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Modification of precipitated calcium carbonate with cellulose esters and use as filler in papermaking

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ABSTRACT

New hybrid materials of precipitated calcium carbonate (PCC) and cellulose esters (cellulose acetate and cellulose acetate butyrate) were prepared aiming to obtain new modified fillers for papermaking. A novel simple procedure based on the mixing of an aqueous suspension of PCC with an organic solution of the cellulose derivative, followed by the addition of the resultant mixture to hot water, was followed. The hybrids were characterized by several analytical and spectroscopic techniques. The organics content in the hybrids determined based on the carbon elemental analysis or by thermogravimetry, was found to be of *ca.* 10 wt%. Due to the presence of the organics the average size of the particles increased slightly in comparison to the unmodified PCC. Results of the modified PCCs as fillers in papermaking showed a slight improvement of some paper strength properties, whereas the structural and optical properties were not affected.

Keywords: PCC; Composites; Cellulose derivative; Paper filler; Papermaking

1. Introduction

The benefits of using mineral fillers in papermaking, particularly for the production of fine printing and writing papers, are widely recognized and thoroughly described in the literature: partial replacement of fibers by a cheaper material and improvement of the paper optical properties and also bulk and smoothness. For this reason, there is a general interest of the papermaking industry in increasing the filler content of paper, but for that it is also crucial to overcome the main drawbacks related to the presence of the mineral fillers: a decrease in fiber-to-fiber bonding and, as a consequence, a reduction of the paper strength properties, as well as additional problems of retention, dusting and white waters recirculation (Raymond et al., 2004; Thorp, 2005; Subramanian et al., 2007; Shen et al., 2009a, 2010). This is why in general, for a fine paper grade with 60 g/m^2 basis weight, values superior to 25% are uncommon and, at present, both fillers manufacturers and academia are focused in finding strategies for increasing the paper filler content. These strategies include, among others, the fillers surface chemical modification, with the objective of contributing to a better fiber-to-filler-to-fiber bonding so that no relevant negative impact on paper resistance occurs.

Several works have been developed on the modification of precipitated calcium carbonate by inorganic compounds (*e.g.* calcium-chelating agents, weak acids, aluminum salts, zinc chloride, and sodium silicate) (Passaretti, 1991; Tokarz et al., 1991; Chapnerkar et al., 1992; Wu, 1997; Snowden et al., 2000; Jaakkola and Manner, 2001; Shen et al., 2009a,b,c). However, these were mostly directed to obtain calcium carbonate-based filler with improved acid-resistant properties which are required for papermaking in weakly acid to neutral conditions. Recently, promising results have been obtained when using a modified PCC containing a dense film of silica on the surface of calcium carbonate crystals produced by sol–gel method (Gamelas et al., 2011; Lourenço et al., 2013). The main strength properties of kraft fibers based handsheets produced with this modified PCC have improved in comparison to those obtained using the unmodified PCC.

Nonetheless, most of the reported modifications of PCC regarding the improvement of its filler performance are those related to the modification of the PCC surface using

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organic compounds. Precipitated calcium carbonate has been treated/modified by organic compounds such as starch, starch derivatives, cellulose, carboxymethylcellulose, xanthan gum, water-soluble synthetic polymers, and polymer latexes, among others (Gill, 1991; Fairchild, 1995; Chen et al., 2005; Van Der Horst et al., 2005; Zhao et al., 2005; Myllymaki et al., 2006; Fairchild, 2008; Laleg et al., 2008; Nelson and Deng, 2008; Shen et al., 2010; Deng et al., 2011; Fan et al., 2012; Huang et al., 2013; Yang et al., 2013). In particular, in what concerns polysaccharides, an increase of Scott bond and breaking length was found for handsheets produced with the PCC treated with anionic polysaccharides (xanthan gum and anionic guar gum) (Fairchild, 1995). In another study, the handsheets produced with starch gel-coated PCC showed much better tensile strength than those produced from unmodified PCC, while the optical properties were not significantly affected (Zhao et al., 2005). In this context, it was claimed that the bonding strength between wood fibers and polysaccharides, namely starch, cellulose nanowhiskers, and regenerated cellulose nanospheres depended inversely on the crystallinity of the latter (Nelson and Deng, 2008).

Regarding cellulose derivatives, the use of carboxymethylcellulose (CMC) to modify PCC and its effect in papermaking properties has been reported. CMC-treated PCC could improve paper brightness in comparison to untreated PCC (Fairchild, 2008). CMC/alum modified PCC could greatly increase the filler retention in comparison to unmodified PCC (Shen et al., 2010). In certain conditions of alum dosage, the brightness and opacity of the produced handsheets were also found to increase while the main strength properties (tensile, burst and tear indexes) gave similar values. Besides, the use of CMC-treated PCC promoted an improvement of the sizing efficiency in papermaking (as measured by the Cobb test), in comparison to the untreated PCC (Van Der Horst et al., 2005).

In spite of the developments achieved so far there is still room to study the modification of PCC filler with cellulose derivatives (others than CMC) due to the relative low cost of the latter and ability to improve the filler-to-fiber interactions, since more strong interactions could be expected between the cellulosic pulp and the cellulose derivatives than with the PCC alone. In the present work, PCC was modified, by the first time, with cellulose acetate and cellulose acetate butyrate, which were chosen for their additional potential to establish hydrogen bonds with cellulosic fibers through the carbonyl groups of the ester bonds. The resultant new materials were characterized by several spectroscopic and analytical techniques and, besides, their papermaking performance as fillers was evaluated. The main objective of this work was to study alternative PCC-based materials to improve the paper strength properties when used as fillers.

2. Experimental

2.1. Materials and methods

Industrial scalenohedral PCC constituted by 95 wt% of calcium carbonate and 5 wt% of impurities was used (Gamelas et al., 2011). Cellulose acetate ($M_n \sim 30{,}000$, 40 wt% acetyl) and cellulose acetate butyrate ($M_n \sim 30{,}000$, 12–15 wt% acetyl, 36–40 wt% butyryl) were purchased from Sigma–Aldrich.

Thermogravimetric analysis was performed in a TGA-50 Shimadzu thermobalance under air atmosphere between 25 and 900 °C, with a heating rate of 10 °C/min. Carbon elemental analysis was done using a Fisons-EA-1108 CHNS-O analyzer. FTIR spectra were obtained in a Mattson 7000 FTIR, using KBr pellets. The spectra were measured in the 400–4000 cm^{-1} range with a resolution of 2 cm^{-1} and a number of scans of 64. Scanning electron microscopy (SEM) images were obtained on a Jeol JSM-5310. The samples were previously sputter coated with gold before the SEM images acquisition. Powder X-ray diffraction data were collected using a Philips X'Pert diffractometer operating in the Bragg-Brentano configuration with Co-kα ($\lambda = 1.79$ Å) radiation at a current of 35 mA and an accelerating voltage of 40 kV. Intensity data were collected by the step counting method (step 0.025° and time 0.5 s) in the range $2\theta = 5$–80°.

The particles size was measured by laser diffraction spectroscopy using a Mastersizer 2000 from Malvern Instruments (Antunes et al., 2008; Gamelas et al., 2011): aqueous suspensions of the modified PCCs containing a small amount of ammonium polycarbonate (Targon) were stirred, firstly with magnetic stirring during 20 min and then using ultrasounds during 15 min (50 kHz). A certain volume of the prepared suspension was added to water in the equipment vessel until a 10–20% obscuration was observed, and the tests were carried out setting the pump speed to 2000 rpm.

2.2. PCC modification by cellulose derivatives

1.75 g of cellulose acetate or 1.40 g of cellulose acetate butyrate was dissolved in 140 mL of acetone and to this solution a suspension of 14 g of PCC in 126 mL of water was added dropwise. The resultant mixture was added slowly to 350 mL of previously heated water at 40 °C. After 30 min of stirring, the solid was separated by filtration and dried in a vacuum exsiccator for 5 days.

The amount of cellulose derivatives in the hybrids was estimated either from the carbon elemental analysis results, or from the thermogravimetric weight loss between 220 °C and 500 °C, after subtracting the PCC impurities degradation contribution (Gamelas et al., 2011) to this loss. The synthesis of each new PCC-cellulose derivative was repeated at least two times to check for its reproducibility and, similar results, regarding the amount of cellulose derivative in the hybrid, were always obtained. The hybrid materials were characterized by the techniques mentioned in Section 2.1.

2.3. Retention tests in the dynamic drainage analyzer, handsheets production and papermaking properties

Drainage tests were performed with the unmodified PCC and with the different modified PCCs. Two different retention agents were also evaluated in each case, namely a linear cationic polyacrylamide (L-CPAM) and a branched cationic polyacrylamide (B-CPAM), in order to select the most appropriate one for the papermaking experiments. The drainage tests were performed in a dynamic drainage analyzer (DDA, AB Akribi Kemikonsulter, Sweden) with formulations containing fiber (*Eucalyptus Globulus* bleached kraft pulp, beating degree: 33 °SR, viscosity: 1010 cm^3/g, brightness: 85% ISO), unmodified PCC or modified PCC, starch, alkenyl succinic anhydride (ASA), and the retention agent. The amounts added (wt%) were 79.1, 19.8, 1.0, 0.1 and 0.02, respectively. A 60 mesh screen was used and a constant vacuum of 300 mbar and stirring of 800 rpm was applied. After drainage, the wet pad was collected and calcined at 525 °C for 16 h to determine the filler retention (adapted from the Tappi Standard T 211 om-93). All drainage

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