-fiber bonding in the case of fiber loading than in direct loading, most likely due to less interference from inter-fiber bonding when minerals are deposited within the fiber. The tensile index values for fiber-loaded pulp were about 10% to 40% higher than those for direct-loaded pulp, depending on the type of pulp or filler used. No trend in the data for direct loading or for pulp type was noted. Cationic wet end starch increased the strength of handsheets made from both direct-loaded and fiber-loaded pulps with PCC.

Kumar et al. (2009) found that in-situ precipitation of calcium carbonate caused a greater drop in strength properties of bagasse pulp than the drop caused by the direct filler loading, when compared at an equal ash level. The strength properties of in-situ precipitated bagasse pulp could be improved by blending with other pulps. The strength

properties of in-situ precipitated bagasse pulp could also be improved by refining the in-situ precipitated bagasse pulp once again. The effect of in-situ precipitation of calcium carbonate on pulp fibers was quite different for bagasse pulp from the hardwood pulp. Ciobanu et al. (2010) also noted that precipitation of calcium carbonate into the fiber lumen and cell wall pore by in-situ precipitation resulted in a lower tensile strength than those sheets made with conventionally loaded pulp fiber. Allan *et al*. (1998) have shown that the *in-situ* precipitation of filler within the fiber wall could be utilized to obtain gains in strength properties of a newsprint furnish consisting of blends of semichemical soda bagasse pulp and semibleached kraft softwood pulp at equal strength levels of the fiber-wall loaded sheets and conventionally loaded sheets.

Bulk and Stiffness

Usually the bulk of a paper sheet decreases as the amount of filler is increased in conventional loading, but the bulk has been found to show an increase when the filler is loaded within the fiber lumen or cell wall. Klungness *et al*. (1995, 1996), based on the results of pilot paper machine studies, observed about a 10% increase in bulk by fiber loading. Chauhan et al. (2007) also observed an increase in paper bulk when aluminosilicate was precipitated in-situ on the fibers. A decrease in the collapsibility of fibers loaded in the lumen or cell wall resulted in an increased thickness of the paper.

Bending stiffness of paper sheets made from fiber-loaded pulp is found to be greater than the conventionally loaded sheets because the fiber-loaded sheets have a greater bulk (Green *et al.* 1982, Miller and Paliwal 1985, Chauhan et al. 2007). However, Klungness *et al*. (1994 and 200) observed that, at equal filler level, the bending stiffness of fiber-loaded pulps was not much different from the direct-loaded pulps in case of calcium carbonate loading.

Optical Properties

Filler addition has a very significant effect on optical properties of paper as it enhances the specific scattering coefficient of the paper. Miller and Paliwal (1985) found that paper made from bleached soft wood fibers whose lumens had been loaded with TiO_2 by mechanical dispersion showed a slightly lower opacity and lower brightness than the conventionally filled paper. Middleton *et al*. (2003) observed an increase in light scattering coefficient with increasing PCC filler content for both lumen-loaded and conventionally loaded sheets. However, the scattering coefficient of the lumen-loaded sheet was less than that for conventionally loaded sheets. These results contrasted with those of Green *et al.* (1982), who observed nearly equal optical performance of lumen-loaded TiO_2 and conventionally retained TiO_2. They assume this could be due to the very high refractive index of TiO_2, allowing it to make a substantial contribution to light scattering even when it is well bonded to a cellulosic surface.

Klungness *et al*. (1993, 1996, 1999, and 2000) observed that when fibers loaded with calcium carbonate by in-situ precipitation were used in papermaking, all of the optical properties such as opacity, scattering coefficient, and brightness were reduced at the same filler level. They suggested that the decrease in the light scattering coefficient due to fiber loading could be easily offset by increasing the filler level. They also observed that the effect of fiber loading on optical properties was more significant in the

case of TCF pulps than in case of ECF pulps. Addition of 1% hydrogen peroxide based on dry weight of the pulp helped in preventing the brightness loss of TCF pulps during fiber loading. In fact, a major portion of the mineral was precipitated inside the fibers, and it was not affecting the reflectance of light to the same degree as direct filler addition. In case of direct filler loading, the filler particles were able to increase the amount of air-solid interface, thus creating more opportunities for the scattering of light. When a comparison was made between fiber-loading and direct filler addition, the brightness of paper in case of fiber-loaded pulp was quite low. These results further confirm the hypothesis that by in-situ precipitation an appreciable portion of the mineral gets precipitated inside the cell wall of the fiber, where it is does not contribute appreciably to the scattering of light (Chauhan et al. 2007). Allan *et al*. (1998) also noted that the *in-situ* precipitation of filler within the fiber wall resulted in an enhancement of optical properties for a newsprint furnish, but at equal filler levels this was less than in the case of the conventionally loaded sheets.

Kumar et al. (2009) found that in-situ precipitation of calcium carbonate on bagasse fibers resulted in a very significant increase in specific scattering coefficient and consequently large improvements in opacity and brightness of the handsheets made of such pulp. By contrast, in-situ precipitation of calcium carbonate on hardwood fibers did not show much improvement in optical properties. Ciobanu et al. (2010) observed that in-situ precipitation of $CaCO_3$ on bleached softwood kraft pulp fibers resulted in greater opacity than those made of conventionally loaded pulp fibers.

The in-situ precipitation of $CaCO_3$ on bleached pulp caused a slight yellowing of the pulp because of the highly alkaline conditions used in the process (Klungness et al. 1995, 1996). Addition of a small amount of hydrogen peroxide during the fiber-loading process was suggested as a means of reducing the yellowing effect (Klungness et al. 1994, 2000).

Offset Printability

Kumar et al. (2011) compared direct-loaded bagasse pulp with in-situ precipitated bagasse fiber loaded by calcium carbonate filler and showed favorable effects on both the print density and the print-through when the sheets were printed in a laboratory using offset ink. For a given amount of ink on the printing disk or on the paper, the print density was more and the print-through was less for in-situ precipitation of filler than with the direct filler loading. The observed behavior on printability parameters is largely attributable to a significant improvement in light scattering coefficient of the bagasse pulp on loading by in-situ precipitation of calcium carbonate in the fibers. Due to the increase in light scattering, both the print density and print-through values decreased, but the reduction in the print-through was more pronounced than the reduction in the print density. For a given print density, the print-through for in-situ precipitated sheets was less than that for the direct-loaded sheets and much less than that for the unloaded sheets.

CALCIUM CARBONATE–CELLULOSE FIBER COMPOSITES

The term "composite" can be used in cases where mineral is precipitated or made to deposit both onto and within the cell walls of cellulosic fibers. Such approaches can be expected to favor efficient retention of the mineral due to a mechanical interlocking that may be achieved by in-situ precipitation at a fiber surface. However, since no effort is made to remove mineral from the outsides of the fibers, it is uncertain whether to expect strength benefits relative to conventionally loaded paper. Such cases need to be compared to alternative strategies in which suitable mineral suspensions are deposited onto fiber fines and mixed with pulp suspensions. Examples described in this section pertain to a variety of such treatment strategies.

Silenius (2002) observed that the tendency of calcium carbonate to precipitate into the lumen or inside the cell wall was minor when in-situ precipitation was performed for birch fibers using the reaction between calcium hydroxide and carbon dioxide. The major tendency of calcium carbonate to precipitate was on the surfaces of fibers, and the presumed benefits of fiber loading over conventional loading were not visible. Silenius thought that an effective technique could be to produce a composite of fiber fines and calcium carbonate and use it in paper as filler.

Such composite filler was produced by precipitating calcium carbonate on pulp fines having a size range approximately the same as the diameter of filler particles. A highly beaten pulp was fractionated with a Bauer McNett apparatus, and the fines fraction that passed through the 200-mesh wire screen was used to produce the composite filler. Calcium carbonate was precipitated by pressurizing a mixture of fiber fines and calcium hydroxide with carbon dioxide. The calcium carbonate content of this composite filler (called 'SuperFill') was varied to determine the optimum region in terms of paper properties. Although the technique can be considered as an *in-situ* precipitation, it differs from fiber or lumen loading by the proportions of cellulosic material and calcium carbonate, and by the type of cellulosic material. The composite filler is mainly composed of calcium carbonate, whereas loaded fibers contain relatively low proportions of calcium carbonate. Moreover, the cellulosic part of the new filler is composed mainly of narrow fibrils instead of fibers.

Silenius observed that this new filler provided paper with significantly improved filler retention, formation of paper, and combination of optical and strength properties compared with commercial PCC fillers of the same morphology and crystal size. When adding the filler to the paper, the decrease in tensile strength was only approximately one half of that which occurs with the same amount of commercial PCC of the same crystal size and morphology. On the other hand, the light scattering coefficient of paper was nearly doubled at constant tensile index and Scott bond compared with commercial PCC. The SEM analysis of the composite filler revealed that calcium carbonate crystals were precipitated on fibrils, resulting in chainlike structures in which calcium carbonate crystals were supported by the fibrils.

The mechanism proposed to explain the attributes of the composite filler consists of three elements: (1) There is a more uniform spatial filler distribution and reduced agglomeration in the paper, which may contribute to light scattering coefficient through the combined effect of the pigment itself, interruption of the fiber bonded area, and reduced fines collapse. (2) The fines component of the composite filler contributes to enhanced bonding, resulting in increased paper strength. (3) The composite filler

influences paper in such a way that a more optimum pore structure with respect to paper light scattering is achieved.

Subramanian *et al*. (2005, 2006, 2007), following the approach of Silenius (2002), prepared composite fillers by precipitating calcium carbonate on finely ground nonwood and wood pulps. They used a special grinder (Masuko Supermass Colloider) that produces a suspension of fines and externally fibrillated fibers. The refined pulp was mixed with slaked lime and treated with carbon dioxide gas to precipitate calcium carbonate composite filler. Paper sheets were prepared after adding the composite fillers having different PCC-to-fiber ratio to a base pulp furnish. They observed that for given filler content in the paper sheet, the bending stiffness, internal bond strength, and tensile index were greater for sheets loaded with PCC-cellulose composite than the sheets conventionally loaded with PCC. However, the light scattering coefficient of the PCC-cellulose composite filler loaded sheets was somewhat lower than that of conventionally loaded sheets.

Subramanian *et al*. (2007) showed that the effects of loading on paper properties depended on PCC morphology. They prepared pulp composite fillers with varying crystal habits of precipitated calcium carbonate and compared their effects on the papermaking properties of printing and writing paper. In their study, three different types of PCCs — colloidal (c-PCC), rhombohedral (r-PCC) and scalenohedral (s-PCC) — were precipitated in-situ with fines produced from a bleached kraft pine pulp. Similar experimental conditions were employed for the production of composite and reference PCC fillers. The effects of adding composite fillers on the properties of handsheets made from bleached softwood (pine) and bleached hardwood (birch) base pulps were compared with the effects of reference PCCs. A cationic polyacrylamide (C-PAM) retention aid was added to the furnish. Their major observations were:

1. Fibrillar fines PCC composite filler gave higher first pass retention than reference PCC due to higher flocculation of fibrous fines with C-PAM retention aid (Solberg 2003). The c-PCC composite filler showed the highest first-pass retention, probably due to its morphology and agglomeration. A mixture of PCC and fibrous fines had a higher retention than reference filler, but lower than the composites. Mixing of filler with fines trapped the filler into the fines network, resulting in higher retention than with addition of reference filler by itself.
2. The draining characteristics of different furnishes were determined in terms of the dry solids content after the handsheets were pressed twice in a Material Testing System (MTS) press at a pressure of 3.3 Mpa for 0.02 seconds with two blotting papers on each side. Loading with the composite fillers gave the poorest drainage, direct loading gave the best drainage, while loading with a mixture of PCC and fibrous fines gave an intermediate drainage behavior. Among the reference fillers, structured s-PCC showed lower drainage because of the water retention in the pores of the particles. Among the composites, at lower handsheet filler content the colloidal composite showed the poorest drainage, probably due to the homogeneous distribution of fillers in the sheet. At higher filler contents, the drainage of colloidal fillers increased due to the expansion of the network structure. At high filler contents, greater than 20%, the

drainage of s- and r-PCC composite samples decreased significantly, probably due to the higher amount of film-forming fines in the structure.

3. Loading with PCC showed a decrease in apparent sheet density and an increase in air permeability. Among the PCC types, addition of s-PCC caused the most significant effect, and addition of colloidal PCC caused the least effect. In contrast to loading with PCC alone, loading with composite filler containing fibrous fines resulted in an increased sheet density, due to enhanced Campbell's forces (Retulainen 1997).
4. Direct loading of PCC resulted in a decrease of bending stiffness that decreased further with increased addition of filler. The addition of composite filler or a mixture of fines and filler showed an increase in stiffness. Mixing of fines and PCC gave the highest bending stiffness resistance due to stronger bonding and improved sheet consolidation.
5. Composite fillers gave higher tensile strength than the reference fillers. These results were consistent with earlier findings (Xu et al. 2005) showing that fines contributed to strength by acting as a sealant-glue that increased the bonding area in filled paper.
6. Increased addition of filler enhanced the light scattering of paper for all types of fillers studied. Improvement in light scattering, even with increased sheet density, could be due to the higher number of optical pores generated in the paper sheet and the composite filler network structure. The light scattering was similar for composite fillers as well as for PCC alone, in contrast to their earlier observations (Subramanian, et al. 2005). In-situ precipitation could lead to lowering of surface area and particle size of the composite particles to such dimensions that did not contribute to the light scattering.

EFFECT OF FIBER LOADING ON BAGASSE PULP

Bagasse generally yields pulps with low tear strength, opacity, and bulk but acceptable tensile strength. Kumar et al. (2009) found that the *in-situ* precipitation of calcium carbonate on bagasse fibers resulted in a very significant increase in specific scattering coefficient and consequently large improvements in opacity and brightness of the handsheets made of such pulp. At the same level of filler loading, the scattering coefficient of *in-situ* precipitated pulp was much greater than that of the directly loaded pulp. However, i*n-situ* precipitation of calcium carbonate caused a drop in strength properties of bagasse pulp, which could be improved by blending with other pulps or by refining the in-situ precipitated pulp once again. The effect of *in-situ* precipitation was quite different for bagasse pulp from the hardwood pulp. *In-situ* precipitation on hardwood fibers neither showed much improvement in optical properties nor much reduction in strength properties.

Subramanian *et al*. (2005), in their study of composite fillers produced with different nonwood and wood pulp fines, found that the z-directional bond strength was highest when the paper contained bagasse composite. It was remarkably higher than that of direct loading, and even better than for the unfilled paper. This was attributed to the increased bonding caused by the short fibers and fines and the morphology of the bagasse pulp substrate.

SUMMARY

1. Fiber loading by mechanical dispersion or by in-situ precipitation has potential to produce paper sheets having greater tensile strength and nearly equal and slightly lower optical properties than commercially loaded paper at equal filler content. Increasing filler content causes a reduction in tensile strength for both lumen-loaded sheets and conventionally loaded sheets; however, the loss in conventional loading is generally greater.
2. A key to the success of mechanical lumen-loading strategies involves careful management of electrolyte conditions. Both the mineral particles and the fiber type need to be selected based on the size of pit openings in the fibers, allowing access of the mineral to surfaces within the lumen. Efficient deposition of mineral particles onto cellulosic surfaces can be achieved by adjustment of a soluble aluminum additive, pH, and other factors so that the particles have a positive charge and the fiber surfaces are negative. Agitation of such a suspension for a sufficient length of time can promote release of externally adhering particles, allowing them to reposition themselves on surfaces within fiber lumens. Post-treatment with a cationic polyelectrolyte can be effective for holding the lumen-loaded particles in place during subsequent papermaking operations.
3. In-situ precipitation strategies leading to cell wall filling may offer some unique features and advantages for specialty grades of paper. However, the required processing conditions may be demanding. Typically the cellulosic fibers are exposed to one saturated solution, the excess solution is removed, and then the fibers are exposed to a second solution, resulting in precipitation of an insoluble mineral. Because such precipitation tends to occur both within and outside the fibers, including within the bulk of solution, it is usually considered necessary to rinse away the portion of mineral that is not within the cell walls. The effect of cell wall filling on paper optical properties is typically negative, making it an unfavorable option for production of typical printing grades of paper.
4. Composite filler, formed in combination with cellulosic fines, can achieve significantly higher light scattering of paper than conventional addition and refiner-addition of filler. Light scattering increases as a function of refining. Moreover, light scattering and opacity tend to be higher for handsheets prepared with composite filler, compared to reference samples. Addition of PCC composite filler to the furnish can enhance the Scott bond and tensile strength of printing paper compared with conventional loading of calcium carbonate filler. Because such approaches do not require any rinsing step to remove externally-adhering particles from fibers, it is reasonable to expect that this type of strategy can be utilized during the production of conventional grades of filled paper.

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