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PRINTING QUALITY OF PAPERS COATED WITH A MODIFIED PIGMENT OBTAINED BY *IN SITU* SYNTHESIS OF SILICA FILM ON PCC

Ana F. Lourenço, José A. F. Gamelas*, Pedro Faustino, Paulo J. Ferreira*

Chemical Engineering Department, University of Coimbra, Pólo II – R. Sílvio Lima, 3030-790 Coimbra, Portugal

* jafgas@eq.uc.pt; Tel.: +351 239798740; Fax: +351 239798703
* paulo@eq.uc.pt; Tel.: +351 239798747; Fax: +351 239798703

SUMMARY

The surface modification of the particles of precipitated calcium carbonate (PCC) with silica formed *in situ* by sol-gel method is presented by the first time. The new materials were characterized by infrared absorption spectroscopy (FTIR), thermogravimetry, scanning electron microscopy (SEM), and particles size distribution using the light diffraction scattering (LDS) technique, among other techniques. The FTIR spectra of the new modified PCC's, showed the presence of bands that were clearly assigned to vibrations of Si-O bonds, indicating the presence of silica. SEM images were slightly different of those of the original calcium carbonate particles, showing the typical scalenohedral shape of the PCC crystals with a dense and thin film of silica at its surface. The amount of silica formed at the PCC surface, as determined by thermogravimetric analysis, was found to increase with the increase of the ammonia concentration of the reaction medium (between 5% and 30% for [NH_3] of 0.05 and 0.5 M, respectively). LDS granulometric distributions of the new modified PCC's were close to the distribution of PCC, even that some variation in the average size of particles was noted. Preliminary results of the inkjet printing on papers coated with the new modified PCC's as pigments using polyvinyl alcohol and starch as binders are presented.

Keywords: coating, inkjet printing, PCC, silica, sol-gel.

INTRODUCTION

Different grades of silica (mostly fumed and precipitated silica) and precipitated calcium carbonate (PCC) are commonly used as pigments for the coating of printing and writing papers aiming to improve the inkjet printability. These pigments present high reflectance in all the visible wavelength range, superior brightness and refractive index, and also good compatibility with the other components used for the coating process (such as binders, co-binders, dispersants, etc.), which are important characteristics to consider in order to immobilize them at the paper surface and to obtain better printing quality properties. In particular, for the silica, its high porosity and hydrophilicity may help on a better retention of the dyes molecules at the paper surface [1-5].

Papers coated with porous silica particles are considered to have better performance regarding inkjet printing quality. On the other hand, PCC, a much cheaper material, is not so effective in the printing process. In this context, a new material which enhances the properties of both silica and PCC could be of great interest. Therefore, the purpose of this project is a) to effectively change the surface of PCC particles with small amounts of silica, and b) to use the modified PCC's for paper coating in order to improve printability and paper optical properties.

Several works have been reported on the modification of precipitated calcium carbonate, most of them directed to the application of PCC as a filler in papermaking, by inorganic compounds, including calcium-chelating agents (*eg*. sodium hexametaphosphate), weak acids (*eg*. phosphoric acid), sodium silicate, and zinc chloride [6-8], and by organic substances, such as starch, cellulose derivatives, chitin, chitosan, xanthan gum, water-soluble synthetic polymers, surfactants, and polymer latexes [8,9]. To our knowledge, there is no previous report on the modification of PCC by silica. A related work

reported briefly the use of silicone to coat calcium carbonate particles, being the materials characterized by ^{29}Si Nuclear Magnetic Resonance and thermal analysis [10].

In this paper we will report the production *in situ* of silica at the PCC surface by hydrolysis of tetraethyl ortosilicate (silica precursor) in ethanol/water solutions under alkaline conditions. Silica presence at the PCC surface was clearly shown by FTIR and SEM analysis. Their amount, as determined by thermogravimetric analysis, was found to vary between 5% and 30%, depending on the concentration of ammonia used in the reaction medium. The average size of the particles of the new modified fillers was not very different of that of the original PCC particles.

EXPERIMENTAL

Materials

An aqueous suspension of precipitated calcium carbonate was supplied from Specialty minerals, Inc. Tetraethyl ortosilicate (TEOS), absolute ethanol and 25% ammonia aqueous solution were from Sigma Aldrich.

The industrial suspension of PCC was vigorously stirred, and, then, filtered using a Buckner filter (0.2 μm). The solid obtained was dried in an oven at 105 ºC during 24 hours, and ground on a porcelain crucible to be used in the reactions described below.

A commercial calendered uncoated paper (80g/m^2) produced with a *Eucalyptus globulus* Kraft pulp was used as the base paper for the surface treatments. Targon 1128® (ammonium polycarbonate) was used as a dispersant and was supplied by BK Giulini Chemie GmBH. As binders there were used polyvinyl alcohol (PVOH) and native starch, both supplied by the industry. A 10% solution of PVOH in water was prepared to be used in the paper coating. Finally, an acrylic copolymer, Acrosol®, supplied by Clariant™ was used as a co-binder.

Modification of the PCC surface by hydrolysis and condensation of TEOS under alkaline conditions and characterization of the new materials

PCC modification:

Water (13.5 mL), ethanol (126.5 mL) and NH_3 25% (3.37 mL) were mixed inside a 250 mL flask. To the resulting solution, 1.5 g of PCC (in small portions) followed by TEOS (6.75 mL) were added under moderate mechanical stirring (200 rpm.) using a Heidolph RZR 2102 mechanical stirrer. The mixture having an ammonia concentration of 0.3 M was allowed to stand for 24 hours under constant stirring at a room temperature of ~21 ºC. The resultant solid was filtered on a G4 sintered glass filter and washed with 30 mL of ethanol. The solid was then dried in an exsicator under vacuum for about 5-6 days, and, finally, it was gently ground. Experiments with [NH_3] of 0.05, 0.1 and 0.5 M were also carried out.

Characterization:

The 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 4 cm^{-1} and a number of scans of 64.

The thermogravimetric analysis was performed on a TGA-50 Shimadzu thermo balance under air atmosphere between 25 ºC and 900 ºC, with a heating rate of 10 °C/min.

The SEM images were obtained in a Jeol Model: JSM-5310. The samples were previously sputtered with gold before the images acquisition.

The particles size was determined by light diffraction scattering (LDS) technique using a Mastersizer 2000 from Malvern Instruments. Previously to the measurements, suspensions of 1% (w/w) of the PCC samples in distilled water, to which a small amount of ammonium polycarbonate (Targon) was added, were prepared. These were stirred, firstly with magnetic stirring during 20 min., then, using ultrasounds during 15 min. (50 kHz), finishing with magnetic stirring again. A certain volume of the prepared suspension was added to 700 ml of distilled water in the equipment vessel until 10-20%

obscuration was observed, and the tests were carried out setting the pump speed to 2000 rpm. The results analysis was based on the Lorenz-Mie theory.

Porosity, pore size distribution, and density were measured using the AutoPore IV 9500 equipment from Micromeritics. For the surface area determination it was used the ASAP 2000 from Micromeritics.

Preparation of the mixtures for the paper surface treatment

PCC/PVOH suspension**:** 0.7 mL of Targon 1128 (6% of ammonium polycarbonate in water) were added to 10 g of PCC (or modified PCC), with manual stirring. After the dispersion of the pigment, it was added 5 mL of distilled water. Then, to the resulting suspension, 20 mL of a previously prepared PVOH solution (10% solids content) was added at room temperature with vigorous stirring.

PCC/starch suspension: water (at 60 ºC, 18.5 mL) was added to 5 g of native starch. After heating the mixture to 65 ºC with vigorous stirring, more 10 mL of hot water (60 ºC) was added and the heating was extended to 70 ºC. Then, 1,65 μL of α-amylase was added and the mixture was heated again up to about 80 ºC and left at this temperature for 5 min. The starch enzymatic conversion was stopped by the addition of 0.85 mL of a $ZnSO_4$ solution (30 g/L). The colloidal suspension obtained was heated up to 90–92 ºC, and left stirring at this temperature during 15 min. After, it was slowly cooled to 50 ºC and added to a mixture consisting of 15 g of PCC (or modified PCC) with 1.1 mL of Targon 1128 (6%), always with energetic stirring and at a constant temperature of 50 ºC.

Treatment of the paper surface

The formulations obtained were applied in both sides of the paper surface using a Mathis laboratory device, SVA-IR, with a 0,15mm roll and a 6m/min application velocity. The drying process was performed firstly by the device IR dryer and secondly by air-drying for at least 10 min. For the PCC/PVOH formulation the pick-up obtained was 3.9 ± 0.03 g/m^2 and for the PCC/starch it was 6.5 ± 0.25 g/m^2.

Printability

The surface treated papers were printed with a Lexmark x8350 using the plain paper mode and best print quality. The inkjet printing quality was evaluated by measuring the gamut area using the spectrophotometer *i1 Xrite*, and also the optical density (cyan, magenta, yellow and black), print-through and intercolor bleed, using the QEA portable digital microscope equipped with the personal image analysis system (PIAS II).

RESULTS AND DISCUSSION

Characterization of the industrial PCC

A PCC obtained from an industrial suspension was used as the material for the reactions. The FTIR spectrum of PCC showed the characteristic bands of calcium carbonate at 1458 cm^{-1} (ν_3 (CO_3)), 872 cm^{-1} (ν_2 (CO_3)), and 713 cm^{-1} (ν_4 (CO_3)) [11]. Some bands of very low intensity above 1750 cm^{-1} were observed as well, which could be due to the presence of low amounts of reagents and additives used in the industrial preparation of PCC. The thermogram showed a weight loss between about 250 ºC and 500 ºC (2.0%), confirming the existence of some impurities in the solid PCC. In addition, between 580 ºC and 850 ºC, a weight loss of 41.5% was observed, due to the thermal degradation of calcium carbonate to calcium oxide and carbon dioxide. From this value and taking in account that a pure calcium carbonate (100%) should give a weight loss of 44.0%, the purity of the sample was estimated to be of about 94-95%.

PCC was also characterized for its porosity, surface area, and density (Table 1). The values obtained were in agreement with expected values [12]. Optical microscopy photographs showed PCC crystals

with the characteristic scalenohedral shape and individual sizes around 1-2 μm. Some aggregation of the crystals was also noticed.

Table 1. Porosity, density, and surface area for PCC

Porosity (%)	Average pore size (μm)	*Bulk* density ($g/cm^{3)}$	*Skeletal* density ($g/cm^{3)}$	Real density (g/cm^3)	Surface area (BET, m^2/g)
74.5	1.24-1.47	0.42	1.63	2.65	3.9

Silica formed in situ at the PCC surface: synthesis

Formation of silica (or silica oligomers) particles by the sol-gel method is usually based on the reactions of hydrolysis and condensation of tetra-alkoxysilanes as precursors [13-14]. The reactions can be carried out in aqueous medium or more frequently in mixtures of water and an alcoholic solvent (co-solvent), in acidic or alkaline conditions, and are very sensitive to the H_2O/Si molar ratio, pH, co-solvent effect, temperature and time of reaction, among other factors [14-16].

The possibility of growing silica particles at the surface of cellulose matrix was already demonstrated [17,18]. However, to our knowledge, there is no report regarding the surface modification of PCC by silica formed *in situ* by sol-gel method. The preparation of silica-modified PCC particles can confer important optical and chemical properties to the PCC.

To prepare novel PCC-silica composites, the reactions should not be carried out under acidic conditions because of the dissolution of the PCC (unless the contact time of the PCC with the silica sol before the isolation of the composite is kept to a minimal value). In fact, some preliminary reactions carried out in aqueous solutions, using a two-step method, first with nitric acid as the catalyst for the hydrolysis (step 1), and, then, with ammonia to accelerate the condensation reaction (step 2), either afforded premature formation of silica gel and/or originated some PCC dissolution. Moreover, no reproducible results could be obtained.

On the other hand, by performing the hydrolysis/condensation of TEOS in ethanol/water (~9:1, v/v) solutions under alkaline conditions (using ammonia as the catalyst) and at a temperature of ~21 ºC, the formation of silica was clearly detected at the PCC surface without dissolution of the mineral (see below). Experiments with different concentration of ammonia were conducted in order to check any possible influence on the amounts of silica produced at the PCC surface and on the size of the modified PCC particles [18]. It should be noted that, at the end of reactions, the solid was easily separated by filtration, and for each set of experiments, the results regarding the amount of silica formed at the PCC surface were quite reproducible (as demonstrated below).

The thermograms of the modified PCC's showed typically three steps of weight loss: one up to about 120 °C of 0.2% to 2.6% corresponding to the release of the water molecules present in the samples; a second loss from 250 °C to about 500 °C due to the degradation of the additives used in the synthesis of PCC; and, finally, a third loss, between about 580 and 830 ºC, due to the degradation of calcium carbonate. Based on the analysis of the thermogravimetric plots it was possible to obtain the amount of all the components present in the composites, namely the calcium carbonate and silica. Modified PCC's with silica content ranging from 5% to 29% could be obtained.

From the results of the silica content of the new modified PCC's, it seems that the increase of the ammonia concentration (under the other experimental conditions constant) has an effect of increasing the amount of silica formed at the PCC surface (Fig. 1). This could be due to the increase on the extent of the condensation reactions. This result is quite important regarding the application of the modified PCC either as a filler or as a coating pigment in the papermaking. The amount of silica formed on the PCC may, thus, be controlled simply by changing the ammonia concentration in the reaction medium.

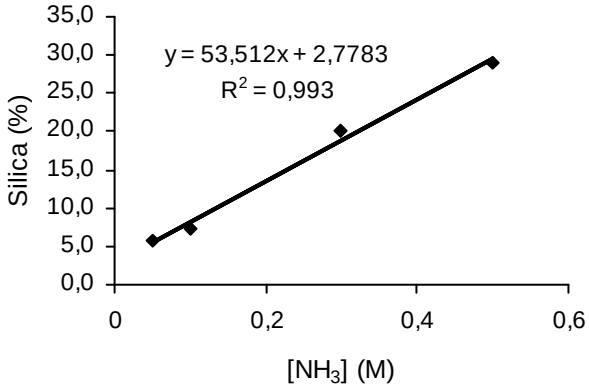

Figure 1. Amount of silica produced at the PCC surface *vs*. ammonia concentration in the medium

Spectroscopic characterization by FTIR and image analysis (SEM) of the new silica-modified PCC materials

FTIR spectroscopy is a good technique to evaluate the presence and the extent of the silica formation at the PCC surface. A few spectra of selected samples are presented in Fig. 2, including the spectrum of industrial PCC for comparison. Infrared spectra of the modified PCC's showed several bands (marked with +), not observed in the spectrum of original PCC (original bands marked with *), which clearly indicate the presence of silica [19,20]. In particular, in the region below 1300 cm^{-1}, a band with maximum at 1080-1085 cm^{-1} was observed which is due to the asymmetric stretching of the Si-O-Si bonds. Bands of lower intensity near 955 cm^{-1}, 800 cm^{-1} (due to the symmetric stretching of the Si-O-Si bonds), and 465 cm^{-1} (due to the δ (O-Si-O) bending mode) were also observed. The relative intensity of these bands in comparison to those of PCC varied with the nature of the sample. It is obviously deduced that in the samples presenting higher intensity silica bands, a larger amount of silica should be present. In fact, the results are in line with the amounts of silica estimated by the thermogravimetric analysis. For the PCC modified with only 5% of silica, all the bands, except that due to δ (O-Si-O), could still be observed.

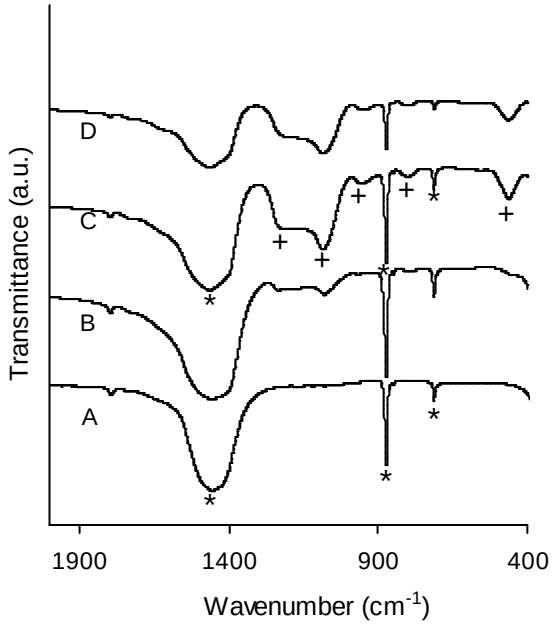

Figure 2. FTIR spectra of PCC (A) and samples of PCC modified with silica (B, 6%; C, 21%; and D, 29%)

SEM images of the modified PCC's were slightly different of those of the original PCC (Fig. 3). It seems that the scalenohedral shape of the PCC crystals is still preserved. However, the crystals are not as "clean" and well-shaped as those of PCC, which must be due to the presence of a coating at their surface. No discrete spherical silica particles could be detected for any of the samples analyzed. Thus,

these results seem to indicate that a dense and thin film of silica must have been formed at the surface of the PCC particles.

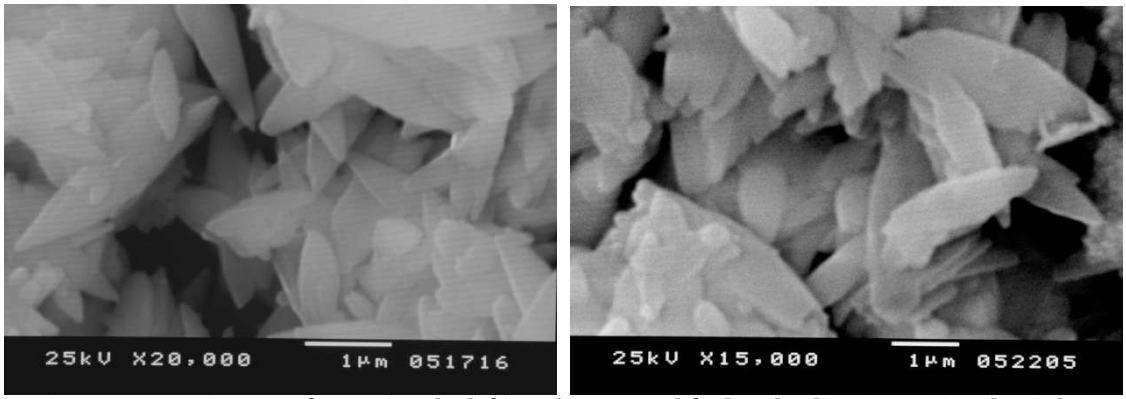

Figure 3. SEM images of PCC (on the left) and PCC modified with silica (27%) (on the right)

Particles size distribution of the new silica-modified PCC materials

The particles size distribution, expressed in terms of particles volume and particles number was determined by LDS for PCC and several samples of PCC modified with silica. The results presented in Fig. 4 show that the shape of the size distributions curves is similar. However, the maximum of the distribution of the particles volume is shifted to higher values of particles size for the silica-modified PCC compared with PCC and for increasing amounts of silica at the PCC surface. The dp50 values have a similar tendency. Average dp50 value was of 4.0 µm for the original PCC particles, 4.4 µm for the PCC with 5% of silica, 5.4 µm for the PCC with 19% of silica and of 6.9 µm for the PCC with 29% of silica. These results indicate that the changes of the particles size after PCC modification with silica are not very significant.

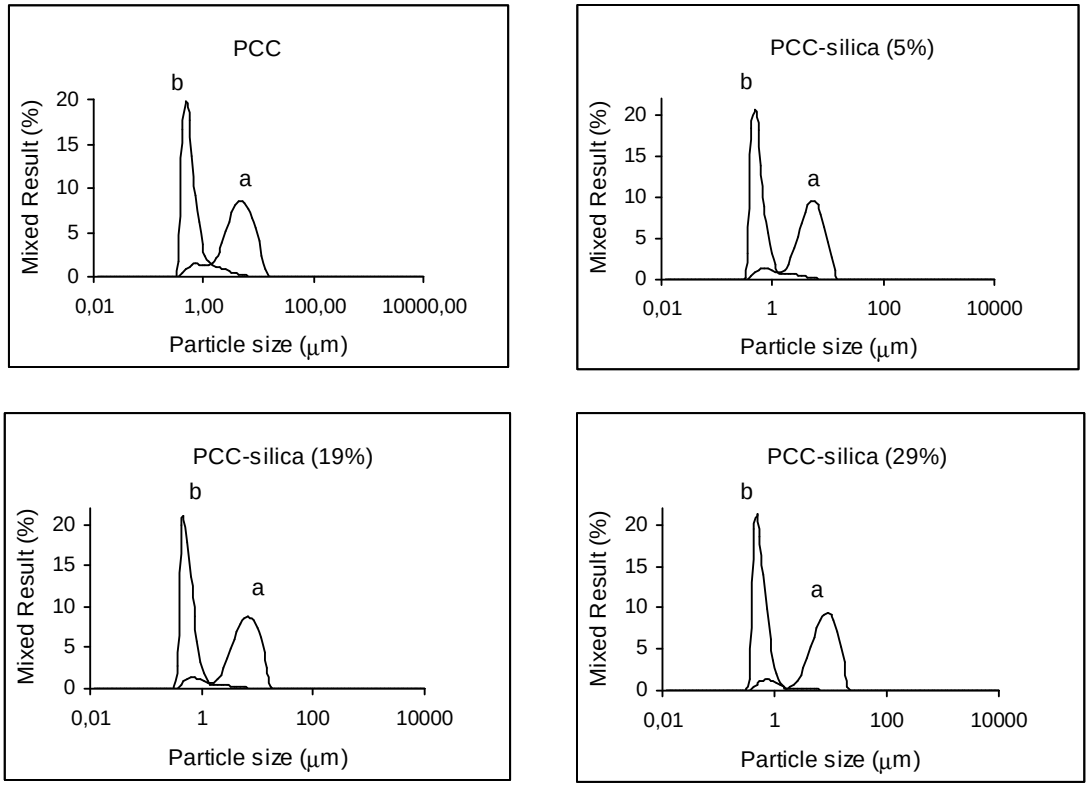

Figure 4. LDS granulometric distributions of PCC and PCC's modified with silica (expressed in terms of particles volume (a) or particles number (b))

It should be noted that the results of particles size expressed in terms of volume may give an erroneous idea of the real size of the individual crystals of PCC. In fact, the results determined from the volume curves indicate the formation of a small number of aggregates having sizes of about 3-10 μm which occupy a comparatively high volume. The major part of the particles, *i.e.*, the individual crystals, is much smaller as can be confirmed by expressing the particles size distribution in terms of the number of particles (Fig. 4).

Printability

The base paper from *Eucalyptus globulus* Kraft pulp was treated with formulations containing modified PCC as pigment (or non-modified industrial PCC for comparison) and polyvinyl alcohol or native starch as binders. The surface treated papers were, then, printed with a Lexmark x8350 and several printing quality parameters evaluated. The results of these parameters are presented in Table 2.

Table 2. Inkjet printing quality parameters for the papers coated with PCC's

Mixtures used in the paper surface treatment	Gamut Area	Optical Density				Print-Through	Intercolor Bleed
		Cyan	Magenta	Yellow	Black		
PCC/PVOH	7579	1,07	1,19	0,85	1,536	0,29	59,8
PCC-silica(20%)/PVOH	6986	0,82	1,13	0,83	1,044	1,05	38,1
PCC-silica(29%)/PVOH	6792	0,79	1,09	0,81	1,182	0,69	33,5
PCC/starch	6862	0,94	1,10	0,83	1,196	0,66	20,1
PCC-silica(20%)/starch	7354	0,97	1,22	0,87	1,242	0,61	63,8

For PVOH as binder, the preliminary results obtained indicate a general decrease of the printing quality parameters when using silica-modified PCC as pigment in comparison to the use of original PCC. However, the intercolor bleed improved significantly, *i.e.*, was lower for the papers treated with the PCC-silica composites and PVOH. On the other hand, for starch as binder, a general improvement in the printing quality was observed by the use of silica-modified PCC for the paper surface coating. In order to improve the quality of these results other experiments are planned based on the use of PVOH with different polymerization degrees.

CONCLUSIONS

The *in situ* synthesis of silica at the surface of PCC particles using sol-gel method is presented. Hydrolysis (and condensation) of TEOS under alkaline conditions was conducted in the presence of the PCC particles. The presence of silica at the PCC surface in the new materials was shown by FTIR, SEM and thermogravimetry. It was found that a higher ammonia concentration of the reaction medium introduced a higher amount of silica on the materials. Modified PCC with silica content near 30% could be obtained by performing the reaction with an ammonia concentration of 0.5 M. Interestingly, the particles size distribution of the modified PCC´s was similar to that of the original PCC, except for a slight increase in the dp50 (expressed in terms of particles volume), meaning that the modification of the PCC particles did not introduce major alterations in the dimensions and aggregation of the individual crystals, as confirmed by SEM. When the new modified PCC's were evaluated as pigments for the paper coating (with polyvinyl alcohol and starch as binders) no improvements on the printing quality parameters evaluated could be detected in comparison to the use of original PCC. However, other experiments have to be performed in order to conclude about the possible benefit or not of the use of the particles of PCC modified with silica for the paper coating.

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