

Inorganic Filler – Modification And Retention During Papermaking : A Review

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ABSTRACT

Papermakers are continuously searching for methods to decrease cost and improve product quality. One approach is increasing the filler content of the sheet, replacing expensive fiber. By increasing filler content, other quality improvements are noticed including increased opacity, brightness, smoothness and printability. However, using conventional means, reduced retention with increased filler loading results in decreased machine performance, as well as reduced strength/physical properties of paper, limiting the papermakers' ability to increase filler content. Many approaches have been proposed by researchers to overcome this problem; filler modification is one of them. The modification of filler is done by pretreating it with different suitable chemicals. The filler modification process can provide improved filler retention, fiber-filler bonding, and optical properties while maintaining or improving the physical strength properties of paper. Filler modification has been a crucial way to develop a paper with higher ash content which will be creating benefits to papermaking industry in the future. The different types of processes used by researchers worldwide to modify papermaking fillers such as kaolin, ground calcium carbonate, precipitated calcium carbonate, titanium dioxide, talc, and silica have been discussed in this paper. New developments in the area of nano-particles and organic fillers have also been briefed.

Keywords: Bonding, Clay, Fiber, Filler, Flocculation, GCC, Modification, PCC, Retention, Sizing, Talc, TiO₂

Introduction

Although the original reason for the use of filler was a question of economy, i.e. the expensive fiber material could be saved, it was soon established that fillers also improved the properties of the paper in many respects. Papermakers use filler to improve product quality with regard to appearance, sheet formation, smoothness, dimensional stability, optical properties like brightness and opacity, and printability of paper. Papermakers have been introducing fillers into paper through the wet-end of the machine which is a common practice for many years. However, with the conventional approach reduced retention with increased filler loading results in decreased machine performance, limiting the ability of papermakers to increase filler content. Fillers are also used in specific applications such as production of

functional papers like deodorant paper (Yokoo and Ogawa 1991; Tsuru et al. 1997), antimicrobial paper (Kim et al. 2005), flame retardant paper (Pearson 1985; Withiam 1989), and magnetic paper (Zakaria et al. 2004 a, b). The conventional and frequently used inorganic fillers are kaolin, talc, ground calcium carbonate (GCC), and precipitated calcium carbonate (PCC). The general physical properties of typical fillers used in papermaking are

shown in table 1. Limited use of titanium oxide and sodium magnesium aluminosilicate is also in practice for achieving some specific properties of paper. The use of inorganic fillers beyond a particular ash level has the following disadvantages:

- Replacement of fibers with inorganic fillers results in loss of paper strength. The paper strength reduces due to two factors; decrease

Table 1. General physical properties of typical fillers (Yoon 2007, Krogerus 1999, Gill 2005)

Parameter	Clay	Talc	GCC	PCC	TiO ₂	Silica, silicate
Formula	Al ₂ Si ₄ O ₁₀ (OH) ₈	Mg ₃ Si ₄ O ₁₀ (OH)	CaCO ₃	CaCO ₃	TiO ₂	CaSiO ₃
Crystal structure	Triclinic, hexagonal, platelets	Monoclinic, lamellae	Trigonic, rhombohedral	Scaleno-hedral, rhombohedral, aragonite	Spheroidal	-
Density, kg/dm ³	2.7	2.8	2.7	2.7	Anatase: 3.9 Rutile: 4.2	-
Refractive index	Hydrous: 1.57 Calcined: 1.60	1.57	1.59	1.59	Anatase: 2.55 Rutile: 2.76	Silica: 1.45 Silicate: 1.55
Scattering coefficient, cm ² /g	Hydrous: 1100-1200 Calcined: 2600-3000	-	1400-1700	2200-2700	4500-6000	-
Hardness (Mohs scale)	2.0-2.5	1.0-1.5	3.0	-	Rutile: 6.5	-
Brightness, %	Hydrous: 78-90 Calcined: 90-95	85-90	Chalk: 80-90 Marble: 85-95	96-100	98-100	93-99
Average particle size, μm	Hydrous: 0.2-2.0 Calcined: 0.7-1.5	1.5-10.0	0.7-3.0	0.3-3.0	0.2-0.4	0.1-3.0
Specific surface area (BET), m ² /g	Hydrous: 10-25 Calcined: 15-25	9-20	2-12	3-25	7-12	45-75
Einleher abrasion (mg of wire loss)	Hydrous: 1-6 Calcined: 15-30	3-5	3-15	2-9	10-30	5-13

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in number of fibers in the sheet, which reduces the number of fiber-fiber bonds, and reduced area of contact between the fibers.

- Calcium carbonate fillers are not suitable for the production of wood-containing or rosin-sized papers due to pulp darkening at alkaline pH and dissolution of calcium carbonate below neutral pH.
- Increase in filler content reduces the filler retention which results in higher solids content in the back water system. Increase in filler content reduces the hydrophobicity of paper thus increases the demand for sizing agents.
- Increase in filler content can increase abrasion and dusting under certain conditions.

As filler loading using conventional approach has many disadvantages, researchers have been studying several techniques to overcome or alleviate them. To increase the proportion of filler without sacrificing paper properties, various methods have been explored viz. use of wet-end chemicals (specifically dedicated dry strength additives), fiber lumen/ cell-wall loading with filler, use of nanostructured and organic fillers, and filler modification/ pretreatment. Filler modification technique is of significant potential for the improvement of the use of inorganic fillers in papermaking to a higher level. The modification techniques used by researchers involved the use of inorganic compounds, natural and synthetic polymers, surfactants, latex, and also hydrophobic, cationic, surface nanostructuring, and physical modification. The filler modification is also carried out by the mechanism based upon surface coating or encapsulation. The techniques used to modify different fillers are reviewed in the present paper.

Modification of Clay

Yoon and Deng (2006 a) modified clay using starch-fatty acid complex. They claimed an increase in tensile strength from 100 to 200% with treated clay as compared with untreated one.

As a specialty filler applied to the sheet mainly to increase scattering/opacity and to reduce ink print-through potential, calcined clay can be prepared from kaolin by applying a calcination process (Holik 2006). In the calcination process, the hydroxylation water is first driven off at temperatures of 500 to

700°C, and the particles begin fusing together into secondary particle aggregates and further agglomerates to tertiary particles at continued heating to 900 to 1000°C, and the end product is a large number of clay-air interfaces and relatively high internal pore volume, hence increased light scattering and opacifying properties (Laufmann 1998).

Withiam et al. (2000) patented the coating of TiO₂ particles on the surfaces of kaolin particles using alum as a pH-reducing agent for enhancing the light scattering and opacity properties of kaolin filler. The addition of alum to the reaction medium containing kaolin and TiO₂ reduced the system pH, and the surface potential of the TiO₂ particles was reversed to cationic, while the surface potential of kaolin retained its cationic charge, and TiO₂ particles were then deposited on the surfaces of kaolin to obtain composite filler with enhanced optical properties.

Starch has been found to be highly effective in filler modification, and it can be anchored on the filler surfaces or used to encapsulate the filler particles to enhance fiber-filler bonding and to improve the strength properties of filled papers (Kurrle 1996; Yan et al. 2005; Zhao et al. 2005; Yoon and Deng 2006 a; Yoon and Deng 2006 b; Yoon and Deng 2007; Yoon 2007; Zhao et al. 2008; Deng et al. 2008; Wang et al. 2008; Shen et al. 2008 c).

Under controlled conditions it is possible to coat starch on filler surfaces using the starch-gel-coating method to obtain modified fillers with enhanced bonding capacities. Yan et al. (2005) improved the starch-gel-coating method by cooking unmodified starch separately i.e. starch was initially cooked at 95°C for 30 min, and starch coating was conducted by mixing cooked starch with clay slurry, followed by drying and grinding treatments. This improved method of starch-gel-coating avoids the need to dewater the mixture before cooking, and it can also significantly improve the strength properties of the filled papers.

Dunham *et al.* (1999) reported that the differences in the chemical nature of the surface of the filler particle had a large impact on the adsorption property of the retention aid. He reported that the value of zeta potential is directly related to the surface chemistry of filler particle or is a result of surface modification.

Liu et al. (2003) have compared the flocculation of kaolin clay using modified and unmodified

montmorillonite in dynamic drainage jar. They found that cationically modified montmorillonite performed better in inducing clay flocculation compared with the unmodified montmorillonite, and the improved performance is related to the cationic charge density of the modified montmorillonite.

Alinec and Van de Van (1993) studied the effect of pH and polyethylenimine (PEI) on stability of clay suspensions. They found that the maximum rate of destabilization by pH control and PEI addition takes place when the net charge of clay particles is close to zero.

The effect of anionic polyacrylamide (APAM) and cationic polyacrylamide (CPAM) on the flocculation of kaolin suspensions have also been studied. Clark et al. (1990) found the similar behaviour of the APAM to that of CPAM of similar molar mass and charge density with respect to the subsidence rates; although the adsorption was considerably less and maximum values were reached at much lower dosages. Gill and Herrington (1988) found that the polymers floc size increases with increasing applied dosage of CPAM. Below a molar mass of 3.8×10^6 g mol⁻¹ the polymer forms smaller and more open flocs. Polymers in this lower molar mass range are less effective as flocculants as they do not bind or hold the clay particles as tightly as the polymers of higher molar mass.

Seppanen et al. (2000) studied the heteroflocculation of kaolin particles by mixing two kaolin suspensions; one stabilized by a cationic polymer and other by a highly charged and low molecular weight anionic polymer. They observed that the floc size and its degradation is independent of primary kaolin particle size. The floc size increased with increasing ionic strength.

Yoon and Deng (2006 b) modified clay with starch precipitate using ammonium sulfate as a precipitation agent. It has been found that clay aggregates with relatively large size can be formed after modification, which may be favorable to the strength development of the filled papers. This method of filler modification is less complicated as compared with starch-gel-coating.

Yoon and Deng (2004) flocculated and reflocculated clay suspensions. For initial flocculation, polyethylene oxide (PEO)/phenol formaldehyde (PFO) system and the high molecular weight and low charge density cationic

polyacrylamide (CPAM) produced larger flocs due to their bridging mechanism. They also found that the floc break-up that took place due to high shear forces can also be reflocculated with conventional or dual polymer retention aid system. Latter gives higher reflocculation than single CPAM system.

Modification of Calcium Carbonate Acid-Tolerant Properties of Calcium Carbonate Fillers

The calcium carbonate fillers have been used since 1980's in woodfree paper grades due to their good optical characteristics and low price. Their use in wood-containing papers is limited due to the negative effects of their alkalinity on high lignin content papers, primarily known as fiber alkaline darkening (Evans et al. 1991). The brightness reversion of mechanical pulp can undergo by 2 to 6 points on increasing pH from 4.5 to 9.5 (Mathur and Lasmarias 1991). The use of rosin size in alkaline papermaking has normally many limitations due to the saponification reaction, making use of calcium carbonate in rosin-sized papers be not industrially feasible (Shen et al. 2007).

The extensive work has been carried out on the modification of both ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) fillers. The efforts have also been made to make them suitable for acid papermaking, improve their retention and decrease negative effect on paper strength.

Starch derivatives can be used in filler modification to improve the acid-resistant properties of calcium carbonate fillers under controlled conditions. Lambert and Lowes (1975) proposed a method of filler modification using a mixture of anionic starch derivative and cationic starch derivative, and the modifiers coagulated or flocculated to coat the particles of filler and caused them to agglomerate. The flocculent filler was claimed to have improved retention in a paper web. More importantly, the filler modification enables calcium carbonate (e.g., chalk and whiting) to be employed as a mineral filler, because the coagulated polymer protects the mineral from the acidic alum in the paper stock.

Wu (1997 a) has shown that the acid-resistant properties of calcium carbonate fillers can be enhanced with a

weak base and a weak acid as modifiers. Alum salt can be used in the modification of calcium carbonate fillers to prepare modified fillers in slurry form, and their acid-resistant properties can be enhanced (Wu 1997 b). Preferred aluminum salts have been claimed to be aluminum sulfate, aluminum chloride, and polyaluminum chloride. After modification, the pH values of filler slurries can be decreased to a certain degree. Also, the use of aluminum salt in combination with anionic salt such as sodium hexametaphosphate (SHMP) in filler modification can also increase the acid-resistant properties of calcium carbonate fillers (Wu 1997 c). Modification of calcium carbonate fillers with a calcium-chelating agent and a weak acid can strikingly improve their acid-tolerant properties (Passaretti 1991), and the modified fillers in the slurry form can be used in acidic or pseudo-neutral papermaking. The mechanism is generally based on the formation of a highly buffered system.

Drummond (2001) patented a method of modification of calcium carbonate filler using an acid-stabilizer of a water-soluble calcium salt, a weak acid, a chelating agent, a weak acid capable of chelating calcium ion, or a mixture thereof under a pH range of 6-7. In this method, an aqueous slurry of calcium carbonate was carbonated to form precipitated calcium carbonate filler and thereafter used in the production of acid paper.

Snowden et al. (1998) patented a method of filler modification using a sodium aluminate and one or more weak acids, and high-solids aqueous acid-resistant calcium carbonate suspensions were claimed to be made at controlled conditions using these modifiers (Rodriguez and Fortier 1999).

Snowden et al. (2000) proposed the modification of calcium carbonate fillers with sodium silicate and a weak acid or aluminum sulfate to obtain modified filler suspension with acid-resistant properties, and it has been found that the inclusion of a silicate and either at least one weak acid or alum confers a higher degree of stability and acid resistance for calcium carbonate in the presence of fiber slurry. Shen et al. (2008 a) have also reported that modification of PCC filler using combination of chemicals can decrease the dissolution of filler to a certain degree, and the dissolution-inhibiting effect of sodium silicate/phosphoric

acid/SHMP is the most striking.

Modification of calcium carbonate fillers with phosphoric acid has also been extensively investigated by researchers (Pang et al. 1998, 2001, 2003; Pang and Englezos 2003). It has been shown that the dissolution of calcium carbonate fillers in water can be decreased with the addition of phosphoric acid as a modifier. Recently, the effectiveness of SHMP and phosphoric acid used as modifiers of a papermaking grade PCC filler has also been further confirmed (Shen et al. 2008 b).

The idea of silica coating used for modification of calcium carbonate fillers has been reported and the modified fillers can be easily stored or conveyed in the form of dry powder, which may facilitate their use in paper mills. Tokarz et al. (1991) have shown that the previously prepared calcium carbonate slurries can be intermixed simultaneously with a solution of a zinc compound and a solution of a silica-containing substance under controlled conditions to obtain modified calcium carbonate fillers with enhanced acid-resistant properties, and the preferred silica-containing substance and zinc compound may be sodium silicate and zinc chloride respectively. Chapnerkar et al. (1992) have shown that the use of sodium silicate, zinc chloride, and carbon dioxide as modifiers can strikingly improve the acid-resistant properties of calcium carbonate fillers, while the amount of costly zinc chloride can be decreased.

Comparison of several different methods for stabilization of PCC filler against dissolution under acidic papermaking conditions has been reported by Jaakkola and Mannu (2001). It has been shown that the modified PCC can exhibit better acid-resistant properties as compared with the unmodified PCC.

Mill experiences have proved that the modified PCC filler can be effectively used to produce wood-containing paper grades, and papermaking system pH can be maintained at 7.2 to 7.3 (Ain and Laleg 1997).

Modification of Ground Calcium Carbonate (GCC)

GCC filler is available commercially in a wide range of particle size distribution. Despite of using GCC of around 20% particles less than 2 micron, papermakers are now using GCC having 60-70% particles less than 2 micron in receipt of enhanced optical properties of paper. Though, there are

some limitations in its use such as lower retention and strength properties, use of such type of GCC has increased the requirement of its modification to retain it within the fiber matrix and to decrease its negative effect on strength properties of paper.

Several advantages have been reported with the use modified GCC filler. Holik (2006) has reported that the modified GCC filler can exhibit extraordinarily high specific surface area, providing high brightness, easy gloss development, and good printability in offset and rotogravure printing.

Lattaud et al. (2006) reported that, using the drop by drop addition of zinc chloride solution into the calcium carbonate filler suspension, the surfaces of filler were coated by zinc carbonate, and the refractive index of the filler was enhanced.

Shiro et al. (1988) chosen specific particle compositions consisting of particles meeting the requirements of i) the zeta potential is negative, ii) the particle size is in between 10 to 150 μm , and iii) the specific surface area is within the range shown by the following formula;

$S > 100,000 / D \rho$; where S is the specific surface area (cm^2/g), D is the average particle size of the composition (μm), and ρ is the specific gravity of the composition. These particle compositions were added to heavy natural GCC fillers using 100 weight parts of heavy natural GCC and at least 0.1 weight parts of chosen particles. They claimed that the particles can strikingly decrease the abrasiveness of fillers, and wire abrasion associated with the use of fillers can, therefore, be reduced.

Fuente et al. (2005) studied that low PEI doses induce a fast flocculation of GCC filler through bridge formation whereas high PEI doses induce a slow flocculation by charge neutralization. They observed that the flocculation mechanism of GCC suspensions induced by high molecular weight modified PEI depends on the polymer dosage.

The effect of shearing forces and flocculant overdose on GCC flocculation and the floc properties was studied by Blanco et al. (2005). They suggested to use flocculant dose based upon zeta potential rather than streaming current. An increase in the PAM dosage would first increase the floc size, but a further increase in the dosage after getting maximum floc size mainly affect floc strength due to an increase of bonding.

Park and Shin (1987) treated GCC filler with high molecular weight CPAM, low molecular weight CPAM, and cationic starch. The initial floc sizes of high molecular weight CPAM pretreated fillers were larger than those of any other pretreated fillers, and low molecular weight CPAM pretreated fillers were the smallest. Cationic starch pretreated fillers were the weakest and high molecular weight CPAM pretreated fillers were the strongest under shear conditions. The retention of pretreated filler was much higher than untreated one. The preflocculation of filler increased tensile index, tear index, burst index, and folding properties, and the strength properties provided by preflocculation were higher when no retention aids were added. In optical properties, high molecular weight CPAM pretreatment gave the poorest opacity, but low molecular weight CPAM and cationic starch pretreatments were good or not significantly different compared to no pretreatment.

Negro et al. (2005) used the phenolic resin/PEO for the flocculation of GCC filler. A plant scale study of GCC flocculation using starch based flocculant shows increased filler retention, strength, and improved formation, opacity, and machine runnability (Mabee and Harvey 2000).

Modification of Precipitated Calcium Carbonate

Zhao et al. (2005) modified PCC filler with raw starch and modified starch using the combined steps of operations including mixing, dewatering, grinding, and aggregate-breaking-up. It has been shown that filler modification using the starch-gel-coating method can strikingly improve the strength properties of filled papers, including tensile, tearing, and folding endurance of paper, and the use of different types of starches can almost give the same physical and optical properties of filled papers.

Laleg (2005) patented a method for the modification of PCC filler using swollen starch-latex compositions prepared in the presence or absence of co-additives. It was shown that swollen starch-latex compositions can be prepared in a batch or jet cooker, or by mixing with hot water under controlled conditions (temperature, pH, shear, mixing time) in order to make the starch granules swell sufficiently to improve their properties as a filler additive but avoiding excess swelling leading to their rupture, and the swollen starch-

latex composition can then be rapidly mixed with the filler slurry, preferably in a static mixer, and added to the papermaking furnish at a point prior to the headbox of the paper machine. It has also been shown that the use of swollen starch-latex compositions can allow the papermakers to increase the filler content in the paper without sacrificing dry strength properties.

Modification of PCC filler with starch-soap complex was patented by Kurrle (1996). Raw or modified starch was cooked using the conventional cooking method, and the starch solution and the soap component comprising sodium or potassium salts of fatty acids were physically mixed, and the mixture was further incorporated into the filler slurry at controlled conditions to induce the precipitation of complexed starch products onto the filler surfaces. The improvement in sizing efficiency and strength properties of the filled papers has been reported.

Gill (1992) treated PCC filler with 0.1-10 (weight % based on dry weight of filler) of a cationic polymer containing a dimer. The use of this modified filler resulted in improved opacity and filler retention, better drainage, and reduced need for sizing agents.

Shen et al. (2008 d) modified PCC filler using chitosan, acetic acid, and hydroxide. Chitosan was reported to be encapsulated on filler surfaces via alkali precipitation, and filler modification strikingly improved the strength properties of the filled papers.

Vanerek *et al.* (2000) reported that the charge of PCC, either positive or negative, depended on its concentration and the purity of the water. From their experiment with water of different degrees of purity (deionized, distilled, doubly distilled), when the concentration and the total surface area were low, the amount of impurities per particle was much larger, thus these impurities significantly affected the surface charge. However, in neither case the charge was strong enough to prevent aggregation of pigment particles.

In the presence of cationic polyelectrolytes, their behavior depended on the type of adsorbed polymers. Highly charged PEI stabilized PCC due to increased electrostatic repulsion which can be explained satisfactorily on the basis of the classical DLVO theory of colloid stability. Polyacrylamide (PAM), on the other hand, flocculated PCC by a bridging mechanism. They also showed that introduction of PEI into the

suspension promotes deposition driven by electrostatic interaction, provided that PEI concentration is not too large. With an excess of PEI, both the fiber and pigment become positive and repel each other. On the contrary, introduction of cationic PAM causes flocculation of the pigment and its deposition on fibers, regardless of the PAM dosage, indicating that electrostatic interaction was not a dominant effect. They concluded that PAM is more effective as a retention aid due to its flocculation ability and the bridging mechanism alone. However, this conclusion was not sufficient to account for the observed interaction between pigment particle and fiber at high PAM dosage.

The influence of PCC characteristics on the flocculation process and floc structure was investigated in the presence of a linear, high molecular weight, CPAM of high charge density by Antunes et al. (2008). They observed that the initial particle size distribution and zeta potential of the filler are important parameters to define the optimum flocculant concentration.

Gaudreault et al. (2009) flocculated PCC filler using eleven different polymers. PEO/cofactor gave faster flocculation rate and larger flocs. The APAM gave strong flocs due to strong binding to PCC. PAM-glyoxal, CPAM, and polyamine cause little or no flocculation because they act as dispersants, similar to PEI. Lu and Pelton (2005) showed the opposite results. They observed that the preformed PEO/cofactor (water-borne phenolic polymer) complexes are not effective flocculants. There is an optimum ratio of PEO to cofactor, whereas the greater the overall PEO concentration, the better the flocculation. They also studied the effect of molecular weight and structure of cofactor on flocculation.

To increase the bonding efficiency of calcium carbonate with fibers, Koper *et al.* (1999) made the poly(propylene imine) dendrimer which was more highly charged than PEI. They reported that the deposition of dendrimer-coated calcium carbonate particle followed Langmuir kinetics as did uncoated or PEI-coated particles. Measured deposition rate constants were twice as large as observed with PEI on calcium carbonate particles. The deposition efficiency increased with particle size and the detachment rate constants were nearly constant. From this they concluded that dendrimers were a somewhat better retention aid than PEI.

Jaakkola and Mannu (2003) have reported that zinc chloride/sodium trisilicate treated PCC filler can result in a slightly better inkjet printability of paper compared with the other fillers.

Modification of Talcum Powder (Talc)

Though talc has been a quality filler mainly available in Asia Pacific, a scanty research has been carried out on its modification. Reason might be that the retention of talc is quite high and it has less negative effect on strength properties than calcium carbonate fillers. Some research has been carried out on its modification to increase its retention and decrease negative effect on strength properties.

Shi (2006) patented a method for improving the optical properties of talc by filler modification with titanium salt and titanium coordination agent. It has been found that by control of dosage of modifiers, reaction temperature, pH, stirring rate, and hydrolysis rate, modified filler particles can be obtained after filtration, washing, drying, and calcination treatments. The method is based on coating of titanium oxide films on the filler surfaces, and the superior optical properties of titanium oxide can be conferred to unmodified talc. The modified talc can potentially be used to substitute the expensive titanium dioxide, conferring significantly enhanced optical properties to papers.

Zhang et al. (2004) modified talc powder using $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} / \text{P}_2\text{O}_5$. It has been shown that the use of $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} / \text{P}_2\text{O}_5$ can improve the retention of talc in the filled papers, and filler retention can be improved by around 30% under the controlled experimental conditions.

Ibrahim et al. (2009) reported that the use of cationic dodecyltrimethyl ammonium bromide (CDTAB) in modification of Egyptian talc enhanced the bonding capacity of talc, and paper strength was strikingly improved. When modified with CDTAB, the charge characteristic of talc may be changed to a certain degree, which is favorable to fiber-filler bonding.

Park and Shin (1987) treated talc filler with high and low molecular weight CPAM, and cationic starch. The initial floc sizes of high molecular weight CPAM pretreated fillers were larger than those of any other pretreated fillers, and low molecular weight CPAM pretreated fillers were the smallest. Cationic starch pretreated fillers were the weakest and high

molecular weight CPAM pretreated fillers were the strongest under shear conditions. The retention of pretreated filler was much higher than untreated one. The preflocculation of filler increased strength properties of paper. High molecular weight CPAM pretreatment gave the poorest opacity, but low molecular weight CPAM and cationic starch pretreatments were good or not significantly different compared to no pretreatment.

Modification of Titanium Dioxide (TiO_2)

Thiele and Sinnott (2006) treated the TiO_2 filler surface using amino organosilane. They claimed that the surface treated TiO_2 filler can increase FPAR and tensile strength of paper by 20 and 30% respectively as compared to the paper made with conventional TiO_2 .

Lee and Cho (2007) showed that when TiO_2 is modified with Ag nano-colloidal solution using hybridization technique, it can be used in functional papers for the purpose of antimicrobial and photocatalytic deodorization functions.

Modification of Silica

Very few researchers have worked on the modification of silica. Peng and Williams (1994) have reported the modification of silica particles with latex dispersions. They showed the effect of agitation intensity, flocculant dosage, and solids concentrations on the floc formation and break-up in a stirred tank. They developed a relationship between the above parameters and demonstrated that the use of on-line measurement provides a powerful means of quantifying the behavior of a friable dispersion when subjected to shear.

Other Approaches

Other techniques used to maintain the strength properties of paper at increased filler content is lumen loading method that held filler mainly within the lumens and/or cell-wall of the fibers. Middleton and Scallan (1985) used excess of TiO_2 , stirred it with pulp slurry and transferred into the fiber lumen. This technique was the physical transfer of filler into lumen through excessive shear force and is applicable for only longer fibers and smaller size fillers. Many other investigators have done the same study using PCC in place of TiO_2 . Several other studies on cell wall loading were

also reported by various research groups in the U.S.A. and Japan. Usually the approach has been to saturate pulp fibers with a soluble calcium salt and to precipitate calcium as carbonate by adding another soluble salt which contains carbonate ions. The salts used can be for example calcium chloride and sodium carbonate (Allan *et al.*, 1992). Chauhan *et al.* (2007) precipitated sodium aluminosilicate in-situ as filler inside the fibers. They have shown the marginal increase in strength properties of paper made with this technique as compared with direct loading of filler.

In addition to the traditional fillers having dimension in micrometers, the use of nanofillers in papermaking has also been a very hot topic (Koivunen *et al.* 2009). In addition to developments of nano-structured fillers for papermaking via certain chemical reactions or routes, the surface nano-structuring of fillers by filler modification can also be feasible. Goldhalm and Drexler (2008) have shown that, under certain conditions, organic nano-particles can be adhered to the surface of inorganic filler particles to obtain nano-hybrid filler particles, and such a filler modification method can potentially improve the surface properties of paper. The nano-hybrid particles may be prepared for example by dissolving the polymer or a copolymer of maleic anhydride with a vinyl monomer in water, adding a RNH₂ compound, R being H, alkyl with 1-18 carbon atoms or aryl and heating the resultant mixture in the presence of filler particles to make the imides. The polymeric particles will settle down on the filler particles. This method of filler modification is very interesting, which may provide papermakers with new insights into the filler modification technology as well as the trouble-shooting strategies for papermaking wet-end applications.

Conclusions

The urge of enhanced filler content in paper and paperboards is ever increasing to desire several benefits viz. optical and functional properties of paper, increased production and decreased cost. Due to limitation of decreased strength properties of paper with increased filler content, papermakers are continuously searching for new methods which could be used to increase filler content in paper without adversely affecting its strength. The filler modification process can provide improved filler

retention, bonding capabilities, and higher optical properties in paper. Papermakers can select an appropriate process for the modification of kaolin, GCC, or PCC depending upon the techno-economic considerations. Further work on the modification mechanism of talc and TiO₂ may also provide interesting results for their increased use in papermaking.

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