

**MODIFICATION OF FILLERS FOR INCREASED
STRENGTH IN PAPERMAKING**

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

Department of Chemical Engineering, CIEPQPF, University of Coimbra, Pólo II. R. Sílvio Lima, PT - 3030-790
Coimbra, Portugal; analourenco@eq.uc.pt

SUMMARY

Mineral fillers have been widely used in papermaking, especially in printing and writing papers, since they add positively to sheet formation, brightness, opacity and printability besides lowering furnish cost. However, by incorporating inorganic fillers in paper the fibre-to-fibre bonding is negatively affected which disturbs the paper strength. Thus, depending on the paper grade, the amount of filler present in the final product is in general inferior to 30%. In order to increase the filler content without losing paper strength the present study presents new methods to modify the fillers surface with polymers that can enhance the intermolecular interactions between fillers and fibres. For that, organic polymers such as cellulose derivatives (cellulose acetate and cellulose acetate butyrate) and polydiallyldimethylammonium chloride, as well as inorganic pigments, such as silica and titanium dioxide were applied at the surface of calcium carbonate. The retention and flocculation of the modified fillers in the fibre mat (containing fibres and sizing agent) were evaluated in a Dynamic Drainage Analyzer, by testing different retention agents. After, paper sheets prepared in lab with the functionalized fillers, for increasing filler levels up to 40%, were evaluated regarding the most relevant papermaking properties. In the present paper the most promising modified filler, among those that were studied, was PCC-silica synthesized by a sol-gel method. This approach proved also to be efficient when modifying GCC with silica. Besides, the results were validated in a pilot paper machine. It is believed that this work is one of the most comprehensive and open study undertaken so far on modified fillers and their influence on paper properties since, contrary to other studies, different parameters were evaluated simultaneously such as retention, formation, drainage and paper properties.

Keywords: Cellulose esters, fillers, precipitated calcium carbonate, silica, titanium dioxide.

INTRODUCTION

Approximately 32% of the total paper and board production in Europe refers to printing and writing papers grade [1]. These papers must have excellent optical properties and enough wet and dry tensile strength in order to enable productions speeds up to 1500 m/min. Thus, pulp fibres with good performances are required. However, in addition to fibres, the production of printing and writing papers usually includes mineral fillers, being precipitated and ground calcium carbonate (PCC and GCC, respectively), kaolin, talc, and titanium dioxide the most common. The increase of the filler content in paper is desirable not only for economic reasons since fibers are commonly more expensive and sheets with higher levels of filler are easier to dry, but also for environmental reasons, as mineral resources are spared [2-4]. Besides that, fillers can be used to control important properties such as opacity, surface smoothness and printability. However there is no filler capable of achieving the desired properties without a negative impact in the physical properties of paper, namely a strength reduction caused by disruption of the fiber-to-fiber bonding network in the sheet. The loss of bonding due to the increase of mineral fillers also leads to retention problems since fillers are harder to retain and it is necessary to use more retention agents which also leads to formation and printing problems (sheet delamination, picking, linting, dusting). Therefore, the filler content in paper is limited to values rarely superior to 30% [2-4]. If it were possible to increase by 5% the filler content of a paper grade with, on average, a filler content of 30% for a paper mill producing 1800 tons/day, then a considerable amount of 90 tons/day of fiber could be replaced.

Several strategies to overcome some of these drawbacks and increase the filler content while improving the final product characteristics and also runnability have been pursued over the years. The simplest solutions, however not completely efficient, are based on the addition of the filler in different areas of the machine in order to increase the contact time between fibers and fillers [5] or on the incorporation of new additives (preflocculation, sizing and retention agents, among others) [6,7]. Nowadays the filler modification is becoming an important subject of several studies [3,8-15]. Several authors have investigated the modification of filler particles with starch or its derivatives by coating or by filler particle encapsulation with a starch gel. Both techniques are very effective at improving the paper mechanical properties, such as tensile index, without sacrificing the optical properties [3,8,9]. An alternative to starch is cellulose and some of its derivatives. Coating filler particles with cellulose, aims at creating a pseudo inter-fiber interface by promoting the formation of hydrogen bonds between the filler particles and cellulose fibers. Theoretically, encapsulation with cellulose increases the filler binding ability, improving therefore the mechanical properties of paper. Myllymäki et al. (2006) showed how the encapsulation process can be performed using an ionic liquid as a cellulose solvent [10]. Although this technique is industrially feasible, the ionic liquids are very expensive and difficult to remove. Other molecules, such as chitin and chitosan, are also a very interesting alternative since they have a structure similar to that of cellulose [3]. Recently, Chen et al. (2014) using a combination of cationic chitosan and carboxymethyl chitosan to modify PCC improved brightness and opacity of the handsheets as well as the tensile strength [11]. Some work has been also developed aiming to obtain calcium carbonate-based filler with improved acid-resistant properties which are required for papermaking in weakly acid to neutral conditions [12,13]. However, when considering the modification of fillers with inorganics, just a few studies include the evaluation of the impact of the treated fillers on the mechanical properties of the papers [3,13,14] and in most of them only the optical properties were enhanced while the mechanical properties and/or retention did not improve.

The present paper introduces new methods to modify the fillers surface, in order to improve filler-to-fibre bonding, and also paper strength, overcoming at the same time the problems of retention. Some of the results presented were already published, namely the production of new composite materials of PCC and cellulose esters (cellulose acetate and cellulose acetate butyrate) [16] and the surface coating of PCC with poly(diallyldimethylammonium) using the layer-by-layer deposition method with alginate as an intermediate bonding polyelectrolyte [17] and their application as fillers in papermaking. Other study published reported to the production of silica at the surface of PCC by sol-gel method using tetraethyl orthosilicate (TEOS) as silica precursor [18]. In this paper it was suggested that the hydroxyl groups present at the surface of silica-coated PCC could provide strong physical interactions with the cellulosic fibres and thus improve the fibre-to-filler interactions and paper strength and, in order to confirm this hypothesis, another work was published in which the silica-coated PCC fillers were applied as fillers in lab handsheets [19]. These results were further explored so that it was possible to increase the paper filler content in 5% without affecting the strength properties [20]. Finally, the results obtained at laboratory were confirmed by up-scaling the experiments to a pilot paper machine using the same furnish, unmodified reference PCC and modified PCC [21]. Besides, a similar improvement of the strength properties was also observed with silica modified GCC [22]. Finally, experiments with PCC milled with titanium dioxide and applied as filler in papermaking were carried out.

EXPERIMENTAL

Filler modification and characterization

For the surface modifications industrial scalenohedral PCC and three different commercial GCC were used. The suspensions of the mineral fillers were filtered using a Buckner filter (0.2 μm) and the solid obtained was oven dried at 105 °C for 24 hours. Four different modifications were conducted:

a) PCC modification with cellulose derivatives: The modification of PCC with low amounts of cellulose acetate (Mn~30,000, 40 wt% acetyl) and cellulose acetate butyrate (Mn~30,000, 12-15 wt% acetyl, 36-40 wt% butyryl) followed the methodology reported elsewhere [16]. Briefly, 1.75 g of cellulose acetate or 1.40 g of cellulose acetate butyrate were dissolved in 140 mL of acetone and a

suspension of 14 g of PCC in 126 mL of water was added dropwise to this solution. 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.

b) PCC modification by the layer-by-layer deposition method: The modification of PCC with several layers of alginate and poly(diallyldimethylammonium chloride) (PDMA) followed the methodology reported elsewhere [17]. In short, 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). After a vacuum filtration and washing with distilled water to remove residual polyelectrolyte not bound, the PCC was dried in an exsiccator for one day. For the second layer, a PDMA solution was added to the aforementioned dried product at a mass ratio of 95:5 ((PCC:alg):PDMA). Again, the resultant solid was filtrated, water washed and dried for one day. The mentioned procedures were repeated until deposition of six alternating layers of the polyelectrolytes, the external one being that of PDMA. The final product was dried in an exsiccator for 4 days.

c) PCC and GCC modification with silica: The modification of the mineral filler with silica followed the methodology reported elsewhere [20]. Briefly, the modified particles were obtained from the dry mineral (PCC or GCC), tetraethyl orthosilicate (TEOS), water, ethanol, and ammonia. For PCC, experiments with [NH₄OH] of 0.05, 0.1, and 0.3 mol dm⁻³ were carried out in order to produce modified PCCs with distinct silica contents. Since with PCC the best papermaking results were obtained with the particles modified with the higher NH₄OH concentration, the GCC modification was conducted using only the latter conditions. Besides, an upscaling (ca. 100x) of the reaction using PCC and the aforementioned [NH₄OH] was performed in order to be used in pilot tests.

d) PCC modification with titanium dioxide: PCC was modified with two different amounts of titanium dioxide (TiO₂). Rutile TiO₂ was mixed with dry PCC in ratios of 90:10 or 75:25 (PCC:TiO₂) using a ball milling technique for 30min. The results were also compared with simple dry mixtures of the two components.

A thorough characterization of the new modified fillers was performed by several techniques: Fourier transform infrared spectroscopy (FTIR) (Jasco Int., 4200), thermogravimetry (Shimadzu, TGA-50), X-ray diffraction (Philips X'Pert diffractometer), laser diffraction spectroscopy (Malvern Instruments, Mastersizer 2000), scanning electron microscopy (SEM) (JEOL, JSM-5310), and electrophoretic light scattering (Malvern Instruments, Zetasizer Nano ZS). Details of these methods as used for the fillers characterization can be found elsewhere [18,19].

Drainage and retention tests

In order to evaluate the behaviour of the new modified fillers in terms of retention in the fiber matrix and influence on drainability, tests were conducted with the unmodified PCC and with the modified PCC-silica (higher silica content) and PCC-cellulose derivatives fillers. The former were performed in a Dynamic Drainage Analyzer (DDA, AB Akribi Kemikonsulter, Sweden) with formulations containing fiber (*Eucalyptus Globulus* bleached kraft pulp refined up to 33 °SR), PCC (unmodified or modified), starch, alkenyl succinic anhydride (ASA), and retention agent. Three polyacrylamides with different structure and charge were used as retention agents: a linear cationic (L-CPAM), a branched cationic (B-CPAM) and an anionic (APAM). The amounts added and the contact times are presented in Table 1. After drainage, the wet pad was collected and calcined at 525 °C for 16 h to determine the effective filler content (adapted from the Tappi Standard T 211 om-93). More details of the procedure can be found elsewhere [19].

Table 1 – Components used in the drainage tests.

Component	Amount (%)	Contact time (s)
Fiber	78.86	300
PCC or modified PCC	20.00	300
Starch	1.00	180
Alkenyl succinic anhydride(ASA)	0.12	180
Retention Agent	0.02	10

Handsheets preparation and characterization

Handsheets were produced in a batch laboratory sheet former (255/SA model, MAVIS) using a 120 mesh screen with the same amounts of those used in the aforementioned drainage tests (Table 1). A procedure reported elsewhere [16,17,19,22] was followed using all of the modified fillers produced along with L-CPAM. Besides that, handsheets with the most promising modified filler (PCC-silica with 29wt% of silica) with nominal filler contents ranging from 20 to 45%, were produced by proportionally decreasing the fiber incorporation. At least two series of experiments were run for each formulation.

The pilot tests were produced with PCC-silica (29wt%) in a pilot paper machine (PM) in which a continuous web of 0.5 m width was produced at a speed of 1 m/min. All the furnish components were mixed in the stock chest, except for the retention agent (L-CPAM) that was added inline. Paper sheets with 30% of filler were produced. The relative amounts of the other components and contact times were the same of the drainage tests and handsheets lab production.

In all the handsheets and paper sheets produced, the structural (basis weight, thickness, bulk, air permeability), mechanical (tensile, stiffness, tear and burst resistance) and optical (light scattering, opacity, brightness) properties were measured according to the corresponding ISO Standard Test Methods. The sheets were also calcined at 525 °C to determine the effective filler content.

RESULTS AND DISCUSSION

Characterization of the modified fillers

Figure 1 shows the SEM images of the modified fillers. For PCC (Fig. 1a to 1d) it is noticed that the scalenohedral original particles (Fig. 1a) are coated by discrete particles and in some cases aggregates of the cellulose derivatives (Fig. 1b) or by a silica film giving the crystals a rounder shape (Fig. 1c). The SEM image of the PCC-TiO₂ composite (Fig. 1d) reveals a smaller particle size, but large aggregates, when compared to the unmodified PCC, probably due to the milling technique used in the modification process. Besides, the presence of particles with sizes inferior to 100nm is detected. For the GCC filler (Fig. 1e), the typical rhombohedral calcite particles are shown together with smaller particles that are normal for GCC and when modified, the presence of silica particles is evident, which somehow hide the typical rhombohedral shape (Fig. 1f).

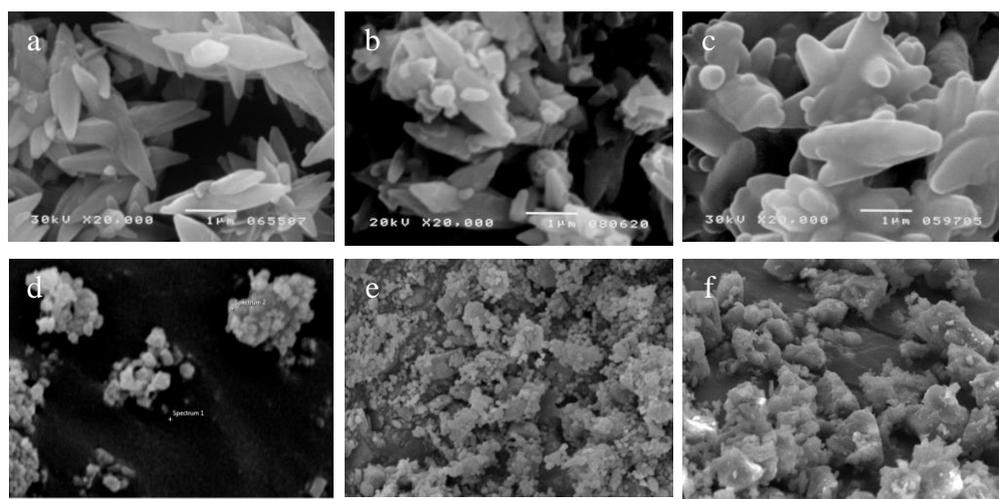


Figure 1. SEM images of (a) unmodified PCC, (b) PCC-cellulose acetate butyrate, (c) PCC-silica (29 wt%), (d) TiO₂, (e) unmodified GCC1, (f) GCC1-silica.

Note: a-d are magnified 20000x and e-f 7500x

Table 2 presents some of the characterization values obtained for the modified fillers. In the case of the new fillers modified by cellulose derivatives and by silica, the amount of modifier present in the composites was estimated by thermogravimetry, from the weight losses correspondent to the degradation of the modifier and compared to the weight loss observed in the unmodified filler, correspondent to the degradation of calcium carbonate. For the PCC modified with PDMA, no differences in the FT-IR spectra between the unmodified and modified particles was observed and therefore an analysis by XPS was performed, which revealed increased amounts of the modifier

compounds, although present in very small quantities. For the new PCC-silica fillers, the amount of silica was found to vary between 11 and 29% and could be controlled based on the ammonium concentration of the reaction medium. Besides, the scale-up experiments, using $[\text{NH}_3]=0,3\text{M}$, revealed an increase of the silica percentage in the modified PCC when compared to the lab synthesis (21 to 33%, respectively). All the new modified materials showed a particle size slightly higher than that of the original PCC and in the case of PDMA this property was found to increase with the increase of the layers deposited at the PCC surface. The high median particle size of PCC-TiO₂ is due to the large aggregates formed, but noteworthy that the size distribution reveals a large amount of particles with $d_{50}<1\mu\text{m}$, as already noticed in the SEM images (Fig. 1d). The brightness of the modified materials was not significantly affected, except for the PCC-TiO₂ composite due to the low brightness of the rutile TiO₂ used and to the grinding process.

Table 2. Characterization of the unmodified and modified fillers

Sample	Modifier content (%)	Brightness (%)	Particle Size d_{50} (μm)	Zeta Potential (mV)
<i>Unmodified PCC</i>	-	95.3	4.5	+8
PCC-cellulose acetate	10.2	95.5	5.0	-19
PCC-cellulose acetate butyrate	9.2	95.9	6.4	+7
PCC-alginate-PDMA (2layers)	< 0.2	-	6.8	+30
PCC-alginate-PDMA (6layers)	< 0.2	93.7	10.6	+40
	11	-	4.7	-32
PCC-silica: lab scale	21	96.2	4.8	-34
	29	95.5	8.6	-35
PCC-silica: pilot scale	33	-	8.6	-
PCC-TiO ₂	25	84.6	10.1	-10
<i>Unmodified GCC1</i>	-	85.4	2.1	-29
GCC1-silica	41	82.6	5.1	-32
<i>Unmodified GCC2</i>	-	88.1	1.3	-29
GCC2-silica	40	87.1	3.7	-33

Regarding the zeta potential, a change from slightly positive to negative values was found in the PCC-silica coated particles. As for the GCC, the values did not change with the silica modification since, contrary to PCC, the surface charge of the unmodified GCC particles was already negative, mainly due to the presence of anionic polyelectrolytes commonly used to stabilize the GCC dispersions. The deposition of the alginate (anionic) and PDMA (cationic) layers at the surface of PCC was controlled by the changes in zeta potential from positive to negative values after deposition of the anionic polyelectrolyte and from negative to positive values after deposition of the cationic one (Fig. 2a).

The presence of modifier in the mineral particles was also confirmed by FTIR analysis (Fig. 2b). In addition to the characteristic bands of calcium carbonate (at 713, 872 and *ca.* 1460 cm^{-1} , marked with *), a few more bands attributed to the presence of the different modifiers (marked with +) were also detected.

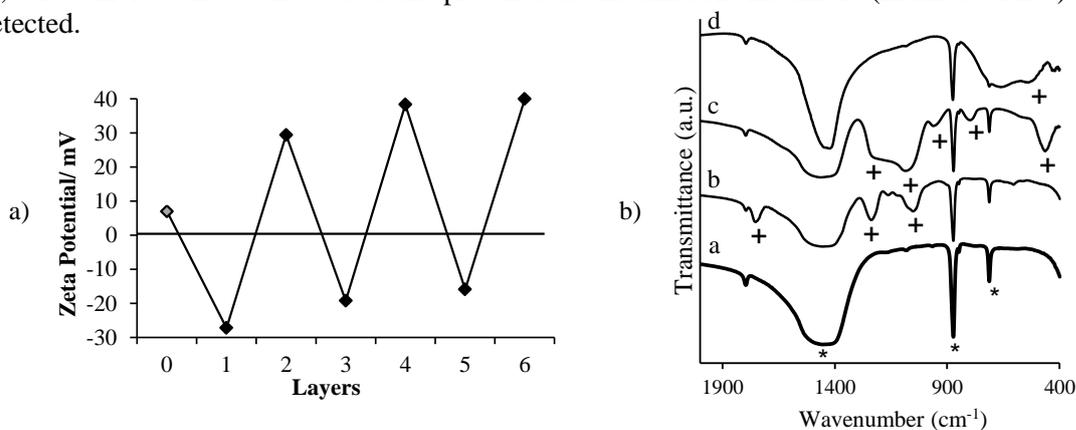


Figure 2. a) Evolution of the zeta potential of PCC in the LbL-coating with alternating layers of alginate (1, 3 and 5) and poly(diallyldimethylammonium) (2, 4 and 6); b) FT-IR spectra of (a) reference PCC and of (b) PCC modified with cellulose acetate, (c) silica (29wt%) and (d) titanium dioxide (25wt%).

Drainage and papermaking tests

Drainage and retention tests were performed in a Dynamic Drainage Analyzer (DDA) with the reference original filler and with the PCC-silica (29 wt%) and PCC-cellulose derivatives fillers. Three polyacrylamides with different structure and charge were used as retention agents. From the results (Table 3), the linear cationic polyacrylamide (L-CPAM), was selected as the most appropriate retention agent (for the handsheets production) giving minimum values of drainage time and filler loss.

Table 3. Retention and drainage times obtained in the Dynamic Drainage Analyzer ^a

		L-CPAM	B-CPAM	APAM
PCC	Retention (%)	94±0.3	90±2	96±1
	Time (s)	4.7±0.1	4.0±0.4	14.5±1.6
PCC-silica	Retention (%)	93±0.3	86±1	90±1
	Time (s)	4.6±0.2	3.4±0.1	16.8±1.9
PCC-cellulose acetate	Retention (%)	87±2	84±4	-
	Time (s)	5.6±0.4	4.4±0.0	-
PCC-cellulose acetate butyrate	Retention (%)	96±1	93±1	-
	Time (s)	4.8±0.1	3.8±0.0	-

^aAll formulations evaluated in the DDA included fiber, filler, starch, ASA and retention agent. L- and B- CPAM refer to linear and branched cationic polyacrylamide, respectively, and APAM refers to anionic polyacrylamide.

The outcomes of the more relevant papermaking results of the handsheets produced with the new modified fillers are summarized in Table 4, in terms of deviation (%) of the results relative to those of the handsheets produced with the unmodified fillers.

Table 4 – Papermaking properties of lab handsheets (and of paper sheets made with PCC-silica at pilot scale) produced with the modified versus the unmodified filler, in terms of increment percentage.

Sample		Retention	Tensile Index	Tear Index	Light scattering
Ca. 17% filler	PCC-cellulose acetate	0.6	4.1	12.6	-2.9
	PCC-cellulose acetate butyrate	-2.3	8.1	7.2	-2.6
	PCC-alginate-Pdadmac (2layers)	0.0	2.6	2.7	2.2
	PCC-alginate-Pdadmac (6layers)	-0.4	11.4	10.3	-3.6
	PCC-silica (11% silica)	0.0	2.9	4.1	-5.2
	PCC-silica (21% silica)	-5.9	7.9	5.6	-7.4
	PCC-silica (29% silica)	-6.3	13.2	7.0	-17.1
	GCC1-silica	-11.4	19.7	-1.2	-9.3
	GCC2-silica	-7.5	18.1	0.0	-7.9
	PCC-TiO ₂ 10%	-1.2	15.6	3.2	-21.6
PCC-TiO ₂ 25%	-2.6	15.0	1.4	-11.7	
Ca. 26% filler	PCC-silica (29% silica)	6.1	15.3	22.7	-18.1
	PCC-silica: pilot scale (33% silica)	-4.2	39.9	47.5	-29.9

When the new PCCs modified with cellulose derivatives were used as fillers a slight improvement of the handsheets tensile and tear indices was obtained, in comparison to the use of unmodified PCC, and the retention and optical properties were not much affected. For the PCC coated with alginate and PDMA (6 coating layers, 3 layer of each PEL), a great improvement of the mechanical properties and no relevant impact on the optical properties were found, if compared to those achieved with the unmodified PCC. As for the new PCC-silica materials (composites with different silica contents were used as fillers in the production of handsheets) a significant improvement of the main strength properties (relative to the unmodified PCC) was found. However, the light scattering coefficient and opacity decreased while brightness was not much affected, probably due to the more closed handsheets (as evidenced by the decrease in sheet bulk – 5% decrease when compared to handsheets produced with unmodified PCC) and by the particles rounder shape (Fig. 1c). As for the GCC modified with silica, an improvement in the main paper strength properties (tensile and burst

strengths) were always found by using the GCC-silica composite but, contrary to the use of the scalenohedral PCC particles, the handsheets bulk increased. As in the PCC-silica results, the optical properties were negatively affected.

The work was continued by studying the influence of increasing amounts of the filler that exhibited overall better results in terms of retention, mechanical and optical properties: PCC-silica hybrid with a silica content of ca 30 wt%. Besides, PCC, and not GCC, was chosen since it is the filler used by the Portuguese producers of printing and writing papers. For that, formulations containing from 20% up to 45% of mineral filler were used to produce lab handsheets, and the main paper strength properties were improved when compared to the same filler contents using unmodified PCC (Fig. 4). As already stated, the handsheets optical properties were slightly negatively affected due to the densification of the paper structure. Even though, it was found that it was possible to increase the filler content in 5 wt% without affecting the paper resistance, when using the new modified PCC-silica material.

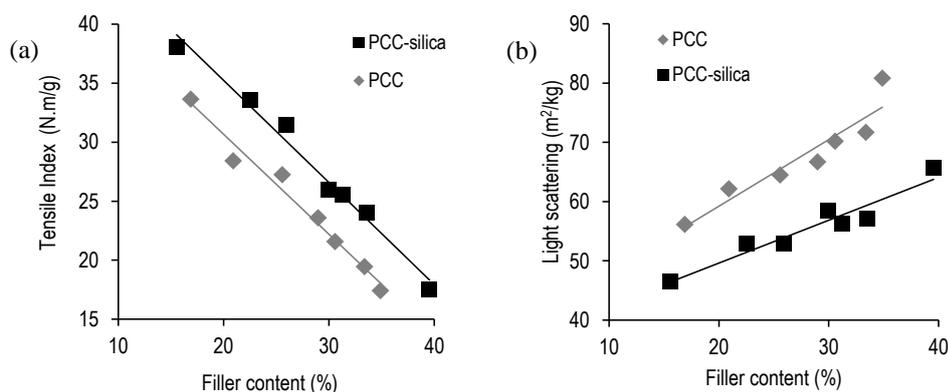


Figure 4. Tensile index (a) and light scattering (b) of handsheets prepared with PCC and PCC modified with 29wt% of silica, at different filler levels.

Considering that the upscaling of the filler modifying process and of the papermaking processes was important to evaluate the feasibility of the new modified fillers, the PCC-silica hybrid with a silica content of ca 30 wt% was chosen, by the reasons mentioned above, to be used in a pilot paper machine. The use of this new material at pilot scale confirmed its huge potential as filler since the improvement of the mechanical properties was even greater than the one obtained at lab scale, using the same furnish composition (Table 4).

As for the PCC-TiO₂ composite obtained by grinding PCC and titanium powder together, papermaking results showed that the mechanical properties were enhanced (ca. 15% for tensile index). If compared with handsheets produced with the same components amounts (10% of TiO₂ and 90% of PCC) but mixed individually in the handsheets production, the new hybrid revealed to be much more efficient since with the individual mixing only a 6.5% increment of the tensile index was found. However, in this case the light scattering was improved (8.2% relative to handsheets produced with unmodified PCC) since the grinding process was not used.

The positive influence of the modified fillers on the papermaking properties results from a better bonding between the mineral particles and the fibres, in most cases by hydrogen-bonding.

When comparing the results obtained with the literature concerning mineral fillers modification that present the most promising values, the main conclusions are that, contrary to the present study, in most cases the modified material is not isolated, or in other words, the modification is performed in the mineral suspension and the latter is directly applied in the papermaking slurry. This limits its utilization and commercialization on other products. Regarding the papermaking properties, improvements of the tensile index of ca. 60% were reported by using a starch-coated PCC [8], but, apart from starch, it seems that all the other modifiers only led to slight increases of the tensile properties and filler retention. The better results were obtained with fillers modified with xantham gum that improved the breaking length by 30% [15] or with PCC treated with cationic and carboxymethyl chitosan that were able to improve the tensile index by 16% and filler retention by 50% [11].

CONCLUSIONS

Mineral fillers (PCC and GCC) were modified with different components in order to improve the filler-to-fibre bonding in papermaking. The characterization of the new composites by thermogravimetric analysis, SEM images and FTIR confirmed the presence of the modifiers - cellulose derivatives (cellulose acetate and cellulose acetate butyrate), polydiallyldimethylammonium chloride, silica and titanium dioxide – at the surface of the minerals particles. The composites were used as fillers in papermaking. A retention and drainage study revealed that a linear cationic polyacrylamide was the best retention agent for use in the papermaking tests. The mechanical properties of handsheets produced with the new modified fillers always improved when compared to that of handsheets produced with the reference filler. The most promising composite was found to be PCC modified with 29wt% of silica and therefore, handsheets with increasing filler contents were produced. It was found that, by using this new composite, it was possible to increase the filler content in 5% without affecting the paper resistance. However, this result was accompanied by a slight decrease of light scattering. Besides, the use of this new material at pilot scale confirmed its good potential as filler. One of the drawbacks of incorporating mineral fillers in papermaking, namely the limit to use higher filler amounts, may now be overcome by using the aforementioned modified fillers.

REFERENCES

1. CEPI. Key statistics, *in*: European Pulp and Paper Industry, Conf. Europ. Pap Ind., Brussels (2014).
2. M.A. Hubbe, R.A. Gill. Fillers for papermaking: a review of their properties, usage practices, and their mechanistic role. *BioResources* **11**(1): 2886-2963 (2016).
3. B Thorp. Engineered fillers: an agenda 2020 goal. *Solutions! for People, Proc Paper*, **May**: 45-48 (2005).
4. J Shen, Z Song, X Qian, W Liu. Modification of papermaking grade fillers: a brief review. *Bioresources*, **4**: 1190-1209 (2009).
5. L Raymond, R Turcotte, R Gratton. The challenges of increasing filler in fine paper. *Pap Tech.*, **July**: 34-40 (2004)
6. W.Cheng, J.Li, Y.Zhao, Q Rao. Method of increasing filler content in papermaking. *US patent* 8088250B2 (2012).
7. M.A. Hubbe. Prospects for maintaining strength of paper and paperboard products while using less forest resources: a review. *BioResources* **9**(1): 1634-1763 (2014).
8. Y. Zhao, Z. Hu., A. Ragauskas, Y Deng. Improvement of paper properties using starch-modified precipitated calcium carbonate filler. *Tappi J.*, **2** (4): 3-7 (2005).
9. X. Huang, Z. Sun, X. Qian, J. Li, J. Shen Starch/sodium oleate/calcium chloride modified filler for papermaking: Impact of filler modification process conditions and retention systems as evaluated by filler bondability factor in combination with other parameters. *Ind. Eng. Chem. Res.* **53**: 6426-6432 (2014).
10. V. Myllymaki, R. Aksela, A. Sundquist, S.M. Karvinen. New composite materials, method for their preparation and use in paper and board manufacturing. *WO Patent* 097571 (2006).
11. Z. Chen, C. Li, Z. Song, X. Qian. Modification of precipitated calcium carbonate filler for papermaking with adsorption of cationically derivatized chitosan and carboxymethyl chitosan. *BioResources* **9**(4): 5917-5927 (2014).
12. D.S. Kim, C.K. Lee. Surface modification of precipitated calcium carbonate using aqueous fluosilicic acid. *Appl. Surf. Sci.* **202**(1-2): 15-23 (2002).
13. J. Shen, Z. Song, X. Qian, W. Liu. Modification of precipitated calcium carbonate filler using sodium silicate/zinc chloride based modifiers to improve acid-resistance and use of the modified filler in papermaking. *Bioresources* **4**: 1498-1519 (2009).
14. J. Shen, Z. Song, X. Qian, W. Liu. A preliminary investigation into the use of acid-tolerant newspaper. *Bioresources* **4**: 1178-1189 (2009).
15. G. H. Fairchild. Treatment of inorganic filler material for paper with polysaccharides. *US Patent* 5458679 (1995).
16. J.A. Gamelas, A.F. Lourenço, M. Xavier, P.J. Ferreira. Modification of precipitated calcium carbonate with cellulose esters and use as filler in papermaking. *Chem. Eng. Res. Des.* **92**: 2425-2430 (2014).
17. A.F. Lourenço, J.A. Gamelas, P.J. Ferreira. Precipitated calcium carbonate modified by the layer-by-layer deposition method – Its potential as papermaking filler. *Chem. Eng. Res. Design* **104**: 807-813 (2015).
18. J.A.F. Gamelas, A.F. Lourenço, P.J. Ferreira. New modified filler obtained by silica formed by sol-gel method on calcium carbonate. *J. Sol-Gel Sci. Technol.* **59**: 25–31. (2011).
19. A.F. Lourenço, J.A.F. Gamelas, C. Zscherneck, P.J. Ferreira. Evaluation of silica-coated PCC as new modified filler for papermaking. *Ind. Eng. Chem. Res.* **52**(14): 5095-5099 (2013).
20. A.F. Lourenço, J.A.F. Gamelas, P.J. Ferreira. Increase of the filler content in papermaking by using a silica-coated PCC filler. *Nord. Pulp Paper Res. J.* **29**: 240-245 (2014).
21. A.F. Lourenço, J.A.F. Gamelas, P.J. Ferreira. Papermaking trials in a pilot paper machine with a new silica coated PCC filler. *Nord. Pulp Paper Res. J.* **31**(2): 341-346 (2016).
22. A.F. Lourenço, J.A.F. Gamelas, J. Sequeira, P. Ferreira, J.L. Velho. Improving paper mechanical properties using silica modified ground calcium carbonate as filler. *BioResources* **10**(4): 8312-8324 (2015).