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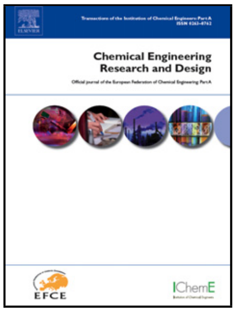

Title: Precipitated calcium carbonate modified by the layer-by-layer deposition method - its potential as papermaking filler

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Graphical Abstract (for review)

PCC

(CaCO$_3$)

+

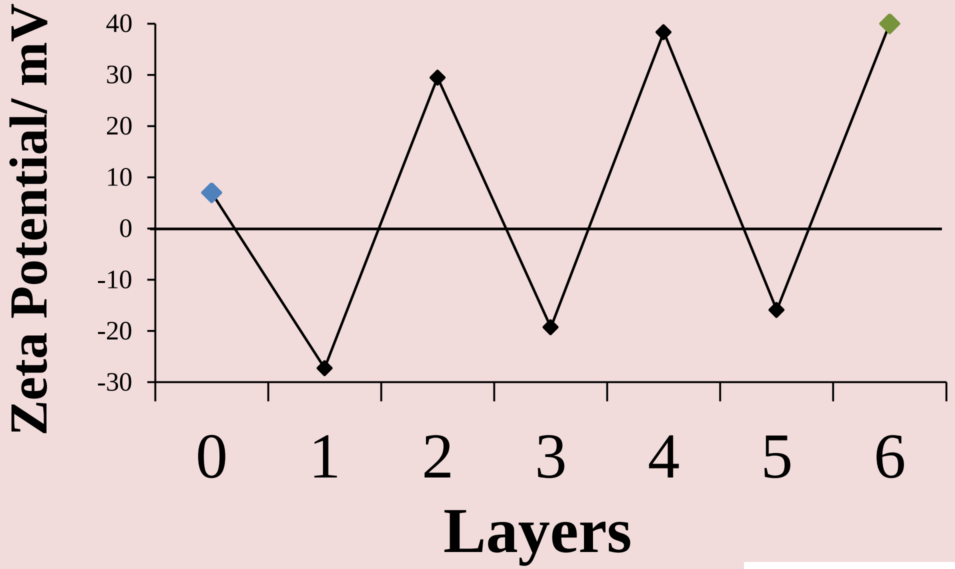
Sodium Alginate

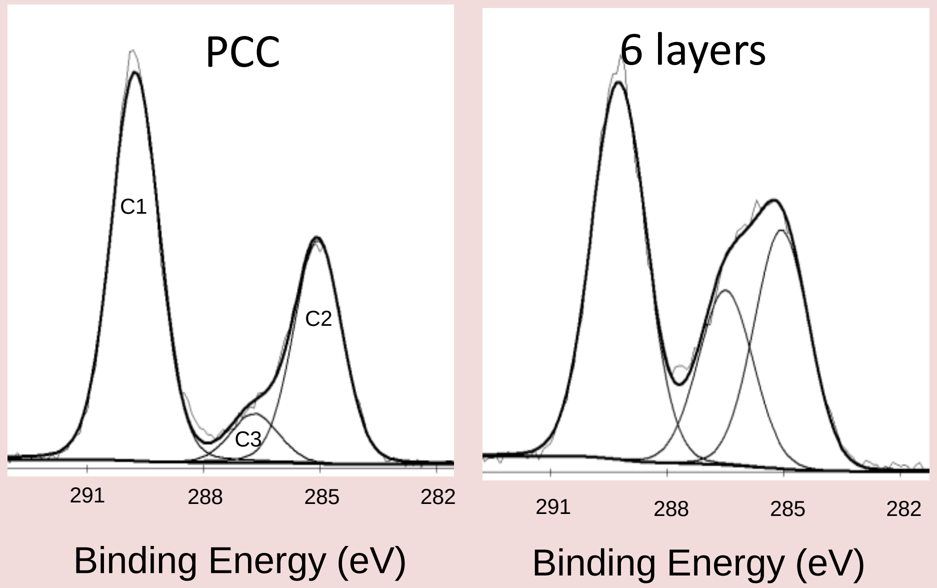
+

Poly(diallyldimethyl ammonium chloride)

Layer-by-Layer Assembly

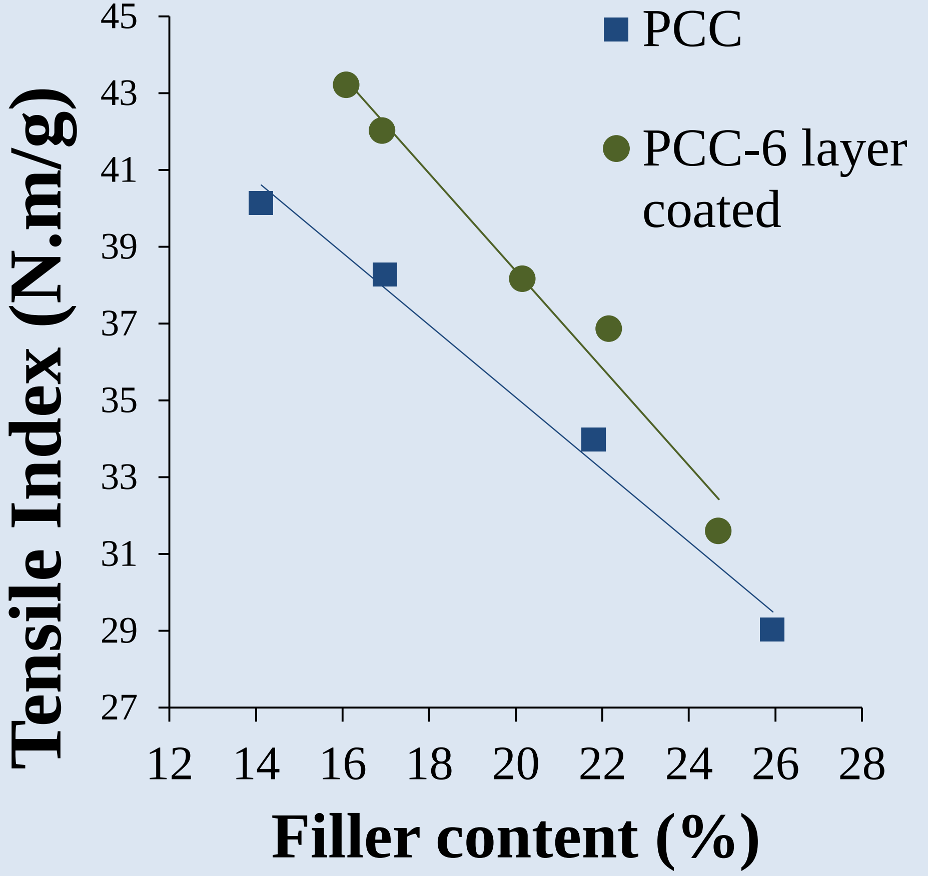
Coated PCC





+ eucalyptus fibres →

Handsheets Tensile Strength



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Highlights:

New PCC-based filler modified by the layer-by-layer deposition method was produced

New filler contained alternating layers of alginate and poly(diallyldimethylammonium)

When used in papermaking, the main handsheets strength properties improved (vs PCC)

The bulk was lower and the optical properties were not significantly affected (vs PCC).

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Precipitated calcium carbonate modified by the layer-by-layer deposition method - its potential as papermaking filler

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Keywords: sodium alginate, poly(diallyldimethylammonium chloride), precipitated calcium carbonate, papermaking; paper strength

Abstract

The surface modification of papermaking fillers with compounds that promote a better bonding with the cellulosic fibres is nowadays one of the strategies used to increase the filler content in paper without sacrificing the mechanical properties. In this study precipitated calcium carbonate (PCC) was surface coated with poly(diallyldimethylammonium) using the layer-by-layer deposition method with alginate as an intermediate bonding polyelectrolyte. The deposition of small amounts of both polyelectrolytes at the surface of PCC was confirmed by different techniques, namely by zeta potential measurements and X-ray photoelectron spectroscopy. The filler particles coated with two layers (one layer of each polyelectrolyte) and with six layers (three alternating layers of each anionic and cationic polyelectrolyte) were used in laboratory papermaking tests. It was observed that the handsheets mechanical resistances were better with the six-layer coated PCC than with the reference PCC whereas the optical properties were not significantly affected. It is therefore possible to increase the filler content in paper using a new PCC-based filler obtained by a cheap and simple modification method.

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1. Introduction

One of the challenges in papermaking is to preserve paper strength while reducing the amount of virgin fibres. Several approaches to use less fibres are available, depending on the paper grade, such as reducing the basis weight, using recycled fibres or replacing fibres by mineral fillers, all of them having however a detrimental effect on paper strength. Fillers, such as calcium carbonate or clay, are often less expensive than virgin fibres and the increase of their content in papermaking has been reported over the years (Raymond et al., 2004; Lourenço et al., 2014). Nonetheless, the filler content is limited to values close to 30% (w/w) due to their significant negative impact on paper strength since they interfere with the fibre-to-fibre bonding. On the contrary, they have a positive effect in bulk, opacity and brightness (Hubbe et al., 2008).

From an economical point of view, considering the market prices of 100 and 500 $/ton for calcium carbonate and kraft pulp, respectively, then a 5% increase of the filler content would lead to savings of 20 $/ton of paper (Cheng et al., 2011; Schaefer et al. 2015). This means that a mill running at 1800 tons/day with 20% of filler, would save more than 13 M$/year if 25% of filler was employed.

One way to increase the filler content in paper and keep good strength properties is based in the filler surface treatment/modification. Many reports in the literature can be found concerning the modification of precipitated calcium carbonate (PCC) aiming at using the filler in acidic papermaking conditions (Passaretti, 1991; Wu, 1997; Shen et al., 2009a; Jaakkola and Manner, 2001), improving retention (Gill, 1991; Laleg et al., 2008; Shen et al., 2010; Huang et al., 2013) or enhancing the optical properties of the filler (Withiam et al., 2000; Fairchild, 2008). The most promising modifications to improve the paper strength properties are those with starch at the surface of PCC, since the handsheets tensile strength is greatly improved when compared to that obtained with

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unmodified PCC, while the optical properties are not significantly affected (Zhao et al., 2005; Shen et al., 2009b). With the same purpose, other filler modifications with organics also afforded interesting results (Laleg et al., 2008; Fairchild, 1995; Gamelas et al., 2014). Recently, the authors of the present paper have produced by the sol-gel method a new PCC-based filler containing a film of silica at the surface of the mineral particles that can mitigate the negative influence of higher filler contents in the mechanical properties of paper (Gamelas et al., 2011; Lourenço et al., 2013). With this modified PCC, it was possible to increase the filler content in 5% without affecting the tensile strength properties (Lourenço et al., 2014).

A strategy for the modification of PCC may be based on the treatment of the mineral particles with polyelectrolytes that promote the filler-to-fibre bonding, such as poly(diallyldimethylammonium chloride) (Fig. 1a), hereafter noted as PDMA. This polyelectrolyte is commonly used in wastewater treatment, mainly as a flocculant, and also as a retention and drainage aid in papermaking (Roach et al., 2011; Allen and Lyman, 1999; Taipale et al., 2010, Allen and Lapointe, 2005). The quaternary amine fraction of this compound provides a constant positive charge to the polymeric strand and bridging and patching aggregation mechanisms are expected to occur with negatively charged particles, such as cellulosic fibres.

However, no specific bonds are expected to occur between the ionic structure of the mineral and the polymeric structure of PDMA. Besides, PCC has a slightly positive surface charge in aqueous medium, that is, of the same signal of PDMA, which, obviously, does not favor the attraction between these two substances. This difficulty may be overcome by using a layer-by-layer (LbL) method, in which an intermediate negatively charged polyelectrolyte able to electrically interact both with the positive sites of the calcium carbonate particles and with PDMA is firstly deposited on the

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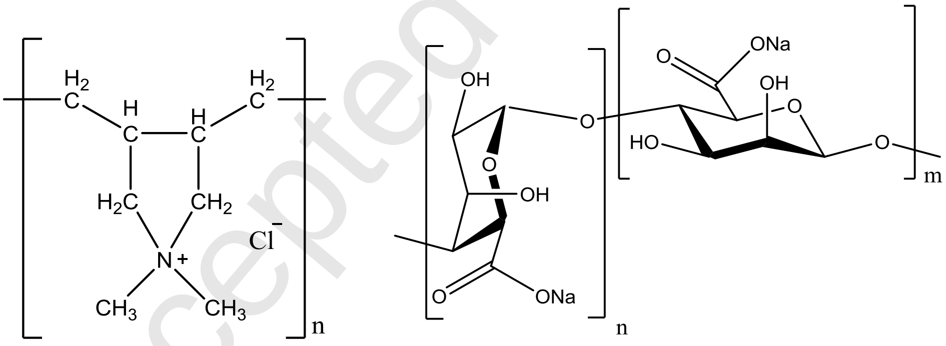
surface of PCC. Alginate may be chosen for the first layer (anionic layer). Alginate (Fig. 1b) is an abundant linear polysaccharide obtained from brown algae with a great affinity between its guluronic and mannuronic acids to calcium ions (Gombotz and Wee, 1998) and therefore it is already used with calcium carbonate in several applications, namely for capsules fabrication, hydrogels to control mineralization processes, nanoparticles for codelivery of genes and drugs, among others (Antipov et al., 2003; Ma and Feng, 2011; Zhao et al., 2012). Besides, alginate has a rigid molecular chain and good film forming ability (Siddaramaiah et al., 2008) which makes it a good candidate for the PCC modification.

In the present work the authors propose the modification of PCC with PDMA in order to promote better filler-fibre bonding in the papermaking process. The modification was performed using the LbL method, in which alternating layers of alginate and PDMA were deposited at the surface of PCC particles.



(a) (b)

Figure 1. Chemical structure of (a) poly(diallyldimethylammonium chloride) and (b) sodium alginate.

2. Experimental Section

2.1. Materials and Methods

Industrial scalenohedral PCC constituted by ca. 95 wt% of calcium carbonate and 5 wt% of impurities was used (Gamelas et al, 2011). Sodium alginate from brown algae

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and poly(diallyldimethylammonium chloride) solution (20 wt% in water) were purchased from Sigma-Aldrich. Aqueous solutions at 0.1 wt% of these two components were prepared: sodium alginate was dissolved in hot water (60 ºC) and the concentrated aqueous solution of PDMA was diluted in water.

X-ray photoelectron spectroscopy (XPS) analyses were carried out on pellets of 1 mm thickness prepared in duplicate by pressing the samples at ≈40 MPa during 2 min. The XP spectra were obtained using a Kratos AXIS Ultra HAS equipment. The analysis was carried out with a monochromatic Al Kα X-ray source (1486.7 eV), operating at 15 kV (90 W), in fixed analyser transmission mode, with a pass energy of 80 eV. Wide scan survey spectra were recorded at a take-off angle of 90º and binding energy between 0 eV and 1350 eV, with a step size of 1 eV and dwell time of 200 ms. 3 different survey areas were averaged. High-resolution C1s spectra were obtained with a step size of 0.1 eV and a dwell time of 1000 ms. Peak fitting of the C1s spectra was performed using Gaussian-Lorentzian peak shapes and Shirley-type background subtraction.

Scanning electron microscopy (SEM) images were obtained in a Jeol JSM-5310. The samples were previously sputter coated with gold before the SEM images acquisition. The particles size was measured by laser diffraction spectroscopy (LDS) using a Mastersizer 2000 from Malvern Instruments. A small amount of ammonium polycarbonate (Targon 1128, BK Ladenburg, Germany) was used as dispersant. The zeta potential was determined by measuring the electrophoretic mobility in a Zetasizer Nano ZS from Malvern Instruments. For both measurements, aqueous suspensions of the modified PCCs were stirred, firstly with magnetic stirring during 20 min. and then using ultrasounds during 15 min. (50 kHz).

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2.2. Modification of PCC by LbL method

Several layers of alginate and PDMA were alternately deposited on the PCC particles surface. For the first layer, a solution of sodium alginate was mixed, at 60°C, with PCC at a mass ratio of 95:5 (PCC:alg) and cooled to room temperature under vigorous stirring. After a vacuum filtration the solid was thoroughly washed with distilled water to remove residual polyelectrolyte not bound to the PCC. The final product was dried in an exsiccator for one day. For the second layer, a PDMA solution was added to the aforementioned dried product a ratio of 95:5 ((PCC:alg):PDMA). Again, the resultant solid was separated by filtration, water washed and dried for one day. The mentioned mixing, filtration, washing and drying procedures were repeated until deposition of six alternating layers of the polyelectrolytes (PCC:alg:PDMA:alg:PDMA:alg:PDMA), with the objective of increasing the surface coating of the PCC particles with PDMA and therefore their potential to interact with the cellulosic fibres. In fact, with the LbL methodology only minor amounts of each modifier remain attached to PCC (Peng et al., 2010; Sasaki et al., 2011) and therefore several layers of both polyelectrolytes have to be applied to efficiently coat the PCC particles. The final product was dried in an exsiccator for 4 days.

Table 1 lists all the produced LbL samples. Note that some of the samples were obtained only as intermediate materials and have not been considered for full characterization and further papermaking tests. Considering that the objective is to use positively charged fillers, emphasis was put in the two-layer coated PCC (S2) and six-layer coated PCC (S6).

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Table 1 – LbL samples produced with PCC, alginate and poly(diallyldimethylammonium)

PCC	S0
PCC:alg	S1
PCC:alg:PDMA	S2
PCC:alg:PDMA:alg	S3
PCC:alg:PDMA:alg:PDMA	S4
PCC:alg:PDMA:alg:PDMA:alg	S5
PCC:alg:PDMA:alg:PDMA:alg:PDMA	S6

2.3. Handsheets production and papermaking properties

Before producing the handsheets, several suspensions and solutions of the different paper components were prepared. *Eucalyptus globulus* bleached kraft pulp (refining degree 33 ºSR; viscosity 1010 cm^3g^{-1}; brightness 85% ISO) was used as the cellulosic fibre source. Aqueous suspensions of the unmodified and modified PCC containing 1 wt% of filler were prepared and stirred, first with magnetic stirring (20 min) and after with ultrasound (15 min, 50 KHz) before use. Alkenyl succinic anhydride (ASA) was used as the internal sizing agent after stabilization by adding it to a 3% starch suspension standing at 60 ºC (Saraiva et al., 2010). A 0.025% aqueous solution of a linear cationic polyacrylamide (C-PAM) used as retention agent was prepared by dissolving the solid in water. These additives were supplied by the industry.

Handsheets were produced in a batch laboratory sheet former (255/SA model, MAVIS) using a 120 mesh screen with formulations containing all the aforementioned constituents. The aim was to achieve a basis weight of 80g/m^2. The added amounts of fillers ranged from 17 to 30% of the total furnish composition. Amounts of 1.00, 0.12 and 0.02 wt% for starch, ASA and C-PAM, respectively, were used. For the handsheets production, a mixture of the fibre suspension with the PCC suspension was first prepared. After 120 s of stirring, the starch/ASA mixture (at *ca.* 60 ºC) was added. C-

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PAM was then added after a total time of 290 s and allowed to stir for more 5 s. The mixture was transferred into the sheet former and after 10 s of air agitation drainage was performed. The total contact time of the retention agent with the other components in the mixture was *ca.* 30 s. The sheets were collected from the web and pressed, dried and conditioned according to the ISO 5269-1 standard. The basis weight, bulk, tensile, tear and burst resistances, light scattering, opacity and brightness were measured according to the corresponding ISO Standard Test Methods. The internal bond strength was also measured using the corresponding Tappi Standard. Finally, the handsheets were calcined at 525 ºC for 16 h to determine the effective filler content of PCC or modified PCC, based on the Tappi Standard T 211 om-93 for ash determination (equation (1)). The loss intrinsically due to the filler occurring during the thermal treatment at 525 ºC was also accounted for, as a correction factor (Lourenço et al., 2013). The filler retention in the handsheets, defined as the ratio between the effective and the nominal (target) filler content, can also be obtained.

$$\text{Filler content (\%)} = \frac{\text{weight at } 525^{\circ}\text{C}}{(\text{weight of dry handsheets}) \times (100 - \text{correction factor})} \times 10^4 \quad (1)$$

3. Results and discussion

3.1 Characterization of the new modified PCCs

The new PCC fillers were characterized by several techniques in order to confirm the deposition of the polyelectrolytes on the surface of PCC and to verify if they did not differ much from the unmodified particles in terms of size and shape, since these are important parameters to maintain in the papermaking process.

The adsorption process of the several layers on PCC was monitored by measuring the electrophoretic mobility after deposition of each layer. Starting from PCC particles

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with a zeta potential in aqueous solution of +7 mV, the zeta potential alternated between ca. -30 mV and +40 mV during the deposition of the 6 polyelectrolyte layers (Fig. 2). These results show convincingly the alternate adsorption of alginate (giving negative zeta potential) and poly(diallyldimethylammonium) (giving positive zeta potential) on the surface of PCC. Besides, a slight increase of the zeta potential with the number of deposited layers from layers 2→ 6 seems to occur, what may be considered an evidence of the increase of poly(diallyldimethylammonium) adsorption in the course of the layer-by-layer assembly.

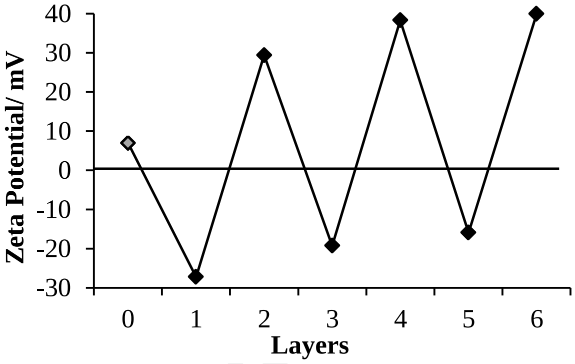

Figure 2. Evolution of the zeta potential of PCC in the LbL-coating with alternating layers of alginate (1, 3 and 5) and poly(diallyldimethylammonium) (2, 4 and 6).

The surface of the modified PCCs was analyzed by X-ray photoelectron spectroscopy (Table 2). With the modification, the amount of carbon, in atomic percentage, slightly increased while the amount of oxygen slightly decreased, confirming increased amounts of the organic modifiers added to the surface. After the PDMA deposition (samples S2 and S6) it was expected to find some nitrogen (Fig. 1a). However, the later was not detected, probably due to the small amount of the polyelectrolyte that is effectively present at the surface of PCC. Low amounts of magnesium were also shown at the surface of PCC (present due to the PCC synthesis).

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Table 2 – XPS atomic percentages and results of peak fitting of C1s signal for unmodified PCC (S0) and PCC modified with 1, 2 and 6 alternating layers of alginate and poly(diallyldimethylammonium) (S1, S2 and S6, respectively).

Material	C	O	Ca	Mg	C1s*		
					C1(%)	C2(%)	C3(%)
S0	35.2	49.8	13.6	1.4	57.5	35.4	7.1
S1	35.9	49.4	13.8	0.9	57.8	29.3	12.9
S2	36.7	48.5	14.1	0.8	54.8	29.9	15.3
S6	37.4	48.3	13.9	0.4	47.6	29.7	22.7

*C1 refers to carbonate species; C2 to C-C and C-H bonds and C3 to C-O bonds.

Additional information on the presence of the polyelectrolytes at the surface of PCC was obtained from the high-resolution C1 s spectra (Fig. 3). The peak fitting of the C1 s spectrum of the original PCC revealed three individual signals at ca. 290 eV, 285 eV and 287 eV with approximate relative intensities of 57.5, 35.4, and 7.1%, respectively (Table 2, Fig. 3a). The former, C1, is attributed to carbonate species; the one at lower binding energy, C2, is attributed to the adventitious aliphatic (C-C; C-H) carbon; and the intermediate one with low relative intensity, C3, is attributed to C-O bonds (Surface Science Western, 2014; Belgacem et al., 1995), which may arise from impurities present at the surface of PCC. After the deposition of the alginate layer, it was found that C3 increased in intensity to 12.9%, while C2 decreased to 29.3% (Table 2). This confirms the presence of alginate chains (Fig. 1b) at the surface of the PCC particles. The further coating of PCC with one layer of PDMA (sample S2) provided results similar to those obtained after the deposition of the alginate first layer, except for a slight decrease of the signal due to carbon from carbonate (Table 2, Fig. 3b). For the coating with PDMA a slight increase of C2 and a decrease of C3 (C-O bonds) could be predicted based on the structure of this polyelectrolyte. The different trend observed for C3 may indicate a not fairly homogeneous coverage of filler particles by PDMA in the two-layer coated-PCC.

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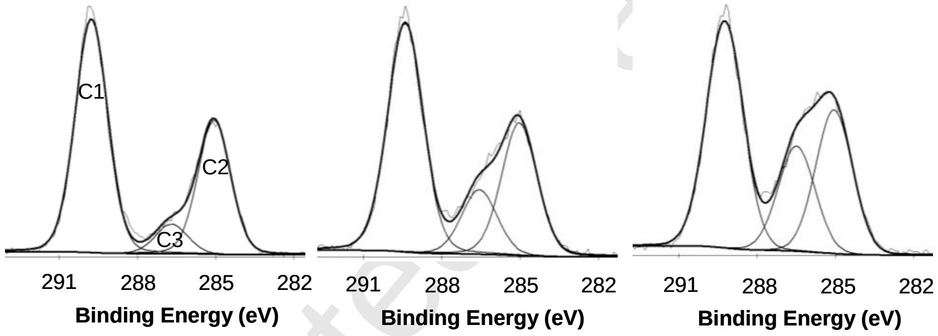
After coating the PCC with a total of six layers (sample S6), the C3 relative percentage reached the highest value (22.7%) while the one due to the carbonate species, C1, was the lowest (47.6%), in agreement with the more extensive modification of the PCC surface (Table 2, Fig. 3c). Note that the core level of carbon atoms from carboxylate groups of alginate should also contribute to the observed XP spectrum, especially in the case of the six-layer coated PCC. However, since the corresponding signal appears at the same binding energy of carbonate (Surface Science Western, 2014; Belgacem et al., 1995) it could not be distinguished in the peak fitting. The fitted component C1 has thus a small contribution from alginate: considering the C3 results shown in Table 2 and the polyelectrolyte structure (Fig. 1b), it can be estimated to be roughly ≤3% for sample S6.



(a) (b) (c)

Figure 3. Peak fitting of the high-resolution XP spectra in the region of carbon binding energies of: a) PCC, b) two-layer coated PCC and c) six-layer coated PCC (respectively S0, S2 and S6).

The SEM images showed no structural differences between the unmodified and the modified PCC (Fig. 4): not only the scalenohedral shape of the particles remains the same but also the size is of the same magnitude. As said, these are important parameters that should be kept as constant as possible since large differences in the PCC

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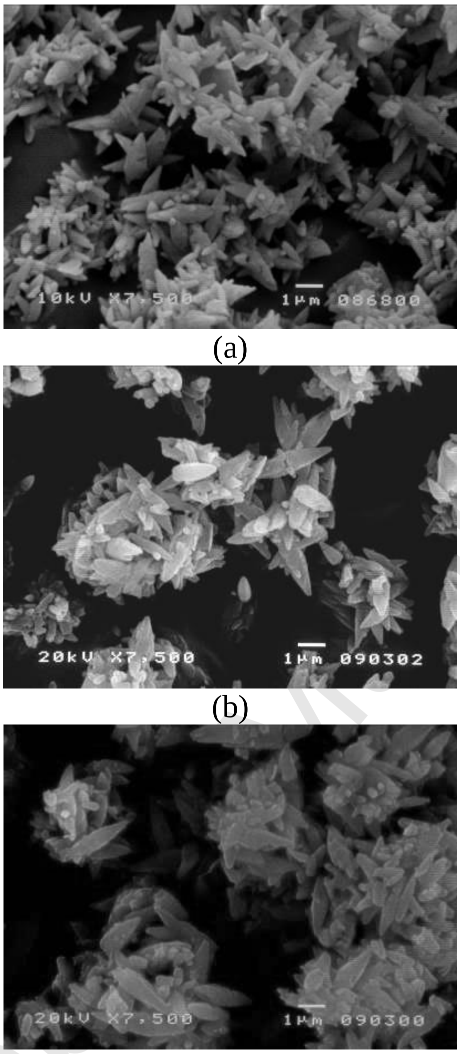
morphology could cause retention, dusting and formation problems in the papermaking process.



(a)

(b)

(c)

Figure 4. SEM images of a) PCC, b) two-layer coated PCC and c) six-layer coated PCC (respectively S0, S2 and S6).

With the PCC modification, an increase of particle size was found in the size distribution of the particles, as measured by laser diffraction spectroscopy (volume weighted) (Fig. 5): the median particle size, d_{50}, increases from 4.1 μm (reference PCC) to 6.8 μm (two-layer coated PCC) and finally to 10.6 μm (six-layer coated PCC). It should be emphasized that PCC has a high tendency to aggregate in aqueous suspensions with time and this behaviour is much more pronounced for the coated

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particles (especially the six-layers one) than for the unmodified PCC which partially explains the larger median values.

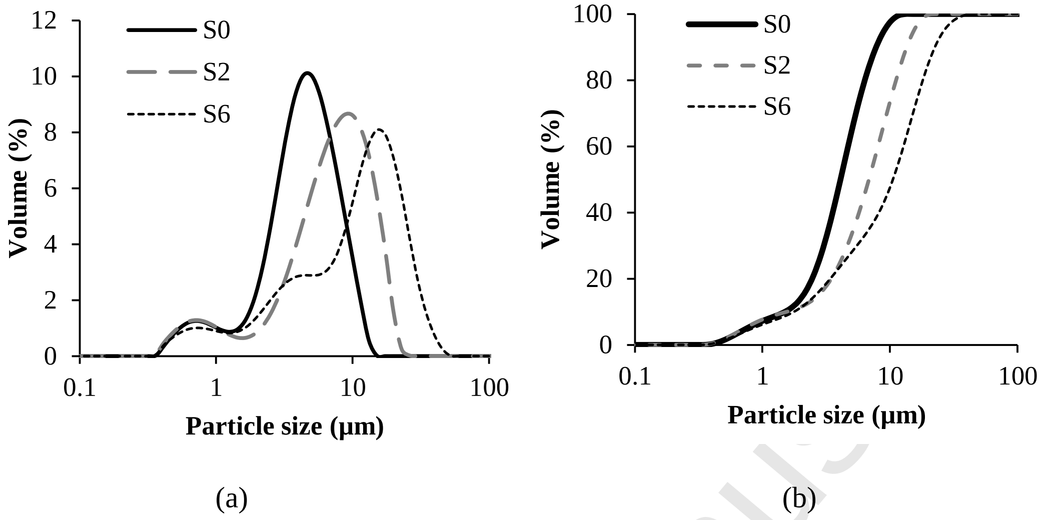

Figure 5. Particle size distribution for PCC (S0), two-layer coated PCC (S2) and six-layer coated PCC (S6): a) relative distribution, b) cumulative distribution.

3.2 Papermaking properties of the new modified PCCs

Laboratory handsheets were produced with unmodified PCC as reference and PCC modified with 2 and 6 layers of polyelectrolytes (S2 and S6). The PCC retention in the handsheets varied from 83-87% (reference PCC) to 79-86% (S2) and to 80-85% (S6) and the basis weight was in the same range for all the prepared handsheets (79-83 g/m^2), making it possible to compare paper properties. The most relevant properties are presented in Figs. 6 to Fig. 9 as a function of the effective filler content. The bulk of the handsheets produced with the modified PCCs was smaller than that of the handsheets produced with the reference PCC, for all studied filler contents (Fig. 6), which is in accordance with previous studies of the authors using other modified PCCs (Lourenço et al., 2013; Lourenço et al., 2014; Gamelas et. al, 2014). This effect is more pronounced for sample S6, i.e., the one with the higher number of layers and, expectedly, the higher amount of PDMA deposited at the surface of the PCC. This

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indicates a more closed fibrous matrix structure. The handsheets tensile resistance was not enhanced when one layer of PDMA was used (S2), but increased significantly with 3 layers of PDMA at the surface of PCC (S6): with this new filler an increase of 12%, relative to the unmodified PCC, was found for the smaller filler content (Fig. 7a). However, for the higher filler levels, the modified PCC is no longer so favorable. The other paper mechanical resistance properties exhibited similar trends: the internal resistance (Scott bond, Fig. 7b) improved 14% when compared to handsheets produced with the reference PCC and the burst and tear indexes showed maximum improvements of 9% and 11%, respectively (Fig. 8). The results reveal that when PCC is coated with PDMA, using alginate in alternating layers to promote a better PDMA adsorption, the bonding between the mineral filler and the fibres is enhanced. However, this positive effect is not detected when only one layer of PDMA (and an intermediate layer of alginate) is used, due to the very small amount of polyelectrolyte at the particles surface, and thus it becomes necessary to coat PCC with more than two alternating layers.

The effect of the PCC modification on the handsheets optical properties was not so evident but a slight tendency to decrease the light scattering and opacity with the LbL treatment was detected (Fig. 9). The aforementioned more closed structure will probably have fewer interfaces for the light to scatter. The brightness of the handsheets was not affected (ca. 87-88 % ISO).

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It must be noted that, in addition, other papermaking tests using PCC treated with only PDMA (3 successive "layers" of PDMA) were also conducted and no significant differences were obtained for the paper properties, in comparison to those with unmodified PCC. This confirms the need to use alginate to promote the effective deposition of PDMA at the surface of PCC, which is reflected on the papermaking results of the six-layer coated PCC.

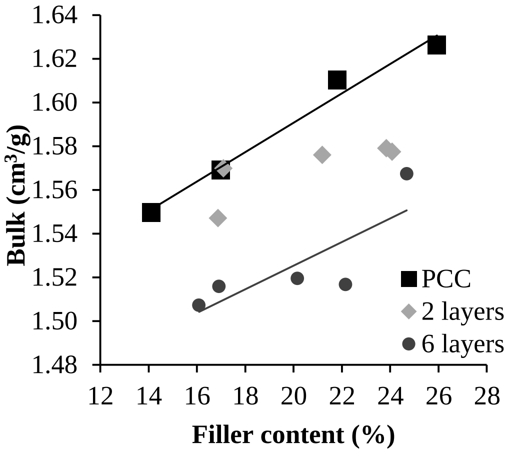
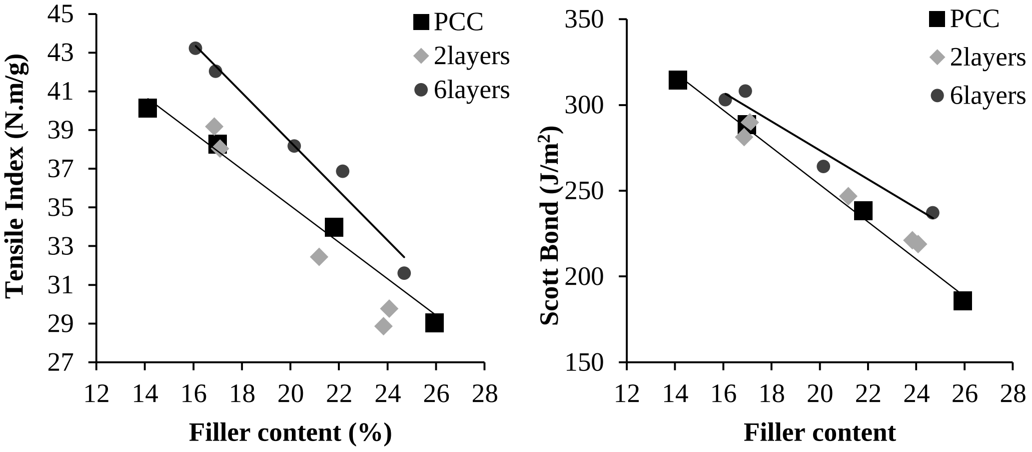


Figure 6. Bulk of handsheets produced with reference PCC and PCC modified with 2 and 6 alternating layers of alginate and PDMA (S2 and S6).



(a) (b)

Figure 7. Tensile index and internal resistance (measured by the Scott Bond) of handsheets produced with reference PCC and PCC modified with 2 and 6 alternating layers of alginate and PDMA (S2 and S6).

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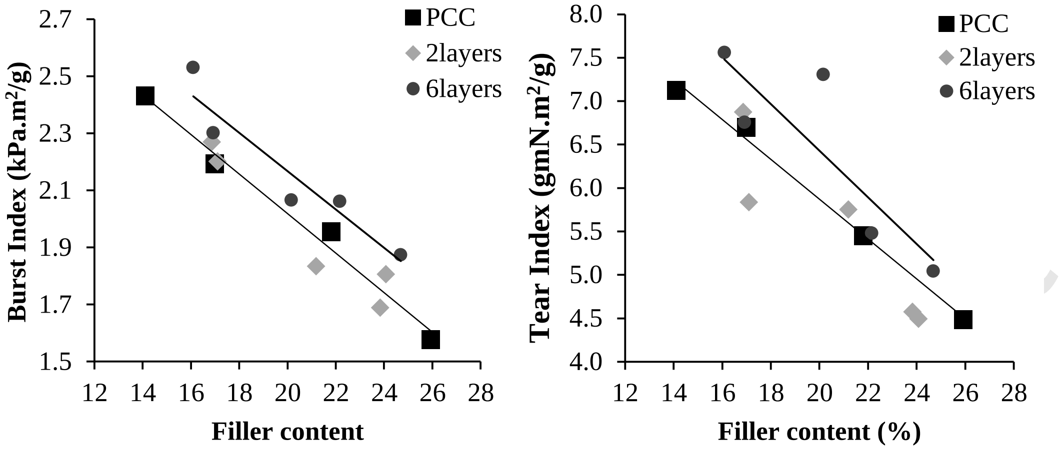
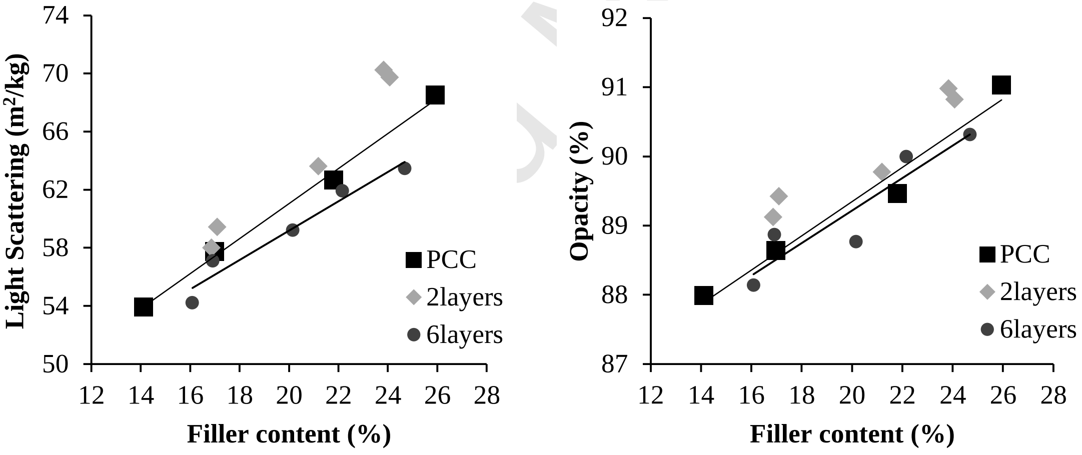


(a) (b)

Figure 8. Burst and tear indexes of handsheets produced with reference PCC and PCC modified with 2 and 6 alternating layers of alginate and PDMA (S2 and S6).



(a) (b)

Figure 9. Light scattering and opacity of handsheets produced with reference PCC and PCC modified with 2 and 6 alternating layers of alginate and PDMA (S2 and S6).

From the results presented it seems that modifying PCC with alternating layers of PDMA and alginate by the layer-by-layer method is a good approach for use in papermaking when compared to the usual use of untreated PCC. It is a simple process

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that uses relatively low amounts of reagents already employed in the papermaking industry. Moreover, further studies can be performed in order to diminish the amount of each polyelectrolyte used. In this study it was shown that it is possible to increase the effective filler content from ca 17% to 20% without reducing the tensile index (38.2 N.m/g) and preserving the optical properties.

4. Conclusions

A new PCC-based filler for use in papermaking was produced by coating PCC with three alternating layers of alginate and poly(diallyldimethylammonium). During the layer-by-layer assembly, the zeta potential of the PCC particles changed to highly negative and positive values when alginate and poly(diallyldimethylammonium) were deposited, respectively, confirming the presence of small amounts of the organic modifiers at the mineral surface. The high-resolution X-ray photoelectron spectra in the region of carbon binding energies of the modified PCC showed an increase of the component due to the core level of carbon atoms from C-O bonds of alginate.

The bulk of handsheets produced with the six-layer coated PCC filler was inferior to that of handsheets with the reference PCC, while the most relevant strength properties improved (tensile, tear and burst resistances, and internal bonding) and the optical properties were not significantly affected. These results can be explained in terms of a better bonding between the cellulosic fibres and the poly(diallyldimethylammonium) layer coating PCC than with the PCC alone.

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