Carbohydrate Polymers 85 (2011) 17–22

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Review

Carbohydrate-based fillers and pigments for papermaking: A review

Jing Shen[a], Zhanqian Song[b], Xueren Qian[a,*], Yonghao Ni[c]

[a] Key Laboratory of Bio-based Material Science andTechnology of Ministry of Education, Material Science and Engineering College, Northeast Forestry University, Harbin, Heilongjiang 150040, China
[b] Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Key and Open Laboratory on Forest Chemical Engineering, State Forestry Administration, Nanjing 210042, China
[c] Department of Chemical Engineering & Limerick Pulp and Paper Centre, University of New Brunswick, Fredericton, NB, Canada E3B 5A3

ARTICLE INFO

Article history:
Received 11 January 2011
Received in revised form 2 February 2011
Accepted 12 February 2011
Available online 18 February 2011

Keywords:
Carbohydrate
Papermaking
Filler
Pigment
Paper recycling
Bioenergy production

ABSTRACT

The replacement of traditional mineral fillers and pigments with environmentally friendly carbohydrate-based organic materials is beneficial to paper recycling, bioenergy production from paper or deinking sludge, alleviation of abrasion of paper machine wire and paper cutters, etc., yet there are still some technical barriers or challenges associated with the use of these organic materials in such aspects as manufacturing costs and structural stabilities. In this paper, the emerging technologies of carbohydrate-based fillers and pigments for papermaking are reviewed. The carbohydrate-based fillers and pigments available in the literature are based on starch, cellulose, disaccharide, xylan, or carbohydrate-rich lignocellulosic forest residues, while the starch-based fillers and pigments have been the most frequently reported. The mineral fillers surface-modified with carbohydrate-based materials is not included in this paper as inorganic minerals are the major component of the modified fillers.

Contents

1. Introduction

In the papermaking industry, mineral-based fillers and pigments are widely used to improve the brightness, opacity, gloss, dimensional stability, printability, and writability of various paper products (Hubbe, Pawlak, & Koukoulas, 2008; Song, Dong, Ragauskas, & Deng, 2009a), and these materials can either be used as fillers in the production of, for example, super-calendered (SC) paper (Dai, Ni, & Li, 2011), or coating pigments in the production of coated paper (Hu, Ni, & Zou, 2007). The benefits associated with the use of minerals also include cost and energy savings, increased furnish drainage rate, machine speed, etc. (Dong, Song, Patterson, Ragauskas, & Deng, 2008; Song et al., 2009a). In addition to their use in the traditional printing/writing paper, mineral-based fillers and pigments can also be used to produce cellulosic paper with functional applications (Shen, Song, Qian, & Ni, 2011; Wu, Qian, Shen, & Song, 2008).

For the recycling of the mineral filler/pigment-containing paper, large amount of inorganic deinking sludge can be formed. For example, it was reported that when 1000 kg of paper is recycled, 50–80 kg inorganic deinking sludge was formed (Raukola, 2007). The deinking sludge is usually land-filled, incinerated, or composted (Raukola, 2007). In these cases, the inorganic fillers/pigments can cause significant problems because they are not readily biodegradable, and they are incombustible and undesirable in the composting materials. On the other hand, if organic fillers/pigments, such as carbohydrate-based products, would be used, they can be incorporated readily into the conventional boiler system in replacing oil for energy production (Raukola, 2007); alternatively, they can be land-

---

* Corresponding author. Tel.: +86 451 82192081; fax: +86 451 82192081.
E-mail address: qianxueren@yahoo.com.cn (X. Qian).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.02.026

filled because these organic fillers/pigments are bio-degradable, thus decreasing the environmental impact of paper recycling. Also, some mineral fillers/pigments usually have much larger density (e.g., ground calcium carbonate) than pulp fibers, and their use considerably increases the weight of the paper, which can increase the transportation cost, for example, for packaging materials (Johansson et al., 2007).

Synthetic plastic-based pigments derived from fossil resources have been used in paper coating under certain conditions, but they are rarely used as fillers for paper. When properly chosen and formulated, they can provide a coating with excellent smoothness, brightness, opacity, as well as a superior printing quality (Holik, 2006). However, a disadvantage associated with the synthetic plastic pigments is that they are not suitable as coating or filler pigments for paper; instead, they are usually used as doped mineral pigments (Johansson et al., 2005). Also, the polystyrene-based pigment does not withstand the heat of the dryer of the paper machine without melting, and the urea–formaldehyde pigment decomposes, leading to the formation of formalin (Mikkonen et al., 2007). A further limitation of the synthetic organic pigments is that they are based on non-renewable fossil resources, and their use is accompanied by the increase in carbon footprint.

Recently, much research effort has been made to develop biodegradable carbohydrate-based organic fillers and pigments derived from renewable bioresources (Bolivar, Venditti, Pawlak, & El-Tahlawy, 2007; El-Tahlawy, Venditti, & Pawlak, 2007; Karvinen, Mikkonen, & Silvennoinen, 2005; Karvinen, Oksman, Silvennoinen, & Mikkonen, 2007; Koivunen, Alatalo, Silenius, & Paulapuro, 2010; Koivunen, Paulapuro, & Silenius, 2007; Koivunen, Silenius, Laine, & Vuorinen, 2007a; Koivunen, Silenius, Laine, & Vuorinen, 2007b; Krogerus, 1999; Mikkonen et al., 2007; Mikkonen, Putkisto, Peltonen, Hyvärinen, & Koivunen, 2010; Mollaahmad, 2008; Myllymäki, Aksela, Kangaslahti, & Silenius, 2006; Patel, Venditti, Pawlak, Ayoub, & Rizvi, 2009; Patel, Venditti, & Pawlak, 2010; Peltonen, Mikkonen, Qvintus-leino, Varjos, & Kataja, 2007; Penttilä, Lumme, & Kuutti, 2006; Putkisto, Mikkonen, Hyvärinen, & Peltonen, 2009; Saari et al., 2005). The substitution of mineral or petroleum-based fillers and pigments with these renewable organic fillers/pigments has many advantages, for example, it can decrease the environmental impact associated with paper recycling, decreased abrasion to processing equipment (e.g., paper machine wire, paper cutters), and foster the sustainable development of papermaking industry (Shen, Song, & Qian, 2007; Shen, Song, & Qian, 2010; Wu et al., 2008). The use of carbohydrate-based organic fillers/pigments would have strategic significance to the global papermaking industry. This paper is to review the recent technologies of carbohydrate-based organic fillers and pigments for papermaking. Although surface modification (encapsulation/coating) of inorganic fillers/pigments with carbohydrate-based materials has recently been a very interesting research area (Deng, Jones, McLain, & Ragauskas, 2010; Deng et al., 2008; Nelson & Deng, 2008; Shen, Song, & Qian, 2008; Shen, Song, & Qian, 2009; Shen, Song, Qian, & Song, 2008; Shen, Song, Qian, & Yang, 2010; Song et al., 2009a; Song, Dong, Ragauskas, & Deng, 2009b; Yan, Liu, & Deng, 2005; Yoon, 2007; Yoon & Deng, 2006a,b, 2007; Zhao, Hu, Ragauskas, & Deng, 2005; Zhao et al., 2008), it is not to be included in the following sections of the review paper as the surface-coated inorganic fillers/pigments are generally based on the use of minerals, i.e., minerals are the major component of the surface-coated fillers/pigments.

2. Starch-based fillers and pigments

Among the carbohydrate-based organic fillers and pigments available in the literature, starch-based fillers and pigments have been the most frequently researched.

Unmodified starch granules are usually considered to be not suitable for use as fillers and coating pigments, mainly due to the strong hydrophilicity and inferior optical property. As reported in the literature (Mälkki & Lehtilä, 2002), unmodified starch particles have sometimes brightly light scattering spots; however, the light scattering is weakened when contacted with water in an aqueous papermaking system or coating formulations. Also, the use of unmodified starch granules as coating pigments is limited by the fact that even the smallest granules available in nature are bigger than 1 μm, making them unsuitable for use as coating pigments for printing paper that demands a highly smooth surface (Peltonen et al., 2007). Therefore, the chemical, physical, and/or structural modification of starch is necessary to suit for the filling and coating applications, or others, whereby a surface hydrophobicity and/or a high light scattering would be required.

Mälkki and Lehtilä (2002) patented a method for preparing an organic pigment from starch for use in papermaking. According to their proposed method, starch granules are swollen in the presence of water to increase their volume and plasticity, and their stability towards changes in volume and shape upon heating or contact with water is improved by cross-linking (e.g., using glyoxal or epichlorohydrin), derivatization (e.g., by acetylating the surface layer using acetic anhydride), or surface hydrophobization (e.g., by coating the granules with a thin layer of acetyl monoglyceride). The derivatization or surface hydrophobization can be used either separately or for complementing the cross-linking treatment of starch. By releasing impregnated gas, or displacing absorbed water with a solvent (e.g., ethanol), gas bubbles or cavities are formed inside the granules to give the improved light-scattering capacity. Formation of cavities is most simply performed by swelling starch granules, cross-linking them or stabilizing by derivatization including graft copolymerization, and subsequently removing the water rapidly by drying or by displacing it with another solvent.

Johansson et al. (2007) patented a method for preparing a porous starch-based pigment or filler product for use in papermaking, the products are in the form of stable foam, which contains foam bubbles (the average size is less than 10 microns).

Water-insoluble starch esters (e.g., starch acetate) have been made for the preparation of starch-based fillers and pigments for papermaking. Esterification (e.g., acetylation) improves the thermal stability of the starch product when compared with native starches, which is advantageous especially when the product is used at an elevated temperature (Mikkonen et al., 2007). Both spherical and micro/nanoporous (or coral-like) starch-based particles with good optical properties can be made based on the dissolution/precipitation technique, and the process can include the following major steps (Peltonen et al., 2007):

- The starch ester is dissolved in a solvent (e.g., acetone), or several organic solvents, or mixture of these and water.
- Subsequently, water is used as a precipitation agent. If water is added to the polymer solution, spherical starch-based particles are formed. On the other hand, micro/nanoporous (or coral-like) starch-based particles are formed when the polymer solution is added to water.
- After the precipitation stage, the organic solvent (organic solvents) is removed from the dispersion, and the starch-based particles can be separated using such methods as filtration, micro-filtration, decantation, or centrifugation.

During the above preparation process of starch-based fillers and pigments, ultrasonic energy can be used to optimize the particle size and its distribution (Peltonen et al., 2007). For starch esterification, a relatively high degree of substitution (e.g., $DS > 2$) is required not only to improve the hydrophobicity of starch, but also to make it totally dissolvable in the solvent system. The experimental work of

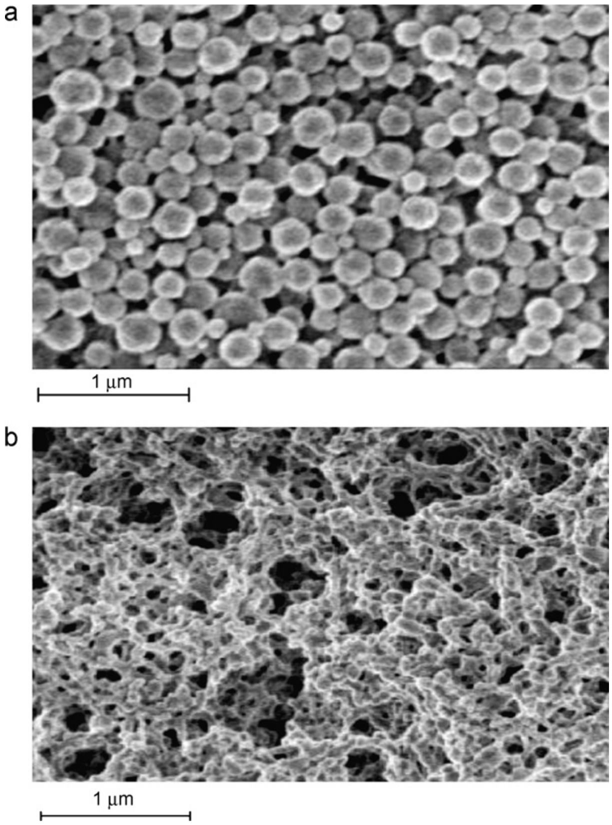

Fig. 1. SEM pictures of starch-based spherical (a) and porous (b) pigments (Kopola et al., 2007).

Mollaahmad (2008) showed that porous starch acetate filler prepared by the dissolution/precipitation technique, could improve the optical properties of the paper, and its effect could be similar to those from ground calcium carbonate under the optimized conditions studied. By following the above mentioned solution precipitation methods, VTT Technical Research Centre of Finland, in cooperation with University of Helsinki and University of Joensuu, has developed starch-based fillers and pigments (see Fig. 1) using chemically cleaved starch acetate as the starting material, and the fillers/pigments were claimed to be suitable for the production of lightweight, non-abrasive, and totally biodegradable paper with good optical properties and printability (Kopola et al., 2007). The pilot coating studies have shown that starch acetate pigment compares favorably to calcium carbonate and kaolin clay in brightness, opacity, gloss, and roughness; also, the mixture consisting of starch pigment and ground calcium carbonate and clay gave even better gloss and opacity (Joyce et al., 2005; Klass, 2005).

When using aromatic esterification agents in the dissolution/precipitation technique for the preparation of starch-based fillers and pigments, the resultant products can have improved optical properties (Mikkonen et al., 2010). These products can include starch benzoate, starch acetate benzoate, starch naphthanoate, starch acetate naphthanoate. The aromatic modification can also improve the hydrophobicity of starch-based particles, thereby enhancing their suitability as fillers and coating pigments.

Another method to prepare starch-based pigments is based on: (1) cooling of starch esters; (2) followed by refining in a jet refiner, and the starch-based particles have a porous surface structure (Mikkonen et al., 2007). Compared with the dissolution/precipitation technique, the cooling/refining process can be applied to starch esters (e.g., starch acetate) with a low degree of substitution. For instance, if starch acetate is used, the degree of substitution of 1 may be suitable for the cooling/refining technique. When the starch acetate is refined at a low temperature (e.g., −50 °C), its fine structure/porosity is maintained, and there is a clear micro-pore structure both within and on the surface of the starch particles; however, refining at room temperature generated a less porous microstructure (see Fig. 2).

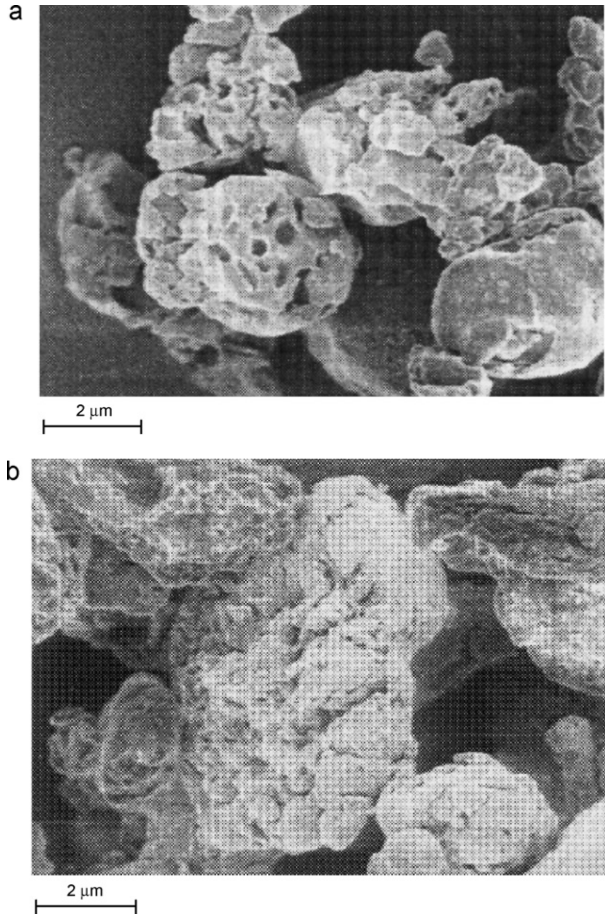

Fig. 2. SEM pictures of starch acetate particles obtained by refining using a liquid nitrogen cooled jet mill (a) and a jet mill without cooling (b). (Mikkonen et al., 2007).

For the development of starch-based fillers and pigments, considerable amount of research work has so far been focused on the preparation of starch-based microcellular foam particles using the so-called solvent exchange technique (Bolivar et al., 2007; El-Tahlawy et al., 2007; El-Tahlawy, Venditti, & Pawlak, 2008; Patel, 2009; Patel et al., 2009, 2010), and the starch-based material is precipitated from the system by ethanol (water is replaced with ethanol). The main illustrative steps for the process include:

- Starch is cooked at a high temperature (e.g., 95 °C) followed by refrigerating treatment to obtain starch aqua-gel, or the cooked starch is blended and/or reacted (e.g., crosslinked) with glutaraldehyde, epichlorohydrin, alkyl ketene dimmer, or polyaminoamide-epichlorohydrin to form a starch-based aqueous mixture.
- The starch-based aqua-gel or aqueous mixture is then contacted with ethanol under sufficient mixing, and starch-based foam particles are then formed. In this process, a higher surface tension solvent (water) is replaced by a liquid of lower surface tension.

By following the above two steps, starch-based microcellular foam particles potentially useful as fillers and coating pigments for papermaking can be prepared. An example of starch-based

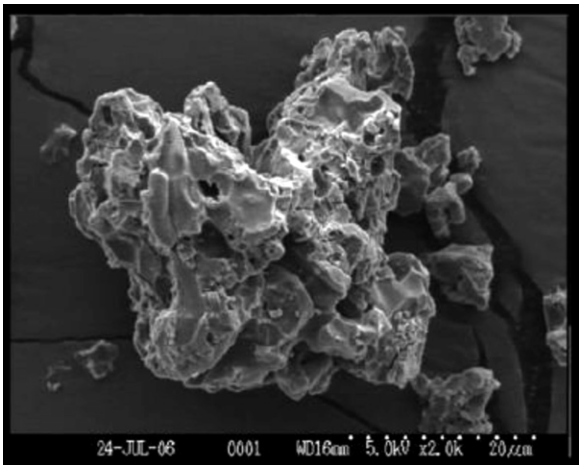

Fig. 3. SEM picture of starch-based microcellular foam particles (Bolivar et al., 2007).

microcellular foam is shown in Fig. 3. The microcellular structure is critically dependent upon the solvent exchange technique, and micro-pores (not macro-pores) can contribute to the optical properties (e.g., scattering coefficient) of starch-based particles. To meet the requirements of practical papermaking applications, in addition to the cost-effectiveness, the preservation of porous structure upon wetting, pressing, and/or calendering is a must.

In addition to the above processes/methods for the preparation of the totally organic starch-based fillers and pigments, the development of semi-organic starch-based fillers and pigments has been reported in the literature. Koivunen et al. (2010) proposed an interesting method for coating unmodified starch granules with aluminum silicate particles having excellent light-scattering coefficient, and the use of silicate-coated starch granules as filler in papermaking was reported to be able to give a good compromise between the optical and strength properties. However, the economic feasibility of silicate-coated starch granules needs to be further evaluated.

3. Cellulose-based fillers and pigments

The use of cellulose particles (or beads) as a coating pigment has been patented by Sone and Matsunaga (1992). The cellulose beads can be prepared using viscose as the starting material, and the process can include: (1) spraying by using two particle nozzles, (2) acid treatment to regenerate cellulose, and (3) drying by hot air to form particles. By following the above process, cellulose beads with grain sizes of 0.1–1000 µm can be produced, and fine beads with the grain sizes of about 1–20 µm would be preferably used as a coating pigment, as claimed by the inventors. The degree of crystallization of the resultant cellulose particles can be as low as 40%, which can result in high degree of swelling of the coating layer, excellent ink absorbing property, and high color forming density (Sone & Matsunaga, 1992). However, smaller particle size relative to the above patent disclosure (e.g., less than 1 µm) of cellulose beads would possibly be required to ensure a highly smooth surface of the coated paper.

Koivunen et al. (2007a) patented a method of using the combined enzyme and alkali treatments to dissolve the cellulose material (e.g., pulp), followed by spraying or mixing the cellulose solution obtained to a regenerating solution for the precipitation of cellulose particles suitable for use as fillers and coating pigments for papermaking. Compared to the method proposed by Sone and Matsunaga (1992), this method can avoid the need to prepare viscose, thus, the use of carbon disulfide. An example of the cellulose particles is shown in Fig. 4. The structure of cellulose particles can also be stiffened in a formaldehyde treatment via crosslinking reactions. In comparison with precipitated calcium carbonate and microcrystalline cellulose, the use of formaldehyde-treated cellulose particles as a pigment filler in papermaking can produce filled paper with better strength properties.

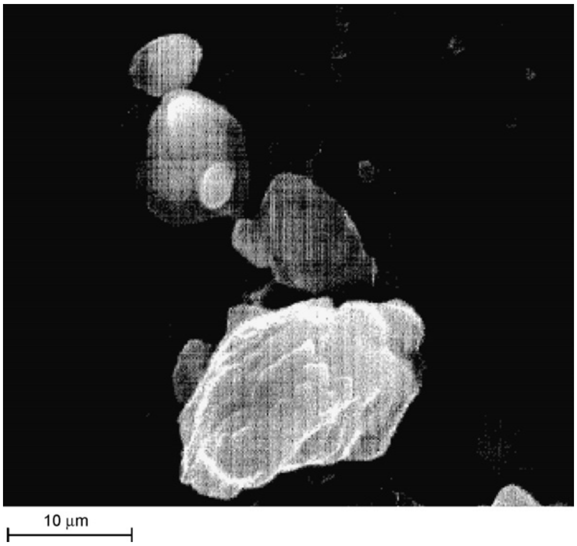

Fig. 4. SEM picture of an example of cellulose particles (Koivunen et al., 2007a).

By incorporating aromatic-based esters in the cellulose structure, and subsequently precipitated and ground to fine particles, Putkisto et al. (2009) have found that the resultant cellulose esters can be effectively used as fillers/pigments for papermaking. These aromatic-based esters can be based on benzoyl, diphenylacetyl and naphthoyl, and their incorporation in the cellulose structure can improve the optical property/hydrophobicity of the cellulosic material.

The cellulose-based fillers and pigments have lower scattering coefficient than inorganic fillers, such as precipitated calcium carbonate and clay. By coating inorganic fillers (e.g., precipitated calcium carbonate) on the surface of cellulose particles, semi-organic particles can be produced, and their light-scattering coefficient would be much higher than the totally organic cellulose-based fillers/pigments, the concept of combining inorganic and organic fillers/pigments was patented by Koivunen et al. (2007b). Different inorganic fillers, including precipitated calcium carbonate and silica, can be used. The semi-organic cellulose-based particles were prepared. The silica-coated cellulose were shown in Fig. 5. Again, similar to semi-organic starch-based fillers (Koivunen et al., 2010), the use of semi-organic cellulose-based particles as a filler pigment in papermaking can give a compromise between the optical and strength properties, as the cellulose component and inorganic component yield the respective strength or optical properties needed for the paper products.

4. Natural disaccharide-based fillers and pigments

The derivatives of some natural disaccharides can be good candidates as bio-based organic pigments for papermaking (Myllymäki et al., 2006; Putkisto et al., 2009). For example, using natural lactose as the starting material, lactose octa-acetate pigments can be produced, and be used as fillers/pigments for papermaking applications (Myllymäki et al., 2006). With acetic anhydride as the esterfication agent, the product can be separated from the reaction mixture by precipitating in water, followed by washing, drying, and refining. The brightness of lactose octa-acetate can be as high as 92% (ISO brightness), and its use as a filler pigment can signif-

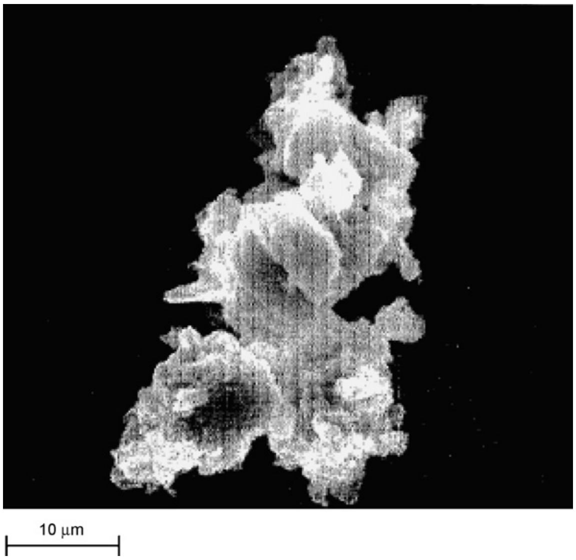

Fig. 5. SEM picture of cellulose particles coated with silica (Koivunen et al., 2007c).

icantly improve the optical properties of the paper. As compared with precipitated calcium carbonate filler, the use of lactose octa-acetate as a filler material can provide the cellulosic paper both a somewhat higher light-scattering coefficient and opacity without notably impairing the tensile index or tensile strength (see Table 1) under the conditions studied; however, the organically filled paper would be favorable for paper recycling, or if the recycled fibers would be used as the raw material for bio-fuel production (higher calorific value, less ash, etc.). In addition to lactose, the esters of sucrose (from sugar cane or beet root), maltose (a hydrolysis product of starch), and cellobiose (a hydrolysis product of cellulose) can also be used as the starting material for the preparation of fillers and pigments for papermaking, as claimed by Myllymäki et al. (2006).

Some disaccharide salts derived from natural resources, such as tri-calcium saccharate, tri-calcium lactose, have a very low solubility in water, and can also be used as fillers and coating pigments for papermaking (Koivunen et al., 2007). These semi-organic disaccharide salts in the form of crystals can be prepared by using disaccharides and calcium oxide as the starting materials.

Table 1
Physical properties of the paper sheets filled with lactose octa-acetate or precipitated calcium carbonate (Myllymäki et al., 2006).

Filler type	Precipitated calcium carbonate	Precipitated calcium carbonate	Lactose octa-acetate	Lactose octa-acetate
Filler content (%)	5.3	9.5	5.2	9
Grammage (g/m^2)	79.4	80.1	80.7	78.8
Total thickness (μm)	164.7	170.7	167.2	167.6
Total density (Kg/m^3)	481.8	469.4	482.4	469.9
Tensile index (Nm/g)	39.3	34.1	36.1	31.1
Opacity (%)	85.5	87.9	88.6	90.6
Gloss (%)	86.1	86.9	84.6	83.9
Light scattering coefficient (m^2/kg)	46.7	55.6	49.9	55.9

Note: The average particles size (d_{50}) of the fillers used was below 2 μm as tested using the instrument for particle size measurement (Malvern).

5. Other carbohydrate-based fillers and pigments

In addition to the above mentioned bio-based fillers and pigments, other types of carbohydrates may also be used to prepare organic fillers and pigments.

For hemicellulose-based materials, in addition to the suitability for use as papermaking wet end additives (Ren, Peng, Sun, & Kennedy, 2009), their use as fillers/pigments for papermaking has also been found to be possible. For example, Putkisto et al. (2009) reported the preparation of ester derivatives of xylan, followed by precipitation and then grinding to prepare fillers/pigments suitable for papermaking.

Carbohydrate-rich ligno-cellulosic particles prepared from forest residues (wood powders) as the starting materials have been reported (Kim et al., 2009; Shin, Kim, Chung, Seo, & Lee, 2008). These particles can be used alone as fillers/pigments in the paper making process, alternatively they can be blended or mixed with mineral fillers (e.g., precipitate calcium carbonate) so that mixed organic and inorganic fillers are used.

6. Conclusions

Although the use of traditional mineral-based fillers and pigments in papermaking has long been a very common/popular practice, the recycling of mineral-containing paper can result in large amount of inorganic deinking sludge, and the presence of the not-easily biodegradable inorganics will cause significant problems associated with such post-treatments as landfilling, incineration, and composting. Mainly for these reasons, quite recently, the development of carbohydrate-based organic fillers and pigments for papermaking applications has been emphasized and implemented by many scientists.

As compared with mineral fillers/pigments, the use of biodegradable, combustable, renewable, and environmentally friendly carbohydrate-based fillers/pigments can potentially provide many benefits for paper recycling, and the deinking sludge or paper can be more suitable for use in bioenergy production; other benefits can also include alleviated abrasion of paper machine wire and paper cutters, etc. Carbohydrate-based fillers/pigments derived from different bio-based materials have been studied, and these bio-based materials can be derived from starch, cellulose, hemicellulose (e.g., xylan), disaccharide, and cellulose-rich ligno-cellulosic forest residues. Among the emerging technologies on carbohydrate-based fillers/pigments, starch-based fillers/pigments have been the most frequently reported. In some sense, it might be considered that compared with other carbohydrate-based materials, starch might possibly be the most suitable and/or industrially acceptable material for the development of organic fillers/pigments for large-scale papermaking applications due to such facts as its less complicated particle formation process, good natural availability, and well-known suitability/popularity of starch derivatives as papermaking chemicals/additives.

Regarding the commercialization of carbohydrate-based fillers/pigments, a lot of technical barriers and challenges still need to be addressed, such as manufacturing costs, structural integrities/stabilities, light scattering capacities, and thermal stabilities. The coordination of worldwide industries with research institutions, and the government policy makers may perhaps also be necessary.

Acknowledgements

The authors would like to acknowledge financial support from the Fundamental Research Funds (DL09BB07) for the Central Universities of China, Foundation (no. 11533009) of the Education Department of Heilongjiang Province of China, and Canada Research Chairs Program.

References

Bolivar, A. I., Venditti, R. A., Pawlak, J. J., & El-Tahlawy, K. (2007). Development and characterization of novel starch and alkyl ketene dimer microcellular foam particles. *Carbohydrate Polymers*, *69*, 262–271.

Dai, Z., Ni, Y., Court, G., & Li, Z. (2011). Mitigating pitch-relateddeposits at a TMP-based speciality paper mill. *Tappi Journal*, *10*(3).

Deng, Y., Jones, P., McLain, L., & Ragauskas, A. J. (2010). Starch modified fillers for linerboard and paper grades: A prospective review. *Tappi Journal*, *9*(4), 31–36.

Deng, Y., Yoon, S. Y., Ragauskas, A. J., & White, D. (2008). Methods and compositions for papermaking. *Pat. Apl. No. 2008/087396 A1*. US Patent Office.

Dong, C., Song, D., Patterson, T., Ragauskas, A., & Deng, Y. (2008). Energy saving in papermaking through filler addition. *Industrial and Engineering Chemistry Research*, *47*(21), 8430–8435.

El-Tahlawy, K., Venditti, R. A., & Pawlak, J. J. (2007). Aspects of the preparation of starch microcellular foam particles crosslinked with glutaraldehyde using a solvent exchange technique. *Carbohydrate Polymers*, *67*(3), 319–331.

El-Tahlawy, K., Venditti, R. A., & Pawlak, J. J. (2008). Effect of alkyl ketene dimer reacted starch on the properties of starch microcellular foam using a solvent exchange technique. *Carbohydrate Polymers*, *73*(1), 133–142.

Holik, H. (2006). *Handbook of paper and board*. New York: John Wiley & Sons Inc. Ch. 2, 59.

Hu, K., Ni, Y., & Zou, X. (2007). Substitution of hardwood bleached kraft pulp with aspen high-yield pulp in LWC wood-free papers, part 2: Impact on coated paper quality. *Tappi Journal*, *6*(1), 26–32.

Hubbe, M. A., Pawlak, J. J., & Koukoulas, A. A. (2008). Paper's appearance: A review. *BioResources*, *3*(2), 627–665.

Johansson, A., Qvintus-leino, P., Varjos, P., Peltonen, S., Mikkonen, H., Miettinen, M., & Luukkanen, S. (2007). Porous filler or coating pigment of paper and cardboard and a method of manufacturing it. *Pat. Apl. No. 20070163737*. US Patent Office.

Joyce, M. K., Saari, J. S., Kataja, K., Mikkonen, H., Peltonon, S., & Qvintus-Lieno, P. K. (2005). Coating trial results with non-mineral based pigments. *TAPPI Coating Conference*.

Karvinen, P., Mikkonen, H., & Silvennoinen, R. (2005). Determination of the refractive index of starch acetate: Biodegradable pigment of paper. In *Technical digest of the sixth Japan–Finland joint symposium on optics in engineering (OIE05)* (pp. 5–6).

Karvinen, P., Oksman, A., Silvennoinen, R., & Mikkonen, H. (2007). Complex refractive index of starch acetate used as a biodegradable pigment and filler of paper. *Optical Materials*, *29*, 1171–1176.

Kim, C. H., Lee, J. Y., Lee, Y. R., Chung, H. K., Back, K. K., Lee, H. J., et al. (2009). Fundamental study on developing lignocellulosic fillers for papermaking (II)—Effect of lignocellulosic fillers on paper properties. *Journal of Korea Tappi*, *41*(2), 1–6.

Klass, C. (2005). Coating pigments: from size and shape to nanotech. *Solutions—for People, Processes and Paper*, *88*(9), 34–35.

Koivunen, K., Alatalo, H., Silenius, P., & Paulapuro, H. (2010). Starch granules spot-coated with aluminum silicate particles and their use as fillers for papermaking. *Journal of Materials Science*, *45*, 3184–3189.

Koivunen, K., Paulapuro, H., & Silenius, P. (2007). Use of semi-organic sugar compounds as fillers and coating pigments of paper and board. *Pat. Apl. No. 2007/082985*. World Intellectual Patent Organization.

Koivunen, K., Silenius, P., Laine, J., & Vuorinen, T. (2007a). Method for dissolving cellulose and for producing cellulose particles. *Pat. Apl. No. 2007/003699*. World Intellectual Patent Organization.

Koivunen, K., Silenius, P., Laine, J., & Vuorinen, T. (2007b). Method for coating cellulose particles, coated cellulose particles, and use thereof in paper and board production. *Pat. Apl. No.* 2007/003697. World Intellectual Patent Organization.

Kopola, H., Hurme, E., Kuusisto, J.-M., Smolander, M., Tuomikoski, M., Kololuoma, T., et al. (2007). Technologies, innovations and new business opportunities in printed intelligence. URL: http://www3.vtt.fi/proj/cpi/files/Kopola_plenary__PlasticElectronics.pdf.

Krogerus, B. (1999). *Modified starch pigments as paper additives. Proc. minerals in papermaking–scientific and technological advances in fillers*. Leatherhead, Surrey, UK: Pira International. Paper 14

Mälkki, Y., & Lehtilä, R. (2002). Organic pigment and a method for its preparation. *Pat. Apl. No. 2002144629*. US Patent Office.

Mikkonen, H., Miettinen, M., Kataja, K., Luukkanen, S., Peltonen, S., & Qvintus-leino, P. (2007). Starch-based filler and coating pigment composition for fibre webs and method for the manufacture thereof. *Pat. Apl. No. 2007/020327*. World Intellectual Patent Organization.

Mikkonen, H., Putkisto, K., Peltonen, S., Hyvärinen, S., & Koivunen, K. (2010). Novel polysaccharide-based pigments and fillers. *Pat. Apl. No.* 2010/076392. World Intellectual Patent Organization.

Mollaahmad, M. A. (2008). Sustainable fillers for paper. *Master Thesis of Luleå University of Technology*, Luleå, Sweden.

Myllymäki, V., Aksela, R., Kangaslahti, H.-M., & Silenius, P. (2006). Paper pigment, process for producing a paper product and paper product. *Pat. Apl. No. 2006/134211*. World Intellectual Patent Organization.

Nelson, K., & Deng, Y. (2008). Enhanced bondability between inorganic particles and a polysaccharide substrate by encapsulation with regenerated cellulose. *Journal of Applied Polymer Science*, *107*, 2830–2836.

Patel, S. V. (2009). The effect of processing conditions and composition on starch microcellular foam properties. *Master Thesis of North Carolina State University*, Raleigh, United States.

Patel, S. V., Venditti, R. A., & Pawlak, J. J. (2010). Dimensional changes of starch microcellular foam during the exchange of water with ethanol and subsequent drying. *BioResources*, *5*(1), 121–134.

Patel, S. V., Venditti, R. A., Pawlak, J. J., Ayoub, A., & Rizvi, S. S. H. (2009). Development of cross-linked starch microcellular foam by solvent exchange and reactive supercritical fluid extrusion. *Journal of Applied Polymer Science*, *111*, 2917–2929.

Peltonen, S., Mikkonen, H., Qvintus-leino, P., Varjos, P., & Kataja, K. (2007). Pigment and filler and a method of manufacturing it. *Pat. Apl. No. 20070101904*. US Patent Office.

Penttilä, A., Lumme, K., & Kuutti, L. (2006). Light-scattering efficiency of starch acetate pigments as a function of size and packing density. *Applied Optics*, *45*(15), 3501–3509.

Putkisto, K., Mikkonen, H., Hyvärinen, S., & Peltonen, S. (2009). Aromatic saccharide-derivatives for pigmenting purposes. URL: http://en.scientificcommons.org/54083462.

Raukola, J. (2007). Organic, natural pigments as paper coatings. *European PLACE conference*. URL: http://www.tappi.org/content/events/07europlace/presentation/07europl18.pdf.

Ren, J. L., Peng, F., Sun, R. C., & Kennedy, J. F. (2009). Influence of hemicellulosic derivatives on the sulfate kraft pulp strength. *Carbohydrate Polymers*, *75*(2), 338–342.

Saari, J., Kataja, K., Qvintus-Leino, P., Kuuti, L., Peltonen, S., Mikkonen, H., et al. (2005). Trials with developed non-mineral starch based pigments and fillers. In *Proceedings of the fillers and pigments for papermakers* Pira International, Atlanta,

Shen, J., Song, Z., & Qian, X. (2007). Research progress of filler engineering and new fillers in papermaking. *Transactions of China Pulp and Paper*, *22*(4), 113–119 (in Chinese).

Shen, J., Song, Z., & Qian, X. (2008). Encapsulation modification of PCC filler with starch/oleic acid complex using alum as a precipitation agent. In *Proceeding of international conference on pulping, papermaking and biotechnology* Nannjing, (pp. 380–385).

Shen, J., Song, Z., & Qian, X. (2009). Investigations on the preparation of starch/sodium oleate/alum modified precipitated calcium carbonate filler and its use in papermaking. *Appita Journal*, *62*(5), 360–364.

Shen, J., Song, Z., & Qian, X. (2010). Possible trends of renewable organic fillers and pigments derived from natural resources for sustainable development of paper industry. *BioResources*, *5*(1), 5–7.

Shen, J., Song, Z., Qian, X., & Ni, Y. (2011). A review on use of fillers incellulosic paper for functional applications. *Industrial & Engineering Chemistry Research*, *50*(2), 661–666.

Shen, J., Song, Z., Qian, X., & Song, C. (2008). Chitosan-coated papermaking grade PCC filler prepared by alkali precipitation: Properties and application. In *Proceedings of 2nd international papermaking and environment conference* Tianjin, 2008, (pp. 645–650).

Shen, J., Song, Z., Qian, X., & Yang, F. (2010). Carboxymethyl cellulose/alum modified precipitated calcium carbonate fillers: Preparation and their use in papermaking. *Carbohydrate Polymers*, *81*(3), 545–553.

Shin, T. G., Kim, C. H., Chung, H. K., Seo, J. M., & Lee, Y. R. (2008). Fundamental study on developing lignocellulosic fillers for papermaking (I). *Journal of Korea Tappi*, *40*(2), 8–15.

Sone, M., & Matsunaga, A. (1992). Coating sheet. *Japanese Patent 4041289*. Japanese Patent Office.

Song, D., Dong, C., Ragauskas, A. J., & Deng, Y. (2009a). Filler modification engineering for improved paper properties and papermaking process. In *TAPPI 2nd annual papercon'09 conference—Solutions for a changing world*.

Song, D., Dong, C., Ragauskas, A. J., & Deng, Y. (2009b). Filler modification with polysaccharides or their derivatives for improved paper properties. *Journal of Biobased Materials and Bioenergy*, *3*(4), 321–334.

Wu, S., Qian, X., Shen, J., & Song, Z. (2008). Development trend of pigments and fillers used in papermaking. *Paper and Papermaking*, *27*(2), 43–49 (in Chinese).

Yan, Z., Liu, Q., & Deng, Y. (2005). Improvement of paper strength with starch modified clay. *Journal of Applied Polymer Science*, *97*(1), 44–50.

Yoon, S. Y. (2007). Bonding material coated clay for improving paper properties. *PhD Thesis of Georgia Institute of Technology*.

Yoon, S. Y., & Deng, Y. (2006a). Clay-starch composites and their application in papermaking. *Journal of Applied Polymer Science*, *100*(2), 1032–1038.

Yoon, S. Y., & Deng, Y. (2006b). Starch-fatty complex modified filler for papermaking. *Tappi Journal*, *5*(9), 3–9.

Yoon, S. Y., & Deng, Y. (2007). Experimental and modeling study of the strength properties of clay–starch composite filled papers. *Industrial and Engineering Chemistry Research*, *46*(14), 4883–4890.

Zhao, Y., Hu, Z., Ragauskas, A. J., & Deng, Y. (2005). Improvement of paper properties using starch-modified precipitated calcium carbonate filler. *Tappi Journal*, *4*(2), 3–7.

Zhao, Y., Kim, D., White, D., Deng, Y., Patterson, T., Jones, P., et al. (2008). Developing a new paradigm for linerboard fillers. *Tappi Journal*, *7*(3), 3–7.