



Preparation and characterization of corn starch–calcium carbonate hybrid pigments



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ABSTRACT

This article presents a novel method for integrating native corn starch and calcium carbonate (CaCO_3) into a hybrid pigment, which can be applied in papermaking to increase the amount of starch in paper and improve sheet bonding without impairing dewatering. Starch was first thermally treated to partially gelatinize and swell the granules. The aim of the treatment was to change the surface properties of starch and thus to improve the interaction with CaCO_3 particles. CaCO_3 shell was precipitated around the swollen granules and the encapsulated starch was then cooked to achieve complete gelatinization. When the granules were cooked, the starch became active for bonding, but its solubility was very limited due to the encapsulation. Particle size measurement and scanning electron microscopy were used to analyze the sample properties during the preparation. The hybrid pigment was added to paper sheets and its effect on the paper properties was examined. Starch was shown to be effectively bound to the pigment structure. The hybrid pigment allowed a large amount of native corn starch to be added to paper without interfering with the papermaking process. Furthermore, it gave excellent mechanical paper properties.

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1. Introduction

Starch is one of the most abundant organic polymers on earth after cellulose. Despite being both composed of the glucose monomer ($\text{C}_6\text{H}_{10}\text{O}_5$), starch and cellulose have different molecular structures and properties. Cellulose consists of linear glucose units linked by beta linkages, whereas the glucose units in starch form both linear (amylose) and branched (amylopectin) molecules connected by alpha linkages (Zobel, 1988). Their roles in plants are completely different; starch is in the form of granules and acts as an energy storage, whereas strong cellulose fibers provide structural support for plants. The crystallinity of cellulose is high and it is insoluble in water, while the semicrystalline starch is water-soluble when heated. In paper and paperboard products, cellulosic fibers are the main raw material and provide the strength of the network by bonding to each other via a combination of hydrogen bonds, and van der Waals and electrostatic interactions (Hubbe, 2006; Lindström et al., 2005). Starch is also capable forming hydrogen bonds and it is used in papermaking as an additive mainly to improve both the dry tensile strength and the surface strength. Besides its availability, starch is also inexpensive, biodegradable

(Dipa and Sonakshi, 2012) and is widely used by many industries such as food, paper, textile as well as in adhesives.

Starch is stored in plants in the form of granules and has no binding properties in this form (Bruun, 2009). Prior to its use in papermaking, starch needs to be cooked into a dissolved form before it is added to the wet end of a paper machine. However, because the retention of native starch is very low, the starch is generally cationized to improve its adsorption onto the anionic pulp fibers. The cationic starch is significantly more expensive than native starch. The amount of cationic starch that can be added to the wet end is limited by the adsorption capacity of the other furnish components. Typically the retention of cationic starch reaches a plateau at 1.5–2% and the further addition of wet end starch will lead to a number of production problems such as high biological oxygen demand (BOD) levels, foaming, slime and sticky problems as well as interferences in runnability and drainage (Krogerus, 2007; Yoon and Deng, 2006). If it is desired to increase the starch content of paper or board beyond this amount, the starch must be added to the paper surface with a size press. This approach has a detrimental effect on paper machine speed and energy consumption since the surface starch must be dried with thermal energy.

Gelatinization means the irreversible process of swelling and finally solubilizing the starch granules when they are heated in an aqueous medium, typically in water (Hari et al., 1989; Lund and Lorenz, 1984). It can be ascribed as a reorganization of the

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molecular structure of starch, which is related to the hydration and swelling of the granules, leaching of amylose and changes in viscosity. During gelatinization, the intermolecular hydrogen bonds between the chains break and hydroxyl groups form bonds with water molecules. First the amorphous parts of the granules, which mainly consist of amylose, start to soften and swell. The water molecules and swollen amorphous parts push amylopectin chains apart breaking the crystalline structure of the granules. The swelling and gelatinization are greatly affected by the origin of starch as well as the amylose/amylopectin content (Fredriksson et al., 1998; Liu et al., 2006).

Inorganic minerals, like calcium carbonate (CaCO_3), clay and talc, are the second largest constituent in paper and board used either for filling or coating the product. Mineral pigments give good optical and surface properties to paper whilst improving also the dewatering and economic performance. However, when minerals are added to stock, they prevent fiber–fiber bonding leading to the decreased strength and stiffness of paper as well as increased dusting and size demand (Cao et al., 2011; Zhao et al., 2005).

Recently, improved cost-efficiency via increased mineral content has been the general trend in the paper industry. To minimize the strength reduction effects, paper manufacturers have developed methods to modify pigments with different strength adding polymers, such as starch. To avoid the difficulties which may result when adding large amounts of dissolved starch into the papermaking process, different techniques, such as precipitation of starch on top of the pigment (Yoon and Deng, 2006) or spray-drying of starch-coated pigments (Deng et al., 2011; Zhao et al., 2008) have been examined. Another possibility to prevent the accumulation of molecular starch has been the treatment of starch in a high solids content into a highly swollen (not dissolved) form followed by a rapid mixing with a pigment to give the pigment a shell structure of starch gel before adding it to the papermaking furnish (Hirvikoski and Laakso, 2014; Laleg, 2013a,b; Zhao et al., 2005). However, most of the reported techniques have been rather complex or have faced challenges in scaling up from a laboratory to an industrial level.

Composites from starch and filler for other applications than paper filling have also been widely developed and examined. Mixture of starch, fibers and CaCO_3 have been used to produce food containers from baked foams, where Glenn et al. (2001) have reported CaCO_3 to have negative impact on the mechanical properties of the foams. The replacement of synthetic materials by biodegradable starch-clay nanocomposites for packaging and food industry has also gained a lot of interest (Aouada et al., 2013; Avella et al., 2005; Chiou et al., 2006).

The target of this research is to form an encapsulated native starch hybrid pigment which imparts useful properties to paper and board products. The starch should be activated for bonding, but restricted from full dissolution. This gives increased sheet strength while maintaining good dewatering and wet end characteristics. Because the hybrid pigment is formed from low cost raw materials, i.e. native corn starch, lime (i.e. calcium oxide, CaO), and carbon dioxide gas (CO_2 , typically available from flue gas as a waste product), the potential cost structure of the new type of hybrid pigment is excellent and can be used to improve the overall cost structure of the paper or board where it is used. In addition, the process developed for the pigment preparation has been kept simple in order to generate an industrially feasible technique and a product, which could find use in many applications like as a fiber replacement in paper, additive in coating or packaging and in different composite applications.

2. Materials and methods

2.1. Materials

Lime was provided by Lhoist, Ltd. (La Mède, France) and native corn starch containing 25% amylose (560P) by Roquette, Ltd. (Lestrem, France). Bleached chemical pulps (pine and birch) were obtained from Stora Enso, Varkaus mill (Finland). Kemira Ltd. (Finland) provided cationic polyacrylamide (C-PAM, grade Fennopol K3400R), which was used as a retention aid in hand sheet preparation. As a reference pigment, commercial scalenohedral precipitated calcium carbonate (PCC, grade Syncarb FS-240 from Omya AG, Switzerland) was utilized in hand sheets. Deionized water was used in the experiments.

2.2. Thermal treatment of starch

Starch was thermally treated before using it in the hybrid pigment preparation. Granular starch was suspended in water and heated to initiate the gelatinization. The target of the treatment was to swell the granules, loosen their tightly packed semi-crystalline structure and make their surface stickier and more accessible for calcium ions to adsorb. To determine the temperature of the thermal treatment, the effect of various temperatures on the swelling, solubility and gelatinization of starch were investigated.

To identify the gelatinization parameters, the corn starch was analyzed with the differential scanning calorimetry (DSC, Mettler Toledo DSC821). The thermal transitions, i.e. the onset temperature (T_o), peak temperature (T_p) and the conclusion temperature (T_c), and the heat of gelatinization i.e. the enthalpic change (ΔH) during the endothermic process were determined. Calorimetric measurement was conducted by heating the starch suspension in excess water from 25 °C to 120 °C at a scanning rate of 10 °C/min in a sample pan. ΔH was calculated from the peak area of the endotherm. The degree of starch gelatinization (DG) after the thermal treatment was determined from the DSC data with the following procedure. The starch suspension was heated from 25 °C to the target temperature at a scanning rate of 10 °C/min, held at the temperature for a designated time, cooled to 25 °C and heated again to 120 °C. Various treatment temperatures and times were examined. DG was calculated by comparing ΔH for untreated starch with that for treated starch (Holm et al., 1988; Ratnayake et al., 2009):

$$\text{DG}(\%) = \frac{\Delta H_{\text{untreated}} - \Delta H_{\text{treated}}}{\Delta H_{\text{untreated}}} \times 100 \quad (1)$$

To measure the swelling power and solubility of starch, the thermal treatment of starch was conducted by heating the 8 wt.% starch suspension in a water bath for 10 min at various temperatures around T_o and cooling the starch suspension to room temperature. Swelling power and solubility of starch after thermal treatment were measured with the procedure similar to the method developed by Holm et al. (1988). Treated starch suspensions were decanted into centrifuge tubes and diluted to 3 wt.%. Untreated starch was also weighed into a centrifuge tube and diluted to the same concentration. The tubes were mixed with an overhead shaker (Heidolph Reax 2) for 1 h and centrifuged for 15 min at 3000G. The supernatant was removed from the centrifuged samples and dried in the oven. Swelling power and solubility of untreated and treated starches were calculated according to Leach et al. (1959):

$$\text{Swelling power} = \frac{\text{mass}_{\text{gel}}}{\text{mass}_{\text{starch, total}} - \text{mass}_{\text{solute}}} \quad (2)$$

and

$$\text{Solubility}(\%) = \frac{\text{mass}_{\text{solute}}}{\text{mass}_{\text{starch, total}}} \times 100 \quad (3),$$

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