

PAPERMAKING BEHAVIOUR OF A MODIFIED FILLER OBTAINED BY LAYER-BY-LAYER TECHNIQUE

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Abstract

One way of increasing the filler content in paper without sacrificing the mechanical properties is based on the modification of the filler surface with compounds that promote a better bonding with the cellulosic fibres. In this context, sodium alginate was deposited at the surface of precipitated calcium carbonate (PCC) as a first layer and alternated successive layers of Cationic poly(diallyldimethylammonium) chloride – polyDadmac and alginate were applied using a layer-by-layer (LbL) procedure.

The analysis of the synthesized new materials showed that there is a deposition of the negative and positive polyelectrolites at the surface of PCC. In fact by XPS it was confirmed that small amounts of the polyelectrolytes are present at the surface of PCC.

Papermaking tests were carried out using the new composites. An improvement of the handsheets strength properties was observed when comparing to handsheets produced with the unmodified PCC.

1. Introduction

One of the challenges in papermaking is how to preserve paper strength using small amounts of virgin fibres. Several approaches can be used, such as reducing the basis weight, using recycled fibres or replacing the fibres by mineral fillers. 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 [1,2] - nowadays values of 25-30% of filler can be found in paper. However, the inclusion of fillers has a detrimental effect on paper strength due to the fact that they interfere with the fibre-to-fibre bonding. On the contrary, they have a positive effect in bulk, opacity and brightness [3].

One way to increase the filler content in paper whilst maintaining good strength properties is by the surface filler treatment/modification. A lot of literature can be found concerning the filler modification with the objective of being used in acidic papermaking conditions [4,5,6], improving retention [7,8] or enhancing the optical properties of the fillers [9]. Regarding the filler modification in order to improve the strength properties of paper, the most promising are the claimed to be the ones that use starch at the surface of PCC [10,11]. Recently the authors published the modification in situ of PCC with silica improving the mechanical properties of paper for similar filler content, and as a consequence, improving the filler content without affecting the paper mechanical resistances [2,12,13].

In this work polyDadmac (PD) was chosen to modify the surface of PCC. PolyDadmac (Figure 1a) is a polyelectrolyte commonly used as flocculant in wastewater treatment [14,15]. 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. Since PCC has a small positive charge, an intermediate layer between PCC and polyDadmac is advisable to get an adequate adhesion. In this context, sodium alginate (SA) (Figure 1b), an abundant linear polysaccharide obtained from brown algae, was chosen due to the great affinity between its guluronic and mannuronic acids and the calcium ions [16].

In the present paper, PCC was modified with subsequent layers of sodium alginate and polyDadmac and the obtained composite was applied as filler in eucalyptus bleached kraft pulp handsheets aiming at improving the strength properties of paper.

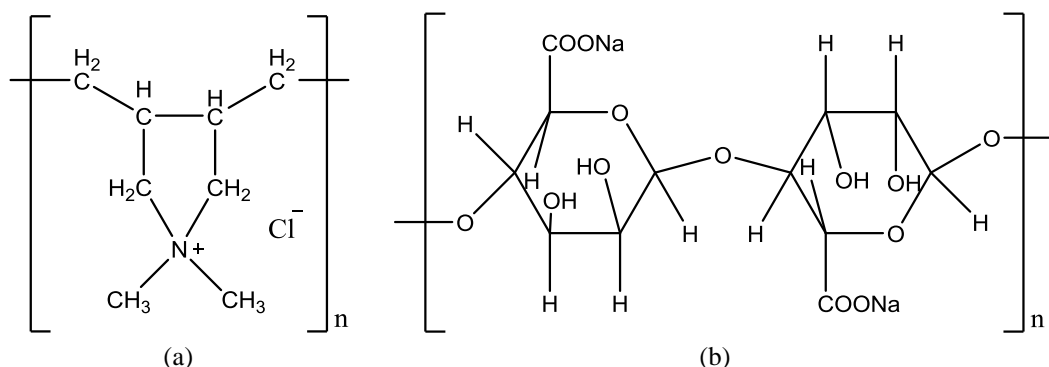


Figure 1. Chemical structure of polyDadmac (a) and sodium alginate (b).

2. Materials and Methods

2.1 Modification of PCC

An aqueous suspension of an industrial scalenohedral PCC was filtered and the solid obtained was dried. Several layers of sodium alginate and polyDadmac were used for the modification. For the first layer, a solution of sodium alginate was mixed with PCC at a ratio of 95:5 (PCC:SA) at 60°C and cooled to room temperature under vigorous stirring. After a vacuum filtration the suspension was washed with distilled water. The final product was dried in an exsiccator for one day. For the second layer the aforementioned dried product was used and a polyDadmac solution was added to the composite at a ratio of 90:5:5 (PCC:SA:PD). Again, the resultant suspension was filtered, washed and dried for one day. The mentioned procedures were repeated until deposition of six alternated layers of the polyelectrolites (PCC:SA:PD:SA:PD:SA:PD), in order to guarantee an efficient modification of the PCC surface.

2.2 Characterization of PCC and modified PCC

The reference PCC and the PCC-SA-PD composites were characterized in order to confirm the presence of the polyelectrolites at the surface of PCC and to assure that the new fillers did not differ much from the reference PCC in terms of shape and size. Table 1 lists the techniques that were used.

Property	Technique
Surface charge	Zeta potential measurement
Identification of the components	X-Ray Photoelectron Spectroscopy
	Infrared spectroscopy
Particle size	Laser diffraction spectrometry
Aspect	Scanning Electron Microscopy

Table 1 – Characterization of the unmodified and modified fillers.

2.3 Papermaking tests

Handsheets were produced in a batch laboratory sheet former (255/SA model, MAVIS) using a 120 mesh screen with formulations containing fibre (*Eucalyptus globulus* bleached kraft pulp refined up to 33 °SR), PCC (unmodified or modified), starch, alkenyl succinic anhydride (ASA), and a linear cationic polyacrylamide (CPAM) as retention agent. The amounts added and the contact times are presented in Table 2. The aim was to achieve a basis weight of 80g/m² and a filler incorporation of 20% (corresponding to a real filler content close to 16%-18%). Tests with filler incorporations of 25% were also carried out.

Component	Amount (%)		Contact time (s)
Fibre	78.86	73.86	300
PCC or modified PCC	20.00	25.00	300
Starch	1.00	1.00	180
Alkenyl succinic anhydride(ASA)	0.12	0.12	180
Retention Agent (CPAM)	0.02	0.02	30

Table 2 – Components and corresponding contact times used in the papermaking tests.

The structural (basis weight, bulk, thickness, air permeability, surface roughness), mechanical (tensile, tear, burst and internal resistance) and optical (light scattering, opacity, brightness) properties were measured according to the corresponding ISO Standard Test Methods. The internal resistance measured by the Scott bond test was performed following the corresponding Tappi Standard. Finally, the handsheets were also calcined at 525 °C to determine the filler retention, according to the corresponding Tappi Standard.

3. Results and Discussion

3.1 Characterization of the particles

PCC particles were coated with alternated layers of alginate and polyDadmac. The process was controlled by measuring the zeta potential by the electrophoretic mobility after each layer deposition. Within the six layers deposited, the zeta potential switched from +7mV (unmodified PCC) to values between -30mV and +40mV (Figure 2), confirming the effect of the polyelectrolyte in the PCC modification.

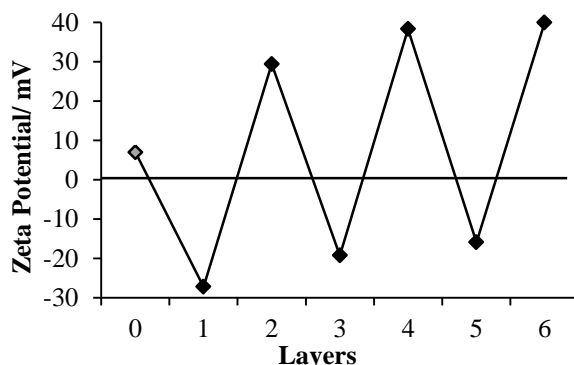


Figure 2. Evolution of the zeta potential with LbL coating of PCC with sodium alginate (layers 1,3 and 5) and polyDadmac (layers 2,4 and 6).

The surface of the modified PCC's was analyzed by X-ray photoelectron spectroscopy (Table 3). With the modification, the amount of carbon increases while the amount of oxygen decreases, confirming increased amounts of the modifiers added to the surface. Due to the presence of polyDadmac it was expected to find nitrogen (Figure 1a); however this does not occur, probably due to the small amount of the polyelectrolyte that is effectively at the surface of PCC. Traces of magnesium (present due to the PCC synthesis) decrease, most certainly due to relative increase of the other modifier components.

Material	C (atom.%)	O (atom.%)	Ca (atom.%)	Mg (atom.%)
PCC	35.2	49.8	13.6	1.4
PCC-SA	35.9	49.4	13.8	0.9
PCC-SA-PD	36.7	48.5	14.1	0.8
PCC-6layers	37.4	48.3	13.9	0.4

Table 3 – XPS results of unmodified PCC and PCC modified with 1,2 and 6 alterned layers of sodium alginate (SA) and polyDadmac (PD)

By the analysis of the infrared spectroscopy spectra, no additional peaks than those present in the unmodified PCC (marked with *, Figure 3a) are found. As suspected, the amount of electrolytes is very small and therefore, with the FT-IR technique, it is not possible to identify these components. However, they are definitely present, as confirmed by the values plotted in Figure 2 and Table 3.

The size distribution of the particles (volume weighted) shows that there are no relevant changes in size (Figure 3b): the median (d50) value of the reference PCC is 3,8 μm and values of 4,8 μm and 4,4 μm for the modified PCC with 2 and 6 layers, respectively, are found. It should be emphasized that the tendency to aggregate in aqueous suspensions with time is much higher for the coated particles than to the unmodified PCC.

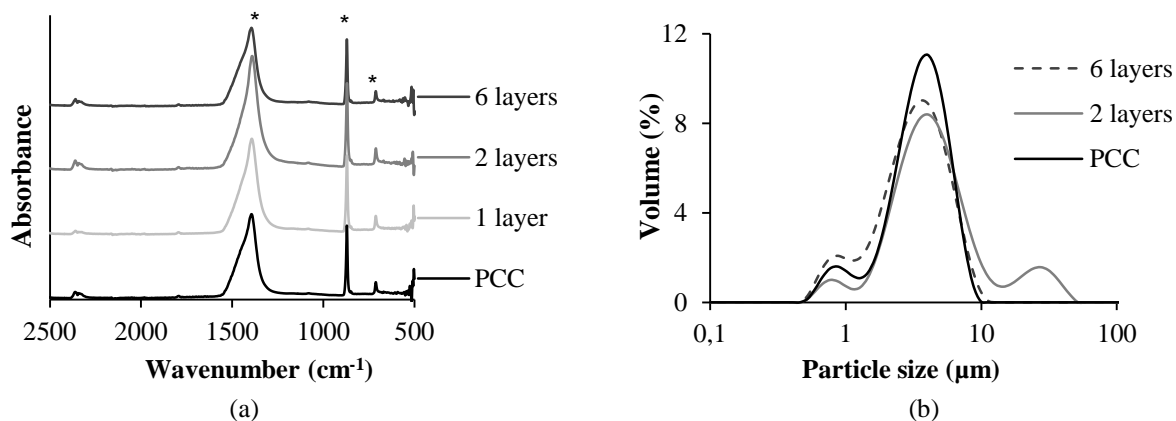


Figure 3. FT-IR spectra (a) and particle size distribution (b) of PCC and PCC modified with 1,2 and 6 alternated layers of sodium alginate (SA) and polyDadmac (PD).

The SEM images show no structural differences between the modified and the unmodified PCC (Figure 4): not only the size (as mentioned before) but also the scalenohedral shape of the particles remains the same. This is an important parameter if the composites are to be used in the process as a substitution of the currently used filler.

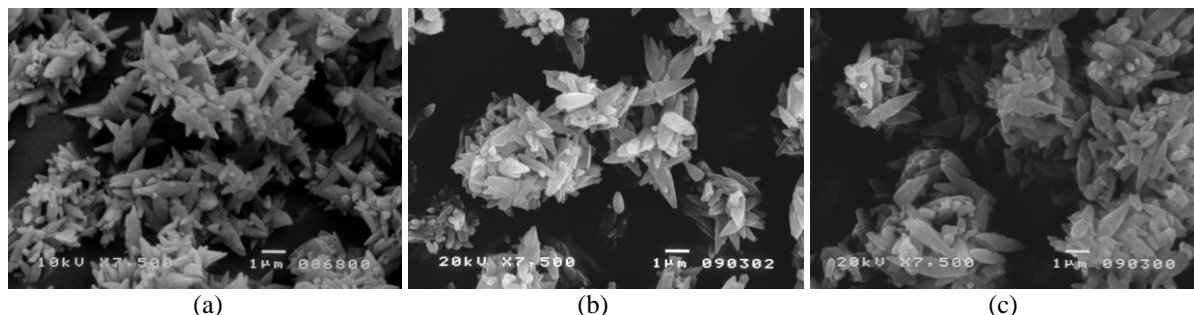


Figure 4. SEM images of PCC (a) and PCC modified with 2 (b) and 6 (c) alternated layers of sodium alginate (SA) and polyDadmac (PD).

3.2 Papermaking properties

Laboratory handsheets were produced with unmodified PCC as reference and PCC modified with 2 or 6 layers of polyelectrolites using the amounts present in Table 2. Other papermaking studies were performed in order to optimize the process. As stated in 3.1. the modified particles have a greater tendency to aggregate with time and stirring, even though the papermaking tests did not show any differences between high and low contact times among the handsheet components. Different amounts of polyelectrolites in the composites were applied and a 5% synthesis amount was chosen to assure a good deposition at the surface of the PCC particles, although it is proved that lower amounts effectively remain in the composite. Tests without alginate were conducted and it was proven that SA is fundamental to attach PD to the surface of PCC. The results presented are those obtained after this optimization process.

The PCC retention in the handsheets varied from 83-88% (unmodified PCC) to 80-86% (modified PCC) and the basis weight was similar for all the handsheets (81-84 g/m²), making it possible to compare the properties. The bulk of the handsheets produced with the modified PCC was smaller than that of the handsheets with the reference PCC (Figure 4a). In fact with the deposition of more layers at the surface of PCC, the lower was the bulk, which is in accordance with values presented for modified PCC [13]. The handsheets tensile resistance

was not enhanced when two layers were used, but increased significantly when six layers of polyelectrolites were deposited at the surface of PCC: with this composite it was possible to increase the unmodified PCC tensile index by 13% (Figure 5b). Other mechanical resistance properties exhibit similar trends: the burst and tear indexes improved 15% and 13%, respectively, and the internal resistance (Scott bond) improved 5%. Therefore, the obtained values seem to prove that when PCC is coated with alternate layers of sodium alginate and polyDadmac, a better bonding between the mineral filler and the fibres is established. However, only one layer of each polyelectrolyte (two layers total) is not sufficient to have this positive effect in the bonding mechanism, thus becoming necessary to coat PCC with more than two alternate layers.

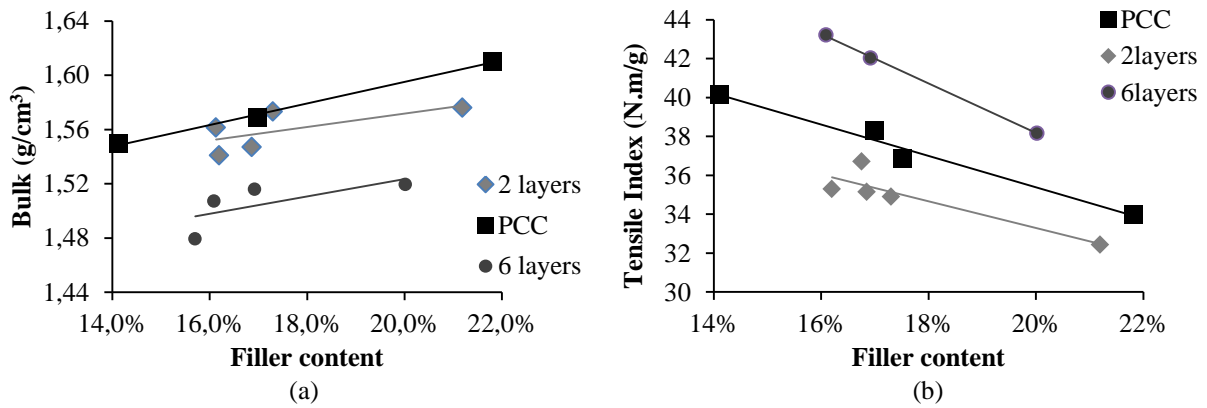


Figure 5. Bulk (a) and Tensile index (b) of unmodified PCC and PCC modified with 2 or 6 layers of polyelectrolites (sodium alginate and polyDadmac).

The effect of the treatment on the optical properties was not so evident but a slight tendency to decrease the light scattering and opacity with the layer-by-layer treatment was detected (Figure 6). In fact, the air permeability was smaller in the handsheets produced with the modified PCC which indicates a more closed structure (in agreement with the lower bulk) and therefore there are fewer interfaces for the light to scatter. The brightness of the handsheets was not affected.

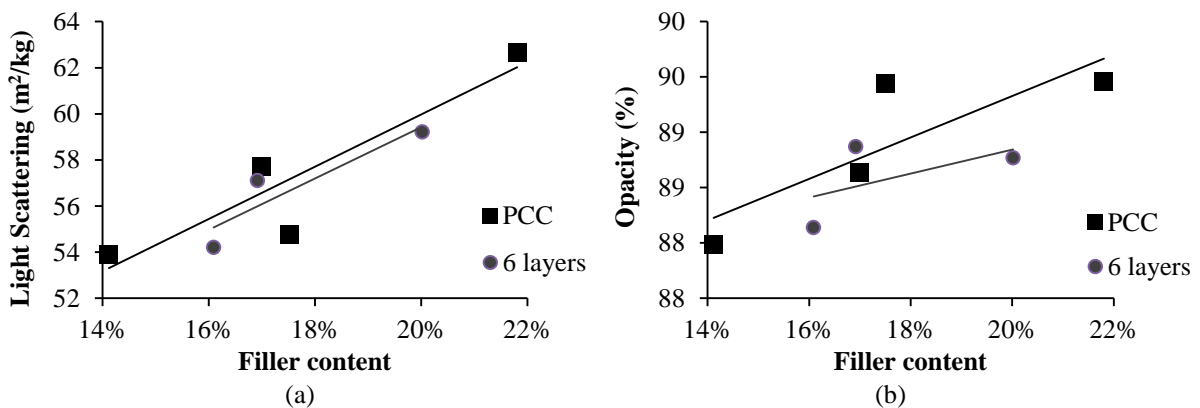


Figure 6. Light scattering (a) and opacity (b) of unmodified PCC and PCC modified with 6 layers of polyelectrolites (sodium alginate and polyDadmac).

The results seem to show that the modification of PCC with polyDadmac (using sodium alginate as an intermediate layer) is beneficial for the fibre-to-filler-to-fibre bonding.

However, some optimization must be done regarding the work developed so far, namely by the reduction of the amount of polyelectrolytes used or/and the recovery of the filtrate to be reutilized in the deposition of the subsequent layers.

Conclusion

The PCC surface was modified with alternated layers of alginate and polyDadmac. The zeta potential varied between negative and positive values, ensuring the deposition of the polyelectrolyte at the surface of PCC. By XPS analysis it was confirmed that small amounts of the polyelectrolytes are present at the surface of PCC.

The papermaking tests show that two layers are not sufficient to improve the mechanical properties in reference to the unmodified PCC, but the composite with 6 alternated layers of polyelectrolytes is capable of increasing the strength of the paper by ~13% (tensile, tear and burst indexes). The optical properties are slightly affected, although the brightness of the handsheets remains the same.

It seems that the new LbL-modified PCC materials have potential to increase the filler-to-fibre-to-filler bonding in papermaking, which can be a way to increase the filler content and save fibre resources.

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