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A Review on Use of Carbohydrate-based Fillers and Pigments in Packaging Paper

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Abstract As one of traditional packaging materials, paper and paperboard are being more popular and beneficial thanks to their environmental sustainability and have been widely used in packaging applications, from light weight infusible tissue for tea/coffee bags to heavy duty boards for the distribution. Papermakers have to design the products having a desired customized function with their paper machine. Globally, the use of filler and pigment in papermaking is now a very common practice to meet the needs of customers. Many benefits can be achieved as a result of filler addition, which mainly includes cost and energy savings. The replacement of traditional mineral fillers and pigments with biodegradable and renewable carbohydrate polymers is a very interesting and promising research topic due to the concern of environmental impact. In this review paper, the use of traditional and novel carbohydrate fillers and pigments in cellulosic paper is highlighted. It is noteworthy that there are still some challenges and technical barriers associated with the use of these organic materials in point of structural stabilities and manufacturing costs, although most of them are available in market as the commercialized products. With the emerging nanotechnologies, it is believed that the use of carbohydrate-based filler and pigment for papermaking will increase and bring technical advantages to industry.

Keywords Packaging paper, Carbohydrate, Filler, Pigment, Papermaking

Introduction

The use of paper and paperboard for packaging dates back to the 17th century with accelerated usage in the later part of the 19th century[1] They are extensively used in various types of flexible, semi-rigid, or rigid packaging[2] due to their unique properties such as high stiffness/rigidity, good printing surface, easy to tear, and well deadfold[3]. In addition, paper and paperboard are economical and the most environmentally friendly material for packaging, in view of its natural sourcing and easy recyclability. Therefore, paper and paperboard are the largest-used packaging material throughout the world, by weight[4]. They are a part of the overall flexible packaging market as in several format; for example, sachets, pouches, bag, multiwall sack, and overwrapping material. Among of several grade of paper and paperboard, machine-glazed, one side coated paper, greaseproof paper, and calendered paper are the major contributed to flexible packaging section[1]. To enhance the properties of paper and paperboard serving the market's demand, the surface sizing on paper machine are usually considered as primary technique.

Generally, paper and paperboard compose of pulp fibers and some inorganic fine particles or plastic-based pigments, which are used as paper fillers and coating pigments during papermaking processes[2] to improve the brightness, opacity, gloss, dimensional stability, printability, writability, chemical resistance, and barrier properties[5,6]. Inorganic fillers and synthetic pigments such as titanium dioxide, silicon dioxside, calcium carbonate, and kaolin clay as well as polyacrylate and polystyrene are applied to produce cellulosic paper for desired applications[7-10]. During papermaking process or recycling process, such inorganic fine particles with some pulp fractions that cannot be retained on paper wire or are rejected during repulping are transferred to paper sludge pond for further treatment[2]. Traditionally, it is dried in air and subjected to incineration; then, its ash is disposed by landfilling. However, these inorganic fillers/synthetic pigments can cause significant problems because they are incombustible and not readily biodegradable in landfill[2,11,12]. Unlike the aforementioned fillers/pigments, a paper sludge with organic based material (i.e., protein or carbohydrate) can be readily incorporated into the conventional boiler system as alternative fuel as well as directly land-filled because these organic fillers/pigments are biodegradable; thus, decreasing the environmental impact from recycling system[11].

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Carbohydrates polymers are the most abundant biopolymers in the biosphere which account for three-fourth of the global available biomass[13)]. The use of biodegradable and renewable carbohydrate polymers (such as starch, cellulose, and chitosan) as modifiers is a very interesting and promising research topic[14)]. Among the carbohydrate-based organic fillers and pigments available in the paper industry, starch-based fillers and pigments have been the most frequently used as internal and external sizing. Starch solution is applied onto dried paper or surface sizing to improve their surface property for water resistance and physical properties for tensile strength and internal bond[15)]. However, in modern papermaking industry, several new and novel carbohydrate-based fillers/pigments have been reported in the recent literatures or commercialized in market. Therefore, this paper is to review the overview of carbohydrate-based fillers and pigments for papermaking including the novel material from emerging nanotechnology.

Starch-based fillers and pigments

From the global non-food perspective, the paper industry generally represents the biggest application of starch[16)]. With the high performance of starch, it is applied in both internal and external sizing. Starch composed of anhydroglucose units with abundant hydroxyl groups that are able to form hydrogen bonds with cellulosic fibers and to increase paper strength[17)]. In its native form, starch is mostly used for as a thickener or binder. Although unmodified starch can be used in surface sizing in some cases, the viscosity of starch solution is usually too high which reduce the allowable solids content of the starch solution for surface sizing[16)]. Moreover, the smallest unmodified starch granule size is larger than 1 μm which cannot provide a highly smooth surface for printing-writing paper[11)]. Therefore, it is not considered for use as fillers and coating pigments for paper industry. However, the modified starch derived from native starch via depolymerization (i.e. chemical, physical, and/or enzymatic modifications) is widely used in the manufacture of paper and paperboard[16,18)] due to their more economic and efficient application.

There are several types of modified starch available to the papermaker to choose from depending on the applications: paper formation control, furnish drainage improvement, filler and cellulose fines retention, size retention, internal paper strength improvement, surface strength enhancement, and reduction of waste water pollution[19,20)]. Table 1 presents the type, function, and application of each modified starch which is used for sizing agent. Cationic starch is highly used in virtually all grade of paper and paperboard. Four major benefits of cationic starch over others are improvement of mechanical strength, better retention of fines and fillers, faster drainage, reduction of waste water pollution (BOD: biochemical oxygen demand)[19,20)]. Acid-depolymerized starch is widely used for solid bleached sulphate (SBS) board, Kraft linerboard, and cartonboard. It can be applied at both water box at the calender to increase the internal bonding between fibers or at the size press to improve the surface sizing. However, it is sensitive to retrogradation and has to be kept at controlled temperature and pH. Oxidized starch is particularly used as the surface size on uncoated paper that requires high surface strength and ink holdout. The cooked oxidized starch must be kept at alkaline condition but too high pH can cause the discoloration. Unlike other modified starch, starch ether and ester are considered as a premium grade. It is usually used for high quality paper such as greaseproof paper and medical paper due to their superior film-forming and water-holding properties. However, the alkalinity and temperature at size press must be well controlled to avoid the saponify effect. Anionic starch provides improvements in film strength, pick resistance, opacity, and air-leak density which is necessary for paperboard, barrier paper and specialty paper with a high content of recycled pulp[20)].

Apart from aforementioned starch grades, there are the relatively newer modified starches such as cross-linked, microcellular foam[22)], liquid or dry pre-gel, and highly charged wet-end starch used for surface applications include hydroxypropylated, acetylated, acid modified, phosphate ester, and dextrins[11)]. Bolivar et al.[21)] succesfully developed the starch-

Table 1. Type and function of modified starched for papermaking applications

Type of modified starch	Functions	Application
Acid-depolymerized starch	Improving surface sizing and internal bonding	SBS board, Kraft linerboard, carton board, and commodity grades
Oxidized starch	Improving surface strength and ink holdout	Uncoated wood-free sheets for offset, book, and text paper grades
Starch ether/ester	Providing superior film-forming and high water-holding	Specialty grades such as greaseproof paper, and medical paper
Cationic starch	Improving paper strength Enhancing film clarity Reducing BOD of waste water	Virtually all grade of paper and paperboard
Anionic starch	Improving pick resistance, opacity, and air-leak density	Paperboard, greeting card stock, barrier paper, and specialty papers

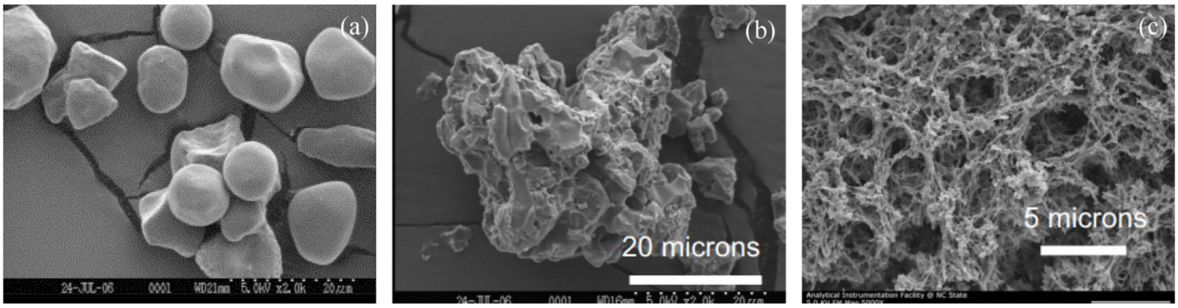

Fig. 1. SEM picture of (a) unmodified starch and (b,c) starch-based microcellular foam particles[21)].

based microcellular foam as illustrated in Fig. 1. The brightness of the particles was significantly higher than that of the unmodified starch, which is most likely due to the development of a porous structure. Besides, the water resistance performance of such starch was given only after blending with alkyl ketene dimer (AKD).

In addition, with an emerging of nanotechnology, starch nanoparticle/nanocrystal has been reported as a great potential for use in papermaking wet-end, surface sizing, and coating. It shows several distinctive advantages over traditional microscale starch[23,24)]. LeCorre et al.[25)] prepared the starch nanocrystal from waxy maize starch and wheat starch via acid hydrolysis. After coating the base paper with such diluted water-based starch nanocrystals, they found that the water vapor permeability (WVP) decreased to 40% compared to the base paper. This works shown that starch nanocrystals are promising fillers for water barrier coating. Swoboda and Wendt[26] patented a use of cationic starch nanoparticle for paperboard sizing to produce a disposable paper servingware container. The particle dimension of these starches is reported to be between 50 nm and 100 mm. In accordance with their invention, the result shown that the obtained paper servingware exhibits high wet-rigidity due to the superior starch concentration at sized surfaces in 20 lbs per 3000 ft^2 per ream.

Cellulose-based fillers and pigments

The use of fillers at high loading levels is usually considered to bring certain disadvantages or limitations such as deteriorated paper strength, poor filler retention, decreased sizing efficiency, and bending stiffness. In order to overcome or alleviate at least one of the drawbacks associated with filler addition, many methods have been reported or industrially practiced, which generally include fiber loading by incorporating fillers into the lumens and/or cell walls of pulp fibers, preflocculation, chemically treated filler with polymer, filler-wood fine composites, and pulp fines-filler complexation by premixing fillers with fines/fibrils or in situ precipitation of filler particles on fines/fibrils[14,27)]. Since the main component of paper is pulp fibers, blending or incorporating the cellulose-based filler/pigment could result in higher efficiency over others. Its compatibility with pulp fibers is surely very good, as strong hydrogen bonds can be formed under typical conditions[6)].

Lavoine et al.[28)] presented a potential usage of microfibrillated cellulose (MFC) as pigment coating agent to improve the barrier and mechanical properties of paper. The air barrier and the bending stiffness were considerably improved 90% and 50%, respectively. However, the improvement of the properties of cellulosic substrates will mainly be influenced by the kind of paper substrates and the type of MFC suspension. Studies from Aulin et al.[29)] and Ankerfors[30)] revealed that carboxymethylated MFC can improve the surface strength by reducing the linting propensity and enhance the barrier properties. Aulin et al.[29)] found that the MFC layer reduced the sheet porosity resulting in very low oxygen permeability as compared with samples prepared from plasticized starch, whey protein, and arabinoxylan. Ankerfors[30)] disclosed that the carboxymethylated MFC can be added at the wet-end process to produce the high-loading paper. Eriksen et al.[31)] reported that adding 4% kraft MFC to thermo-mechanical pulp (TMP) paper as strength enhancer, the tensile index, and air resistance increased; however, the light scattering coefficient, opacity and brightness of the sheets were reduced.

The combination of nanocellulose with paper-based cellulosic materials is quite recent. Interestingly, nanocellulose has shown its potential in surface nano-engineering of cellulosic paper. Using cellulose nanofiber (CNF) and cellulose nanocrystal (CNC) as a paper coating agent have been reported in several study about their performance to improve the print quality and barrier properties[33)]. Kajanto and Kosonen[32)] disclosed the novel development from UPM-Kymmene Corporation about the use of CNF as a reinforcement agent in the paper on a high-speed pilot paper machine represented the condition of paper mill. Two grades of CNF named AS and KS were studied. With the maximum 2% CNF loading together with 1% of cationic starch, the tensile strength significantly improved, enabling up to 8 g/m^2 grammage reduction as reported in Fig. 2(a). Moreover, as shown in Fig. 2(b), the

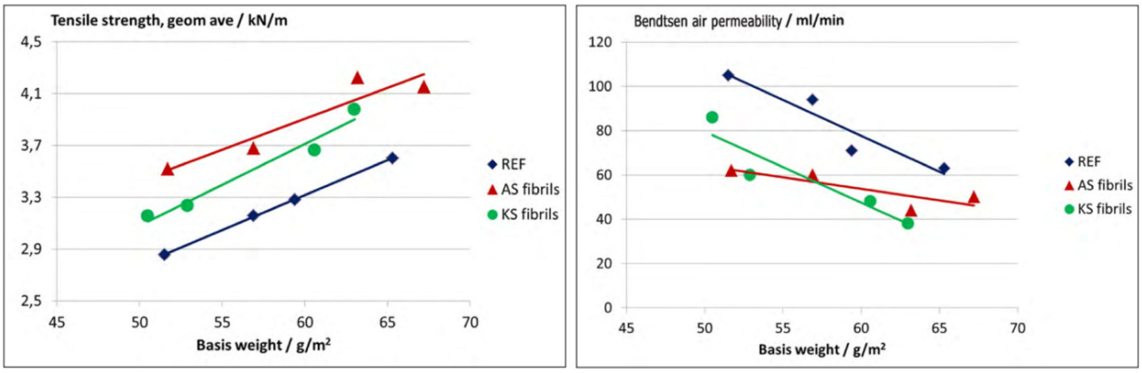

Fig. 2. (a) Tensile strength and (b) Bendtsen air permeability of reinforced paper with two grades of CNF (AS and KS)[32].

result showed that the porosity of paper can be reduced to 20-30% leading an improvement in air barrier properties. Cerenano® is a novel bio-based CNF filler for paper and paperboard manufacturing that has recently been developed by the Cerealus Company and the University of Maine Process Development Center. Their report showed that Cerenano® is a promise filler which dramatically improves the sheet density, porosity, surface quality and Z-direction strength (internal bond). With adding Cerenano® 100kg/ton finished paper at the blend chest, the basic weight and density of paper can be decreased while the caliper and porosity is reduced as illustrated in Fig. 3. From their report; moreover, Cerenano® can be applied at size press to improve the paper dimensional stability, too[34].

To produce CNC, the cellulose is subjected to strong acid to remove the amorphous regions and remain only the crystalline regions with low molecular weight polymer chain. So, the use of CNC as reinforcement poses more challenge than CNF[32]. To enhance the reinforcement performance of CNC, it is suggested to be blended with other long chain carbohydrate. Yang et al.[35] developed a new surface-sizing agent for cellulosic paper from the combination of cationic starch and CNC. The addition of 0.3% CNC improved the heat stability of starch as well as the mechanical properties and the air resistance of surface-sized paper.

Hemicellulose-based fillers and pigments

Unlike cellulose, hemicelluloses are comprised of long chains of various sugar molecules in their molecule chains. The exact sugar composition of hemicellulose can vary depending on the type of plant including glucose, xylose, mannose, galactose, rhamnose, and arabinose. To date, hemicelluloses have found only limited application in industry, and they are primarily used for the production of fine chemicals, such as xylose and other monosaccharides[16,36]. For paper surface engineering, the use of hemicellulose-derived chemicals has recently been demonstrated. They have been used in surface sizing, particularly as a replacement of starch[37]. The surface sizing application of hemicelluloses can result in the improvement of paper's surface strength.

Xylans are the most abundant hemicelluloses which exist in hardwood while galactoglucomannans are the main hemicel-

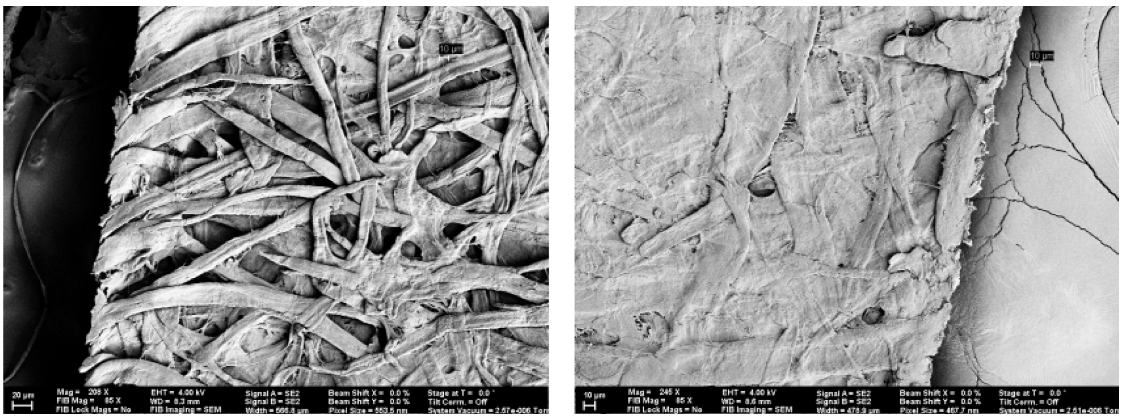

Fig. 3. SEM picture of (a) controlled paper and (b) test paper with Cerenano® 10% loading[34].

luloses in softwoods[36]. Kataja-aho et al.[38] prepared cationized birch xylan for the wet and dry strength of birch kraft paper. The results showed that the addition of 3% xylan improved the initial wet strength of the web by 30% and increased the tensile strength of the dry web by 26%. However, this improvement was not as high as achieved with conventionally used cationized starch. This is most likely because the molecular weight distribution of the hemicelluloses is lower than starch which limit the enhancing. So, the higher molecular weight hemicellulose fillers are considered more attractive and effective than low molecular weight one[39]. Laine et al.[40] investigated the barrier properties of coated paper with medium-high molecular weight xylan derivertive, cross-linked hydroxypropylated xylan. They found that such coated paper delivered the high oxygen permeability which was nearly one third of the polyethylene terephthalate coated paper. Recently, Skalax® from Xylophane (a Swedish company commercialized the production of xylan from cereal husks) has been commercialized as a barrier coating for paper and cardboard. The product claims that Skalax provides a superior performance similarly to traditional barrier coating agent such as EVOH, aluminium and metallised foils[41].

Although the production costs of galactoglucomannans are higher than starch, they have a great advantage in being more water soluble than starch and can easily be modified according to desired end use. Studies from Lindqvist et al.[42,43] revealed that different types of galactoglucomannan present a different pathway for interaction mechanism. The dispersion of native galactoglucomannan in the fiber suspension can create the outstretched fibrils on fiber surface which promote the interaction between fibers. Thereby, the wet tensile strength and the elastic modulus increase. The use of cationic galactoglucomannans can increase the binding site between fibers and fiber fines as well as other fillers. It can be adsorbed to negatively charged surface of fibers via electrostatic attraction. On the other hand, the carboxymethylated galactoglucomannan are assumed to form an ionic bond to metal ions, such as calcium and magnesium contained in wood.

Other carbohydrate-based fillers and pigments

In addition to the above organic-based fillers and pigments, other types of carbohydrates may also be used to prepare fillers and pigments. For di-saccharide-based fillers and pigments, their use as fillers/pigments for papermaking has also been found to be possible[44]. Myllymaki et al.[44] patented the use of ester derivatives of disaccharides for paper surface coating pigment. The brightness of this pigment can be as high as 92% (ISO brightness). Moreover, the coated paper showed higher light-scattering coefficient and opacity without notably impairing the tensile index or tensile strength. Other polysaccharides such as alginates and chitosan also have been used as a papermaking additive and for the surface treatment of paper as well as a bulk paper fillers. It has been reported that the printability and gas barrier of coated paper increases with the addition of chitosan due to the fact that the paper surface becomes denser and smoother as shown in Fig. 4.[45-48] show the coated surface of Moreover, chitosan shows the unique property over other fillers and pigments about the controlling the microbial contamination on paper surface which is imperative for packaging materials[47].

Conclusion

As exemplified in this brief review, the use of organic carbohydrate-based fillers and pigments can reduce and resolve environmental problems, such as chemical recovery, paper sludge disposal in recycling system and energy consumption, caused by the use of non-biodegradable inorganic fillers and pigments in the paper industry. Besides, since such carbohydrate-based fillers and pigments have a similar structure with the host fiber cellulose, they easily bond and deposit onto the surface of the paper and lead to achieve desired cellulosic paper specialties, for instance, brightness, tensile, air and water barrier properties. The challenge in fully implementing this carbohydrate-based fillers and pigments over the inorganic ones in paper industry is their cost and stability. However, with the emerging of recent nanotechnology, it is

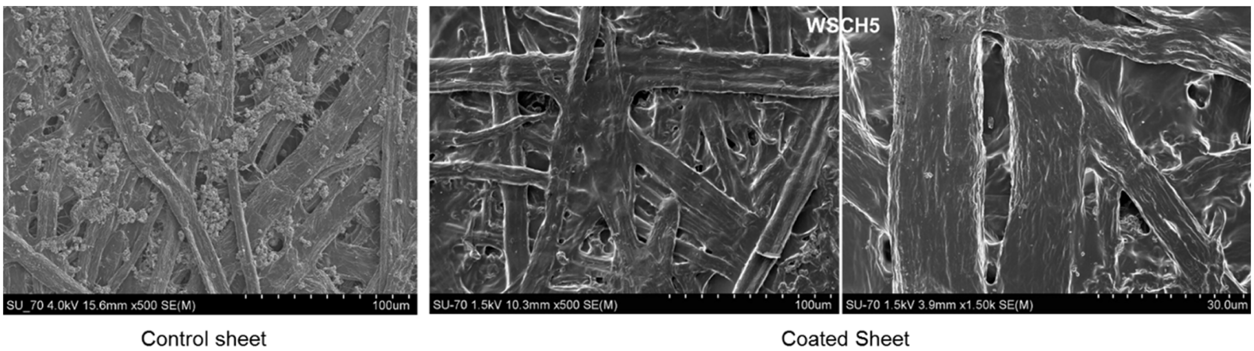

Fig. 4. SEM surface views of a control sheet and water-soluble chitosan with five layers from the coated side (WSCH5).[48]

expected to further decrease these demerits in the near future. Therefore, the use of carbohydrate-based filler and pigments will potentially offer new possibilities to develop new applications for cellulosic paper packaging material without compromising the future of the global environment.

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