

MODIFICATION OF PAPERMAKING GRADE FILLERS: A BRIEF REVIEW

Jing Shen,^a Zhanqian Song,^b Xueren Qian,^{a*} and Wenxia Liu^c

The use of fillers in paper products can provide cost and energy savings, improved paper properties, increased productivities, and specifically desired paper functionalities. There are many problems associated with the use of fillers, such as unsuitability of calcium carbonate fillers in acid papermaking, negative effects of filler loading on paper strength, sizing, and retention, and tendencies of fillers to cause abrasion and dusting. In order to solve these problems and to make better use of fillers, many methods have been proposed, among which filler modification has been a hot topic. The available technologies of filler modification mainly include modification with inorganic substances, modification with natural polymers or their derivatives, modification with water-soluble synthetic polymers, modification with surfactants, modification with polymer latexes, hydrophobic modification, cationic modification, surface nano-structuring, physical modification by compressing, calcination or grinding, and modification for use in functional papers. The methods of filler modification can provide improved acid tolerant and optical properties of fillers, enhanced fiber-filler bonding, improved filler retention and filler sizabilities, alleviated filler abrasiveness, improved filler dispersability, and functionalization of filled papers. Filler modification has been an indispensable way to accelerate the development of high filler technology in papermaking, which is likely to create additional benefits to papermaking industry in the future.

Keywords: Fillers; Papermaking; Filler modification; Acid tolerant properties; Fiber-filler bonding; Filler retention; Sizability; High filler technology

*Contact information: a: Laboratory of Pulp and Paper Engineering Subject, Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Material Science and Engineering College, Northeast Forestry University, Harbin 150040, China; b: Institute of Chemical Industry of Forest Products, CAF; Key and Open Lab. on Forest Chemical Engineering, SAF, Nanjing 210042, China; c: Key Laboratory of Paper Science & Technology of Ministry of Education, Shandong Institute of Light Industry, University Park of Science and Technology, Jinan 250353, China. *Corresponding author: qianxueren@yahoo.com.cn*

INTRODUCTION

Fillers are usually used in papermaking to provide cost and energy savings, and to improve optical properties, sheet formation, printability (smoothness, ink adsorption and show through), dimensional stability, and appearance of papers. Also, in specific applications, fillers can be used in the production of functional papers such as deodorant paper (Yokoo and Ogawa 1991; Tsuru et al. 1997), antimicrobial paper (Kim et al. 2005), flame retardant papers (Pearson 1985; Withiam 1989), and magnetic paper (Zakaria et al. 2004a,b). For many paper grades, fillers are the second most important material of paper

stock, in terms of the amount added, and their consumption in papermaking is enormous. Fillers can generally be divided into two groups, inorganic fillers and organic fillers. The dominant fillers used in papermaking are inorganic fillers. Organic fillers are in two main types, hollow micro-spheres and porous fillers, and they are suitable only for special applications because of high price (Mollaahmad 2008). In addition to the traditional fillers in micrometers, the use of nanofillers in papermaking has been a very hot topic (Koivunen et al. 2009).

The conventional and frequently used inorganic fillers are kaolin clay, natural ground calcium carbonate, precipitated calcium carbonate, and talc. Another noticeable material is titanium oxide; however, it is applied less often due to its high price. It is generally considered that the use of inorganic fillers, especially at high loading levels, has the following disadvantages or limitations:

- Conventional low-cost and high-performance calcium carbonate fillers are not suitable for use in wood-containing or rosin-sized papers due to pulp darkening at alkaline pH and dissolution of calcium carbonate below pH 7.
- Paper strength is inevitably reduced by replacement of the fibers by inorganic fillers, not only because there are less fibers in the sheet, which reduces the number of fiber-fiber bonds in the sheet, but also because the presence of the filler reduces the area of contact between the remaining fibers.
- Increased loading levels of inorganic fillers have negative effects on filler retention, resulting in higher solids content of the circulating system.
- Increased loading levels of inorganic fillers have negative effects on sizing efficiency of the filled papers, increasing the demand for sizing agents.
- Use of inorganic fillers can cause abrasion and dusting under certain conditions.
- Dispersing of fillers in papermaking systems needs to be improved under certain conditions.
- Optical properties of fillers cannot well meet the requirements of paper and paperboard properties under certain conditions.

In order to overcome or alleviate the above disadvantages or limitations, many methods have been proposed, among which filler modification for improving the use of inorganic fillers in papermaking has been a hot topic. Filler modification is of significant potential for the improvement of the use of inorganic fillers in papermaking, and it is highly favorable to the development of high filler technology. Also, for the functionalization of papermaking grade fillers, filler modification is one of the indispensable ways to confer specifically desired functional properties to filler-containing papers.

MODIFICATION WITH INORGANIC SUBSTANCES

Inorganic compounds have been extensively used for modification of papermaking grade fillers to enhance the acid tolerant, optical, retention, and drainage properties.

Modification for Enhanced Acid-Tolerant Properties

Calcium carbonate fillers have been widely used in woodfree paper grades since the 1980's because of their good optical properties and low prices. In woodfree paper grades produced from chemical pulps, the alkaline nature of calcium carbonate is an additional benefit because it creates a stable buffered system and provides some paper strength improvement (Evans and Slozer 2003). However, the alkalinity of calcium carbonate fillers has limited their use in wood-containing papers due to the negative effects of alkalinity on high-lignin-content papers, primarily known as fiber alkaline darkening (Evans et al. 1991). Fiber alkaline darkening is assumed to be caused by quinine chromophores originating from the lignin components in mechanical pulps (Evans et al. 1993). Lignin is very pH-sensitive, and the higher the pH rises, the darker the lignin gets. The brightness of mechanical pulp can undergo reversion by 2 to 6 points, as the pH of pulp is raised from 4.5 to 9.5 (Mathur and Lasmarias 1991). Fiber alkaline darkening is most problematic for production of paper grades made from virgin mechanical pulps, e.g. SGW, PGW, TMP, and RMP (Evans et al. 2005). Also, the use of calcium carbonate fillers in neutral-to-alkaline papermaking may cause further problems associated with pitch deposits (Phipps 2002).

Traditionally, cost-efficient rosin sizes are widely used in acidic and pseudo-neutral papermaking to render the papers resistant to liquid penetration. However, the use of rosin sizes in alkaline papermaking normally has many limitations due to the saponification reaction, making the use of calcium carbonate in rosin-sized papers also not industrially feasible (Shen et al. 2007). Titanium dioxide and calcined clay can be used as filler materials in the preparation of neutral to weakly acidic papers, and the optical properties can be strikingly improved. However, these materials have the disadvantages of being very expensive, resulting in higher manufacturing costs. Talc fillers can also be effectively used in the preparation of neutral to weakly acidic papers, and the price of talc is generally equivalent to calcium carbonate, but calcium carbonate is much superior to talc in many respects such as the optical properties of the filled papers.

The conversion from traditional acid to neutral/alkaline papermaking practices is still challenging (Chabot et al. 2008), and it depends on many factors such as paper grade, pulp furnish, paper mill configuration, and also on the method used to control pH (Evans et al. 1991; Ain and Laleg 1997). Acidic or pseudo-neutral papermaking is still needed for the production of many paper grades. Therefore, there is a need to improve the acid-tolerant properties of calcium carbonate fillers and enable their use in acid or pseudo-neutral papermaking.

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. A calcium-chelating agent, such as sodium hexametaphosphate, is added to the calcium carbonate slurry; it chelates with the calcium ion that is on the surface of calcium carbonate and in solution. When a weak acid, such as phosphoric acid, is added, it forms $\text{Ca}(\text{H}_2\text{PO}_4)_2$, but the pH of the solution stays acidic due to the H^+ formed by the hydrolysis of the $(\text{NaPO}_3)_6$. As more CaCO_3 dissolves, the calcium ion concentration

increases to the point where the system reaches equilibrium and no more CaCO_3 can disassociate. The equilibrium pH is acidic and is dependant upon the amount of sodium hexametaphosphate and phosphoric acid added. Mill experiences of the use of a modified precipitated calcium carbonate filler have proved that the modified 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). Recently, the effectiveness of sodium hexametaphosphate and phosphoric acid used as modifiers of a papermaking grade precipitated calcium carbonate filler has also been further confirmed (Shen et al. 2008b). Wu (1997a) has shown that the acid-resistant properties of calcium carbonate fillers can be enhanced with a weak base and a weak acid as modifiers, where either the weak base or the weak acid is derived from an organic polymeric acid, and the preferred combinations of modifiers are sodium hexametaphosphate/polyacrylic acid, sodium hexametaphosphate/polymaleic acid, and sodium polyacrylate/phosphoric acid.

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 1997b). 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 in filler modification can also increase the acid-resistant properties of calcium carbonate fillers (Wu 1997c).

Drummond (2001) patented a method of filler modification 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. The acid-stabilizer has been claimed to be present in an amount sufficient to provide aqueous calcium carbonate slurry having an increased calcium ion concentration and an acidic pH. 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 able made at controlled conditions using these modifiers (Rodriguez and Fortier 1999).

Modification of calcium carbonate fillers with phosphoric acid has 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. Also, the preferred dosage of phosphoric acid was found to be 0.2g/g, based on the weight of calcium carbonate. Pang (2001) has also shown that the inhibition mechanism involves the formation of Ca-P phases that precipitate on the filler surfaces, acting as barriers and blocking the dissolution sites.

Modification of calcium carbonate fillers with sodium silicate and a weak acid or aluminum sulfate to obtain modified filler suspension with acid-resistant properties has been proposed, 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 (Snowden et al. 2000). Also, Shen et al. (2008a) showed that modification of a papermaking grade of precipitated calcium carbonate filler using sodium silicate/aluminum sulfate, sodium silicate/aluminum chloride, sodium silicate/phosphoric acid, sodium silicate/phosphoric acid/sodium hexametaphosphate, or

sodium silicate/phosphoric acid/sodium polyacrylate can decrease the dissolution of filler to a certain degree, and the dissolution-inhibiting effect of sodium silicate/phosphoric acid/sodium hexametaphosphate is the most striking.

The idea of silica coating used for modification of calcium carbonate fillers has been reported in the literature (Tokarz et al. 1991; Chapnerkar et al. 1992), 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 or zinc chloride. 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 papermaking grade PCC against dissolution under acidic papermaking conditions has been reported in the literature (Jaakkola and Mannu 2001). It has been shown that, for five kinds of modified fillers including $Mg_2CO_3(OH)_2$ /phosphoric acid/polyacrylic acid treated PCC (method A), sodium hexametaphosphate/phosphoric acid treated PCC (method B), zinc chloride/sodium trisilicate treated PCC (method C), sodium hexametaphosphate/calcium nitrate treated PCC (method D), and zinc chloride treated PCC (method E), they can exhibit better acid-resistant properties as compared with the unmodified PCC. Method A and B can give the best stability regarding pH in the water suspension of PCC without the presence of wood-containing pulp, and method A, B, and C can give the best resistance against the dissolving effect of aluminum ions in the aluminum sulfate tests. Also, smoothening of the coarse surface structure can be observed from SEM images with the use of method C in filler modification. Jaakkola and Mannu (2003) have also shown that zinc chloride/sodium trisilicate treated PCC filler can result in a slightly better ink-jet printability of the paper compared with the other fillers.

The industrial applications of acid-tolerant calcium carbonate fillers are already available around the world. Further scientific investigations such as development of more cost-effective modification methods for improved acid-tolerant properties, and elimination or avoiding of the negative effects on papermaking process, are still necessary.

Modification for Improved Optical Properties

Under certain circumstances the optical properties of papermaking grade fillers can be improved by filler modification, and the mechanism is usually based on surface coating or encapsulation. Withiam et al. (2000) patented the coating of titanium dioxide 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 titanium dioxide reduced the system pH, and the surface potential of the titanium dioxide particles was reversed to cationic, while the surface potential of kaolin retained its cationic charge, and titanium dioxide particles

was then deposited on the surfaces of kaolin to obtain composite filler with enhanced optical properties. Shi (2006) patented a method for the 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. 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 calcium carbonate filler were coated by zinc carbonate, and the refractive index of the filler was enhanced.

Modification for Alleviated Abrasion

Paper machine wire abrasion can easily be caused by the use of inorganic fillers. The abrasion potential of fillers is influenced by particle structure, particle fineness, and particle hardness (Holik 2006). Relatively coarse platy fillers tend to be less abrasive than non-platy ones of similar size (Holik 2006). It is not only the general quality of a filler, but the interaction of the filler with, in the first place, the stationary drainage elements, which determines the level of wire abrasion, and the general layout of the wire section, the types of wires used, as well as the overall operating conditions have a great influence on how long the wire will last (Laufmann 1998). Shiro et al. (1988) have shown that the addition of specifically chosen particle compositions to heavy natural ground calcium carbonate fillers can strikingly decrease the abrasiveness of fillers, and wire abrasion associated with the use of fillers can therefore be reduced.

Modification for Improved Filler Retention

Filler retention (Hubbe 1984; Cho et al. 2001; Nystrom and Rosenholm 2005; Antunes et al. 2008) is a very important issue in the field of papermaking wet end chemistry. The retention of papermaking grade fillers can be improved by filler modification. 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 as high as 29.76% under the controlled experimental conditions.

MODIFICATION WITH NATURAL POLYMERS OR THEIR DERIVATIVES

Natural polymers and their derivatives can be used in modification of papermaking grade inorganic fillers to enhance their bonding capacities with pulp fibers, to improve the strength properties of filled papers, or to improve filler retention.

Modification with Starch or Starch Derivatives

Both starch and starch derivatives can be used in filler modification, and the relevant methods tend to be well-suited for industrial applications due to the easy availability and low cost of these polymeric materials.

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 2006a; Yoon and Deng 2006b; Yoon and Deng 2007; Yoon 2007; Zhao et al. 2008; Deng et al. 2008; Wang et al. 2008; Shen et al. 2008c).

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. Zhao et al. (2005) modified papermaking grade precipitated calcium carbonate filler with raw starch and modified starch using the combined steps of operations including mixing, dewatering, grinding, and aggregate-breaking-up. When the mixture of starch powder and filler suspension was cooked at 90°C for 3 h, starch was reported to swell to form a partially cross linked gel, which coated on the filler surfaces and bound the filler particles together. 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 strengths, and the use of different types of starches can almost give the same physical and optical properties of filled papers. Also, the dissolution of coated starch gel from the filler particles during the papermaking process has found to be not serious. 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, as shown from the reports of the authors.

When using ammonium sulfate as a precipitation agent, the coating of filler surfaces with starch precipitate can significantly improve the strength properties of the filled papers, and this method of filler modification is less complicated as compared with starch-gel-coating. Yoon and Deng (2006a) modified clay with starch precipitate using ammonium sulfate as a precipitation agent; i.e., the cooked clay-starch mixture was poured into ammonium sulfate solution under stirring to induce the precipitation of starch on the filler surfaces to obtain clay-starch composites. 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.

Modification of calcium carbonate fillers with starch-soap complex was patented by Kurrle (1996). Raw starch 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. This method of filler modification has been shown to be beneficial to improvement of sizing efficiency of the filled papers, and the strength properties can also be enhanced, allowing high filler loading levels.

Yoon and Deng (2006b) reported a starch-fatty acid complex formation method similar to that of Kurrle (1996) for the encapsulation modification of clay, and the modifiers used were raw starch, palmitic acid, potassium hydroxide, and hydrogen chloride. It has been shown that the modification of clay with starch-fatty acid complex significantly improved its bonding capacity and strength properties of the filled papers, and the water-repellant properties of the filled papers can also be enhanced (Yoon and Deng 2008). Wang et al. (2008) modified precipitated calcium carbonate fillers using such a complex formation method with raw starch, stearic acid, sodium hydroxide, and hydrogen chloride. Shen et al. (2008b) modified the method of complex formation using aluminum sulfate as a precipitation agent, and the modifiers used were raw starch, sodium oleate, and aluminum sulfate.

Laleg (2005) patented a method for filler modification 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 (i.e., temperature, pH, mixing, 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 of the papers without sacrificing dry strength properties or increasing the amount, and hence the cost, of the retention aid added.

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 cause 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 whiting) to be employed as a mineral filler, because the coagulated polymer protects the mineral from the acidic alum in the paper stock. Harvey and Klem (1989) patented the use of cationic starch in filler modification to obtain preflocculated filler of controlled particle size to improve the papermaking process.

Modification with Cellulose or Cellulose Derivatives

Cellulose is an important component of pulp, and its compatibility with pulp fibers is surely very good, as strong hydrogen bonds can be formed under typical conditions. Therefore, if the filler surfaces are encapsulated with cellulose, the resulting particulate materials are theoretically excellent fillers in terms of their bonding capacities. In the literature, the encapsulation modification of papermaking grade fillers with water-insoluble cellulose has been reported only quite recently (Myllymäki et al. 2006; Yoon 2007; Nelson and Deng 2008).

Myllymäki et al. (2006) have shown that, under specifically controlled conditions, when filler particles are dispersed into clear solution of cellulose prepared by dissolving

microcrystalline cellulose into an ionic liquid solvent, the addition of a specific non-solvent miscible with the ionic liquid solvent into the solution under agitation can initiate the formation of cellulose-encapsulated fillers. As shown from the patent descriptions, by use of such a modification method, both highly organic end products with exceptional heat capacities as well as cheap high-filler end products can be manufactured. This modification method was further claimed to be favorable to the improvement of strength properties of the filled papers. The use of various pulps as the cellulose sources in the encapsulation modification of fillers is also feasible, and the fillers can be organically encapsulated with enhanced bonding capacities (Yoon 2007; Nelson and Deng 2008). For filler modification using water-insoluble cellulose, the high cost of ionic liquids should be considered, and the industrial application of such a filler modification technology is possibly feasible and promising if highly effective recovery of ionic liquids can be achieved.

Cellulose derivatives can be used to modify fillers. Wannstrom et al. (2005) patented a method of filler modification using one of the specific cellulose derivatives having a degree of substitution of net ionic groups up to about 0.65. They have shown that modified filler suspensions can be obtained by mixing filler with cellulose derivative (such as carboxymethyl celluloses and quaternary ammonium carboxymethyl celluloses) in water, and the modification or pretreatment of filler with cellulose derivative provides a convenient way of separately processing only one component of the cellulose suspension to produce a modified filler, and the filler modification can be an important way to minimize the negative effects of filler loading on sizing.

Modification with Chitin or Chitosan

The molecule structures of chitin and chitosan are very similar to that of cellulose, and their use in modification of papermaking grade fillers can improve the bonding capacities of fillers, and strength properties of the filled papers can then be enhanced. Myllymäki et al. (2006) have shown that, by use of an ionic liquid and a non-solvent, chitin can be encapsulated on the filler surfaces to obtain organically modified fillers with enhanced bonding capacities. Shen et al. (2008d) modified papermaking grade precipitated calcium carbonate 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.

Modification with Xanthan Gum or Anionic Guar Gum

Xanthan gum and anionic guar gum can be used in filler modification to provide improved strength of the filled papers. Fairchild (1995) showed that filler modification carried out by mixing of one of the fillers with xanthan gum or anionic guar gum in water can improve the strength properties of the filled papers at very low modifier dosages of 0.05% to 0.5%, based on the filler weight, and increasing the temperature at which the filler modification is carried out can provide additional strength improvement. The positive effect of increased temperature on paper strength may be due to enhanced modifier adsorption on the filler surfaces.

MODIFICATION WITH WATER-SOLUBLE SYNTHETIC POLYMERS

Water-soluble synthetic polymers can be used in filler modification to provide paper strength improvements, to improve filler retention, or to improve sizing efficiencies (Gill 1992; Zunker 1985; Gill 1997; Tanaka et al. 2006a; Tanaka et al. 2006b; Tomney et al. 1998; Brown 1997a; Brown 1997b; Ibrahim et al. 2009a; Cheng and Gray 2009; Smith 1981; Riddell and Waring 1980). These polymers include polyacrylamide, vinyl alcohol polymer, cationic melamine-formaldehyde resin, polyamino-amide, polyamide, homo-polymer of diallyldimethylammonium chloride, and copolymer of the diallyldimethylammonium chloride and (meth)acrylamide.

The principles of filler modification with water-soluble polymers can be divided into three groups, i.e., polymer adsorption on filler surfaces, precoagulation, and preflocculation. For a specific modification method, these principles are sometimes combined together. As far as polymer adsorption on filler surfaces is taken into consideration, the adsorption can be induced by one kind of polymer or the combination of different polymers, and multi-layer adsorption can also be feasible. The charge density and molecular weight of polymers play important roles in filler modification. By using low molecular weight and high charge cationic polymers called coagulants in filler modification, precoagulated fillers can be obtained. On the contrary, by using flocculants in filler modification, preflocculated fillers can be obtained. Among the emerging technologies of filler modification with water-soluble polymers, filler preflocculation has been most frequently reported in the literature, and controlled preflocculation can improve paper formation, strength, and machine performance (Mabee 2001), catering to the need of high filler technology.

MODIFICATION WITH SURFACTANTS

Surfactants have found their use in modification of papermaking grade fillers. Recently, Ibrahim et al. (2009a) reported that the use of cationic dodecyltrimethylammonium bromide (DTAB) in modification of Egyptian talc enhanced the bonding capacity of talc, and paper strength was strikingly improved. When modified with cationic dodecyltrimethylammonium bromide, the charge characteristic of talc may be changed to a certain degree, which is favorable to fiber-filler bonding.

MODIFICATION WITH POLYMER LATEXES

Latexes can be used in filler modification under controlled conditions. Latexes can generally be divided into two groups, i.e., cationic latexes and anionic latexes. Anionic polymer latex dispersions do not readily adsorb on pulp fibers; therefore, they are not used alone as papermaking furnish additives. However, it is known in the paper industry that the addition of anionic latex followed by the addition of alum causes the latex particles to precipitate onto pulp fibers. Cationic polymer latex dispersions (Xiao et al. 1999; Liu and Xiao 2000), which can readily adsorb on pulp fibers, are not commonly

used as furnish additives probably due to their high cost (Laleg et al. 2008). In the literature, the use of anionic latex in filler modification has been reported, and it has interestingly been found that the modification process can be carried out by adding the specifically prepared anionic latex, i.e., an acrylic polymer selected from the group consisting of n-butyl acrylate-acrylonitrile-styrene copolymers and n-butyl acrylate-styrene copolymers, into common papermaking filler slurries at ambient temperature, followed by mixing with water of temperature higher than the glass transition temperature (T_g) of the latex used, and this method of filler modification can improve filler retention, sizing efficiency, paper strength, and acid-resistant properties of fillers (Laleg et al. 2008). The use of anionic latex in combination with starch has also been reported in the literature (Codolini 1978; Laleg 2005).

HYDROPHOBIC MODIFICATION

Increasing the concentration of filler in the papermaking furnish results in increased sizing agent demand to maintain the desired hydrophobicity and water repellency in the finished papers (Gill 2000; Shen et al. 2008e). It is believed that the sizing agents may be lost or rendered ineffective from furnish due to a disproportionate fraction of a sizing agents being absorbed on the high surface area filler in the furnish. Therefore, the effectiveness of the sizing agent is reduced and the cost of the papermaking process is increased due to an increase in sizing agent demand. Hydrophobic modification of papermaking grade fillers is one of the effective ways to eliminate the negative effect of filler loading on sizing efficiency. As filler hydrophobicity is enhanced, the demand of wet-end sizing agent is decreased, and sizability of the filler material is increased.

Gill (1995) patented a method of filler modification using water soluble C12-C22 fatty acid salt to improve filler hydrophobicity, and the modified filler material was claimed to be prepared by selecting finely divided particles of an inorganic material and substantially modifying all of the surface of a majority of the particles with a C12-C22 fatty acid salt, forming a hydrophobic coating. Modification of calcium carbonate fillers with starch-soap complex has also been found to be favorable to improvement of filler hydrophobicity and sizing efficiency (Kurrle 1996). Gill (2000) proposed a method of filler modification using a water miscible butyl acrylate-acrylonitrile copolymer, and sizing characteristics of the filled papers were claimed to be significantly improved. Niinikoski et al. (2007) proposed a method of hydrophobic modification of fillers using a hydrophobic polymer made of polymerisable monomers polymerised in the presence of a polysaccharide, and the formation of a hydrophobic film on the surface of the filler particles and/or between adjacent filler particles was claimed, and the polymer was polymerised using a polysaccharide as a stabilising agent, wherein the polymer is formed from monomer or monomers selected from the group consisting of styrene, 1,3-butadiene, butylacrylate, methyl methacrylate, ethyl acrylate, 2-ethyl hexyl acrylate, and acrylonitrile. In addition to the improvement of hydrophobicity, this method of filler modification was also claimed to improve the wet strength and reduce the linting of the paper, board or the like to be made.

Hydrophobic modification of fillers can also directly confer sizing characteristics to the filled papers without the further addition of sizing agents. Dumas (1999) proposed that filler modification carried out by the addition of cationic ketene dimer to the surface of inorganic filler particles improved the sizing characteristics of the filled papers, and the sizing level in the sheet was practically unaffected by the level of filler addition. It was also claimed that this method was of great commercial significance, since the papermaker would be able to control filler loading and sizing independently. Under controlled conditions, paraffin wax, alkyl ketene dimer, styrene-acrylic acid emulsion, phthalic anhydride/urea, and rosin size have been proved to be useful in filler modification, and the modified fillers can be directly used as sizing agents to provide hydrophobicity (Wang et al. 2006a; Wang et al. 2006b; Yang and Liu 2008; Yang et al. 2009; Ibrahim et al. 2009b).

SURFACE NANO-STRUCTURING

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.

CATIONIC MODIFICATION

Cationic modification is a very important branch of filler modification technology, and it can be overlapped with some of the above discussed aspects. Fillers can be cationically modified to increase filler loading in paper while maintaining sheet strength, to improve runnability, filler retention, and filler distribution, and to reduce cationic additive demand (Sang and Xiao 2009). The modifiers useful for cationic modification of fillers can include polyamino-amide, polyamide, homo-polymer of diallyldimethylammonium chloride, copolymer of the diallyldimethyl-ammonium chloride and (meth)acrylamide, chitosan, cationic dodecyltrimethyl-ammonium bromide, cationic polyacrylamide, and cationic starch (Gill 1992, 1997; Tanaka et al. 2006a; Tanaka et al. 2006b; Ibrahim et al. 2009a; Shen 2008d,e). Although there are many benefits of using the cationic modification technology, there are certain drawbacks of

cationic modification, such as slurry instability, formation of agglomerates, and greater susceptibility to sedimentation (Sang and Xiao 2009).

PHYSICAL MODIFICATION BY COMPRESSING, CALCINATION, OR GRINDING

Papermaking grade fillers can be physically modified for improved utilization. After compressing or calendering treatment, finely ground GCC can be specifically modified into a pigment having a completely different morphology and consequently different properties (Holik 2006). The modified GCC can exhibit extraordinarily high specific surface area, providing high brightness, easy gloss development, and good printability in offset and rotogravure. This modified GCC has already found its way into the commercial production of supercalendered papers.

Fillers can be modified by high-temperature calcination treatments to improve their optical properties. As a specialty filler applied to the sheet mainly in order 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 or 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).

Grinding may affect many properties of fillers, such as particle size, size distribution, and shape. Filler color can possibly be influenced by particle size and size distribution, and the color of white filler processed by grinding becomes whiter as particle size decreases (Scott 1990). Grinding can also affect the structure and reflectance from filler surfaces, and its impact is dependant upon the mineral filler species (Christidis 2004). By grinding, the properties of fillers can potentially be optimized.

MODIFICATION FOR USE IN FUNCTIONAL PAPERS

Under certain situations, modification of fillers can enable their use in functional papers. Min and Cho (2004) proposed a method of filler modification by the so-called dry impact-blending and spray vapor-drying to obtain Ag composite-pigment hybrids, which were thought to be useful in functional papers. Lee and Cho (2007) showed that, when modified with Ag nano-colloidal solution and TiO₂ by using the hybridization technique, fillers can be used in functional papers for the purpose of antimicrobial and photocatalytic deodorization functions. Filler Modification to bind a conducting polymer to filler surfaces for use in electrically conductive papers was proposed by Ni et al. (2008), and the functional papers might have applications such as electrostatic dissipation and electromagnetic shielding.

OTHER ASPECTS OF FILLER MODIFICATION

Besides the above-mentioned aspects of filler modification, one can combine use of natural polymer and organic polyelectrolyte (Brooks et al. 1981) for filler preflocculation, modification with cationic aluminum zirconium coupling agent for improved filler retention and paper strength (Chen et al. 2006), and modification for improved dispersability (Atkinson 2002). The strategies of filler modification seem to be diversified with the development of papermaking industry.

CONCLUDING REMARKS

The use of fillers in papermaking can provide many benefits, such as reduced costs, improved paper properties, increased productivities, and unique product functionalities. Among the numerous technologies associated with fillers, filler modification, mainly concentrated on the commonly applied fillers, such as calcium carbonate, clay, and talc, can be regarded as an effective strategy to provide improved functions and alleviate disadvantages. Filler modification is also an indispensable way to accelerate the development of high filler technology. The technologies of filler modification have been focused on the improvement of acid-resistant properties, optical properties, bonding capacities, retention properties, and sizing-compatibility of fillers, and the use of filler modification in the development of functional papers and eliminating filler abrasiveness has also been reported in the literature. Also, the functions of different modification methods have often proved to be overlapping in specific applications. In the future, the improved use of filler modification technology has potential to create countless additional benefits to the papermaking industry.

Depending on the specific filler modification methods, the relevant mechanisms of filler modification can be based on encapsulation, formation of a buffering system, adsorption, structural conformation, physiochemical reaction, physical attraction, ionic/electrostatic action, etc. Such approaches also can be used in combination. Further work regarding the mechanisms of filler modification might provide interesting theories or implications. The technical improvement and/or broadening in the field of filler modification, as well as the underlying mechanisms concerning the filler modification processes and interactions of modified fillers with fibers, fines, additives, dissolved and colloidal substances, etc., can serve the needs of the ever-developing papermaking industry.

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