Increase of the filler content in papermaking by using a silica-coated PCC filler

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KEYWORDS: Calcium carbonate; Silica; Paper filler; Strength properties

SUMMARY: The increase of filler content in paper without significantly sacrificing the paper mechanical resistances is of high interest for papermakers. In this work, precipitated calcium carbonate (PCC) modified with silica was used as filler for papermaking. Handsheets based on a eucalyptus kraft pulp furnish with different amounts of the modified filler, ranging from 16 to 40%, were produced.

For similar levels of filler content it was found that the strength properties of the handsheets produced with the modified PCC were always significantly better than those obtained with the unmodified PCC. In particular, for handsheets with a filler content of 30%, the tensile index and the Scott bond internal resistance improved by ca. 20% and 39%, respectively. Some decrease of the light scattering and opacity values was noted when using the modified PCC, but the brightness was roughly the same, for each filler level evaluated. The enhanced fibre-to-filler bonding can be due to the hydrogen bonding between the cellulosic fibres and the hydroxyl groups of the silica film coating the calcium carbonate crystals, during the sheet formation. The present results with the new modified PCC provide a possibility to increase the filler amount in the papermaking industry.

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After cellulosic fibres, mineral fillers are the most important components used to produce paper. One of the major benefits of using fillers is economical since, in general, they are much cheaper than the cellulosic fibres and they improve drainage in the paper machine, thus reducing drying costs. Besides, the mineral fillers typically improve the paper optical properties and also bulk and smoothness. However, they are harmful for the paper mechanical resistances due to a decrease of the fibre bonding. Besides, additional problems of retention, dusting and white waters recirculation tend to occur when they are used (Raymond et al. 2004; Thorp 2005).

The most common fillers employed in papermaking are kaolin, talc, ground and precipitated calcium carbonate (GCC and PCC, respectively) and titanium dioxide. Titanium dioxide is a very expensive material and is used only when high optical properties of the final product are required. Kaolin and talc may not meet the requirement of acceptable optical properties, namely light scattering. On the other hand, PCC typically shows brightness values higher than GCC and therefore it is increasingly employed for printing and writing papers.

For the aforementioned reasons, there is a general interest of the papermaking industry in increasing the filler content of paper. For that it is crucial to overcome the main drawback related to the presence of the mineral fillers: the decrease in fibre-to-fibre bonding and, thus, the reduction of the paper strength. One of the most important strategies to solve this problem consists in chemically modifying the fillers surface, with the objective of contributing to a better fibre-to-filler-to-fibre bonding, so that the filler negative impact on the paper resistance is mitigated. This is one of the research topics concerning filler engineering (Thorp 2005; Shen et al. 2010a).

Some treatments/modifications of the PCC filler surface have been reported. Precipitated calcium carbonate has been treated/modified by a wide range of organic compounds such as starch and starch derivatives (Zhao et al. 2005; Shen et al. 2009a; Deng et al. 2011; Fan et al. 2012; Huang et al. 2013), cellulose (Myllymaki et al. 2006; Nelson, Deng 2008), cellulose derivatives (Van der Horst et al. 2005; Fairchild 2008; Shen et al. 2010b; Gamelas et al. 2014); chitosan (Shen et al. 2008), xanthan gum (Fairchild 1995), water-soluble synthetic polymers (Gill 1991), and polymer latexes (Laleg et al. 2008), among others, and by inorganic compounds such as calcium-chelating agents (e.g. sodium hexametaphosphate), weak acids (e.g. phosphoric acid), aluminium salts (e.g. aluminium chloride), zinc chloride, and sodium silicate (Passaretti 1991; Tokarz et al. 1991; Chapnerkar et al. 1992; Wu 1997; Snowden et al. 2000; Jaakkola, Manner 2001; Shen et al. 2009b; Shen et al. 2009c). Regarding the modification with inorganic compounds, most of the reported treatments were directed to obtain calcium carbonate-based fillers with improved acid-resistant properties, which are required for papermaking in weakly acid to neutral conditions, and for this reason they have less interest for the present study.

The strength properties of the handsheets prepared with new modified fillers and the effect of the filler content variation on the paper properties have been mentioned in just a few studies. In particular, an increase of Scott bond and breaking length was found for handsheets produced with PCC treated with low amounts (< 1%) of anionic polysaccharides (xanthan gum and anionic guar gum), at two different levels of filler percentage (Fairchild 1995). Zhao et al. reported that handsheets produced with starch gel-coated PCC show much better tensile and tear strength than those produced with unmodified PCC, while the optical properties are not significantly affected, at filler levels ranging from about 5 to 25% (Zhao et al. 2005). Laleg et al. (2008) treated PCC particles with anionic polymer dispersions (latex) and found that the resultant slurries could improve paper internal resistance

and breaking length for filler levels in the handsheets in the range of 10 to 25%, besides improving filler retention, sizing performance and acid-resistant properties of filler in papermaking.

The authors of the present paper have recently reported the synthesis and characterization, by several techniques, of a new type of PCC-based material containing a film of silica at the surface of calcium carbonate scalenohedral crystals (Gamelas et al. 2011). New PCC-silica materials with different amounts of silica were obtained by a sol-gel method under alkaline conditions. The application of these new materials in the papermaking for a target of 20% of filler content in the handsheets was later reported and it was found that, in these conditions, they could improve fibre-filler interactions and, thus, the paper strength properties in comparison to unmodified PCC (Lourenço et al. 2013). In the present article, the PCC-silica modified filler containing 28 wt% of silica was studied with higher detail for its papermaking potential in a wide range of filler levels, aiming at increasing the filler amount in the handsheets without affecting the paper performance.

Materials and Methods

PCC and PCC modification

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

Silica-coated PCC particles with an average silica content of 28 wt% were obtained by firstly mixing water (135 ml), ethanol (1265 ml) and NH_3 25% (33.7 ml). After, 15 g of PCC followed by 67.5 ml of tetraethoxy-silane were added under moderate mechanical stirring to the resulting solution. The mixture was allowed to stand for 24 h under constant stirring at ca. 20ºC. The final solid was filtered using a Büchner filter, washed with ethanol and then dried in an exsicator under vacuum for one week. It should be noted that PCCs with distinct amounts of silica can be obtained by the sol-gel method, but a PCC with ca. 30 wt% of silica was selected for this work since in previous studies it was found to be the most adequate to improve the paper strength properties (when used as filler in handsheets containing ca. 16% of filler content) (Lourenço et al. 2013). The thorough characterization of the new modified filler by several spectroscopic and analytical techniques, such as SEM, laser diffraction spectroscopy, powder X-ray diffraction and FTIR, has been previously detailed (Gamelas et al. 2011).

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 refined up to 33ºSR was used as the cellulosic fibre source. After disintegration it was diluted to a consistency of 1% in demineralized water. Aqueous suspensions of the unmodified or silica-modified PCC containing 1 wt% of filler were prepared by adding water to PCC and stirring, first with magnetic stirring (20 min) and after with ultrasound (15 min, 50 KHz) before use. Alkenyl succinic anhydride (ASA) supplied by the industry was used as the internal sizing agent after stabilization by adding it to a 3% starch suspension standing at 60ºC (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 demineralized water.

Table 1 - Amounts (wt%) of each component used in the handsheets production.

	1	2	3	4	5	6	7
Fibre	79.1	73.9	68.9	64.9	62.9	60.9	53.9
PCC	**19.7**	**25.0**	**30.0**	**34.0**	**36.0**	**38.1**	**45.0**
Starch	1.0	1.0	1.0	1.0	1.0	1.0	1.0
ASA	0.13	0.13	0.13	0.13	0.13	0.13	0.13
C-PAM	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Total	100	100	100	100	100	100	100

*ASA: alkenyl succinic anhydride; C-PAM: cationic polyacrylamide

Handsheets were produced in a batch laboratory sheet former (255/SA model, MAVIS) using a 120 mesh screen with formulations containing fibre, PCC (unmodified or modified with silica), ASA, starch, and the retention agent. The aim was to achieve a basis weight of 80 g/m^2 and target filler contents in the handsheets varying from 20 to 45%. The amounts (wt%) of each component added in each series of experiments are shown in *Table 1*. A mixture of the fibre suspension with the PCC suspension was prepared. After 120 s of magnetic stirring, the starch/ASA mixture (at ca. 60ºC) was added. The cationic polyacrylamide 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 drainage was performed after 10 s of air agitation. 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 structural properties (basis weight, density, bulk, thickness and surface roughness), mechanical properties (tensile strength, stiffness, tear and burst strengths) and optical properties (light scattering, opacity and brightness) were measured according to the corresponding ISO Standard Test Methods. The internal bond strength was measured using the corresponding Tappi Standard. Finally, the handsheets were also calcined at 525ºC for 16 h to determine the retention of PCC and PCC-silica.

Filler Retention

The retention of PCC and PCC-silica was calculated based on Tappi Standard T 211 om-93 for ashes determination. Besides, losses intrinsically due to the PCC and silica-coated PCC occurring during the thermal treatment at 525ºC were also accounted for. For that, experiments were carried out in the furnace using only the unmodified PCC or the silica-coated PCC. For unmodified PCC the weight loss correction factor due to the PCC impurities degradation was found to be 2.2%. For the PCC modified with 28 wt% of silica, the correction factor due to solvent removal, impurities degradation and condensation of hydroxyl groups was 10.3%. Considering these values, the retention (%) of PCC (and PCC-silica) in the handsheets was calculated as

follows: [weight at 525 ºC/ ((weight of initial filler) × (100 - correction factor))] × 10^4.

Results and Discussion

In the present study, a PCC-based material containing a dense film of highly branched silica (28 wt% of silica) at the surface of the particles (Gamelas et al. 2011) was used as filler for papermaking. Different filler contents were tested and the results were compared with those obtained with the unmodified PCC.

Laboratorial handsheets were made using the amounts listed in *Table 1*. In general, the filler retention was higher for the handsheets with the modified PCC: values around 80% and 85% were obtained when the reference PCC and PCC-silica were used, respectively. The effective filler contents were thus inferior to those incorporated in the handsheets preparation (*Table 1*): filler levels of 17, 21, 26, 29, 31, 33 and 35%, and of 16, 23, 26, 30, 31, 34 and 40% were found for handsheets produced with the unmodified PCC and with the PCC-silica material, respectively.

The most relevant results of the handsheets with PCC and PCC-silica are plotted in *Fig 1-5* for all the filler levels evaluated. In addition, and as an example, *Table 2* summarizes the results obtained for effective filler levels of *ca.* 22% and 33%. From the different plots, it is visible that both with the original PCC and with the modified PCC, sheet bulk, surface roughness, light scattering and opacity increase with the filler content. The opposite occurs with regard to the strength properties. This is a consequence of the formation of a more open sheet structure with a smaller relative amount of fibres and also a smaller fibre-to-fibre bonding degree. As can be seen in *Table 2*, an increase of the filler content in the handsheets from *ca.* 22 up to *ca.* 33% promotes an increase of the light scattering values of 15% for the handsheets produced with the reference PCC and of 8% for those produced with the PCC-silica hybrid. On the other hand, the tensile index decreased 32% with the unmodified PCC and 29% with the PCC-silica material. These results are within the expected behavior regarding the effect of the filler content variation in paper production.

When comparing the performance of both fillers (PCC-silica and PCC), for similar filler contents, it is possible to verify that, typically, with the new modified filler the handsheet bulk decreases (*Fig 1a)* and the roughness is not affected (*Fig 1b*). Besides, the tensile index and the tear index greatly increase (*Fig 2a* and *Fig3a)*, with maximum increments of 24% and 18%, respectively. The tensile stiffness and burst index show a similar trend (*Fig 2b* and *Fig 3b*).

Table 2 - Papermaking properties of handsheets produced with PCC and PCC-silica* as fillers.

	PCC	PCC-silica	PCC	PCC-silica
Effective filler content (%)	20.9	22.5	33.4	33.6
Basis weight (g/m^2)	81.2	81.8	78.4	81.4
Bulk (cm^3/g)	1.73	1.65	1.76	1.67
Roughness (smooth side, mL/min)	265	271	281	247
Brightness (R457 C)	88.9	88.4	90.0	89.8
Opacity (%)	89.1	87.3	90.3	87.9
Light scattering (m^2/kg)	62.1	52.8	71.7	57.1
Tensile index (N.m/g)	28.4	33.6	19.4	24.0
Tensile stiffness (kN/m)	442	485	344	401
Burst index (kPa·m^2/g)	1.5	1.7	1.0	1.2
Tear index (mN.m^2/g)	5.6	6.1	3.5	3.6
Scott Bond (J/m^2)	201	277	139	176

* A PCC-silica hybrid with 28 wt% of silica was used.

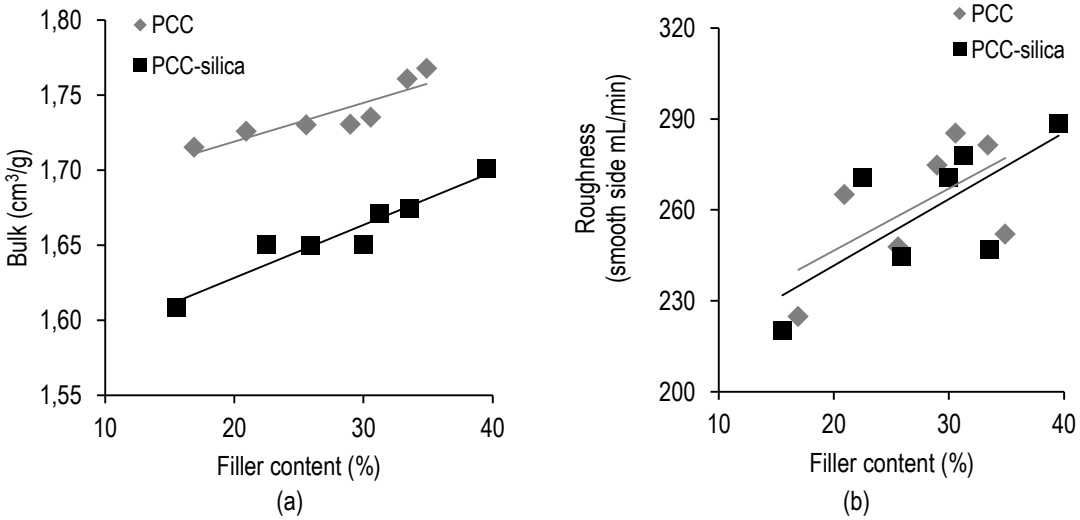

Fig 1 - Bulk (a) and roughness (b) of handsheets prepared with PCC-silica and PCC at different filler levels.

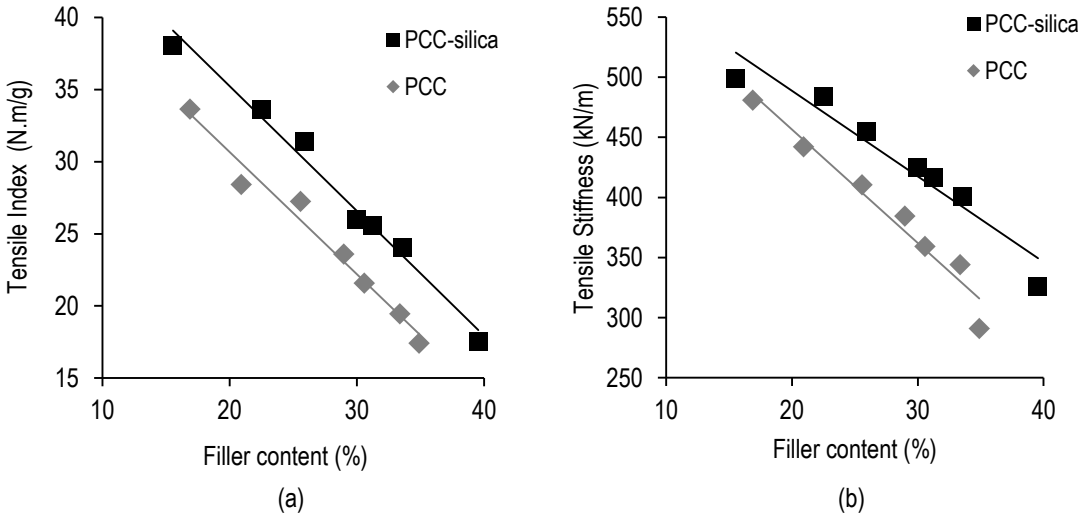

Fig 2 - Tensile index (a) and tensile stiffness (b) of handsheets prepared with PCC-silica and PCC at different filler levels.

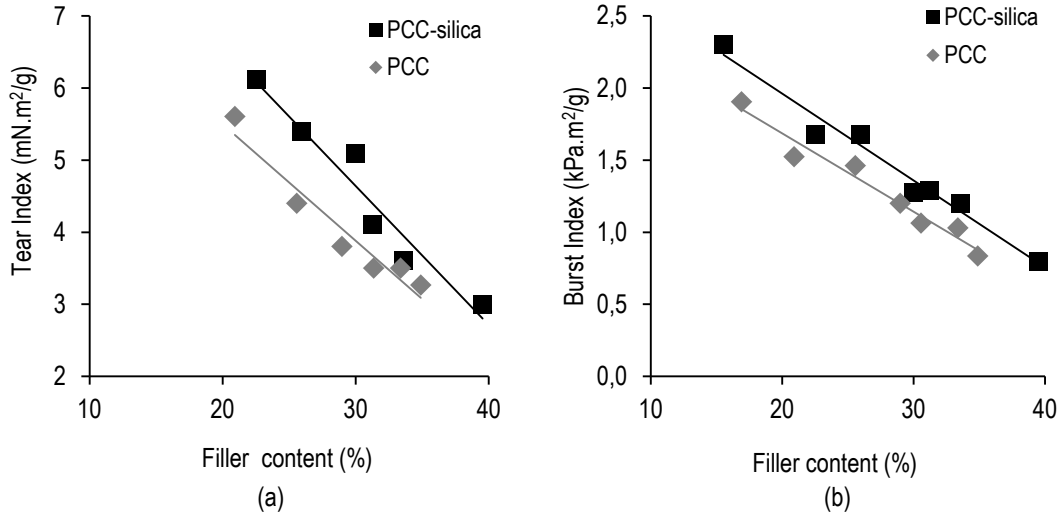

Fig 3 - Tear index (a) and burst index (b) of handsheets prepared with PCC-silica and PCC at different filler levels.

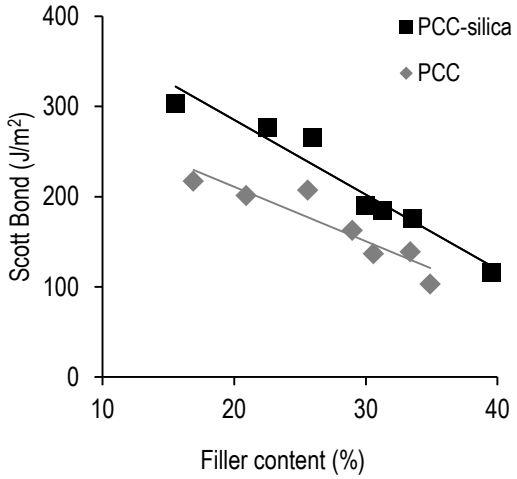

Fig 4 - Internal resistance measured by the Scott bond of handsheets prepared with PCC-silica and PCC at different filler levels.

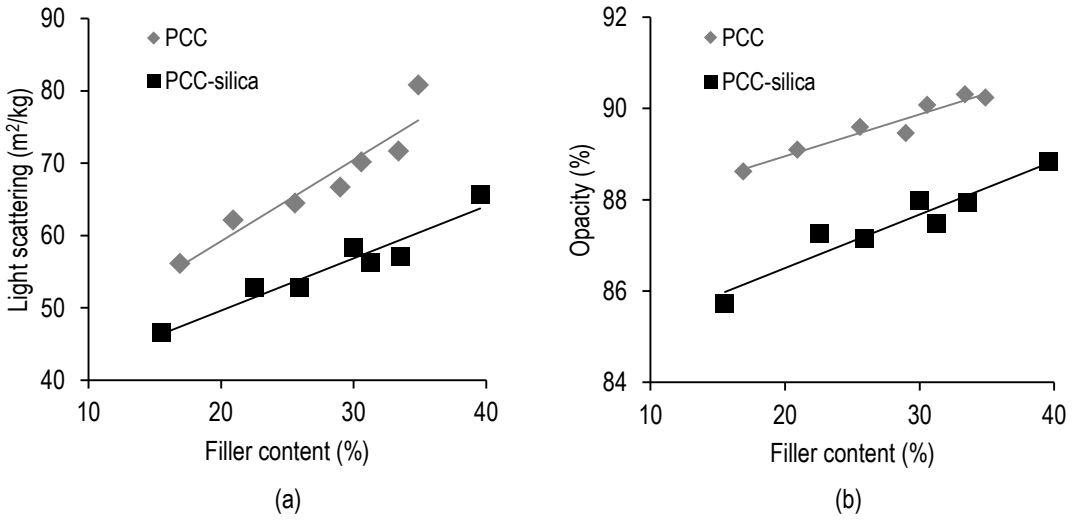

Fig 5 - Light scattering (a) and opacity (b) of handsheets prepared with PCC-silica and PCC at different filler levels.

The Scott Bond value (*Fig 4*) was also found to be considerably higher (with a maximum increase of 50%) for the handsheets produced with the PCC-silica filler. These results show thus that by modifying PCC with silica it is possible to increase the fibre-to-filler bonding and to produce therefore handsheets with strength properties superior to those usually obtained with the unmodified PCC. The hydrogen bonding between the cellulosic fibres and the hydroxyl groups of the silica film coating the calcium carbonate crystals (during the sheet formation) is most probably the main responsible for the enhancement of the fibre-to-filler bonding (Gamelas et al. 2012).

On the other hand, some of the optical properties were negatively affected: for the handsheets produced with PCC-silica the light scattering decreased up to 20% (*Fig 5a*) and the opacity decreased up to 3% (*Fig 5b*). These losses are explained by the fact that the handsheets with PCC-silica exhibit a more closed structure, as evidenced by the decrease of the sheet bulk (*Fig 1a*), so that there are fewer interfaces for light scattering. This effect can be also magnified by the rounder shape and larger size of the modified PCC particles (Hubbe et al 2008) (SEM images of the PCC-silica material can be found in Gamelas et al. 2011). The influence of the slightly smaller refractive index of silica compared to calcium carbonate (1.45 vs. 1.57) on the optical properties of the silica hybrid material is not to be neglected. Notwithstanding, the handsheets brightness was not significantly affected (a maximum relative decrease of 1%), in agreement with the similar brightness values of the original PCC and PCC-silica particles (Lourenço et al. 2013).

The most striking positive effect of the PCC modification with silica was on the paper strength properties, in agreement with the main goal of this study. In spite of these results, which anticipate the possibility of increasing the filler level in paper by using a new modified filler, the process has the drawback of its additional costs, especially considering the comparatively high cost of the tetraethoxysilane precursor employed to produce the PCC-silica material from PCC. Thus, although the new material clearly strengthens the fibre-to-filler-to-fibre bonding in *eucalyptus*-based handsheets in comparison to common PCC, more studies need to be carried out aiming its production at a more competitive cost.

Conclusions

The possibility of increasing the filler content in papermaking was evaluated by studying the performance of a new silica-containing PCC filler and by comparing it to that of a common unmodified PCC filler. For similar filler contents in *eucalyptus* kraft pulp based-handsheets, ranging from *ca*. 16 up to 40%, an improvement of the main paper strength properties (tensile, tear and burst resistances, and internal bonding) was always found by using the PCC-silica hybrid as filler. The optical properties such as light scattering and opacity had a minor decrease on their values, mainly related to the more closed handsheet structure, but brightness was not far from that obtained for the handsheets produced with the unmodified PCC. Remarkably, when using the silica-modified PCC, it is possible to increase the effective handsheets filler content in 5% without affecting the tensile strength properties.

Therefore, it may be concluded that this new material effectively promotes the fibre-to-filler bonding and enables the production of paper with higher amount of fillers.

Acknowledgements

The authors thank FCT (Fundação para a Ciência e Tecnologia) for financial support (PTDC/EQU-EQU/120578/2010) and RAIZ (Instituto de Investigação da Floresta e do Papel) for the laboratory facilities and some furnish components (fibres, starch, ASA and C-PAM).

Literature

Chapnerkar, V.D.; Lasmarias, V.B. and Matur, V.K. (1992): Method for preparing acid resistant calcium carbonate pigments. US Patent 5,164,006.

Deng, Y., Yoon, S., Ragauskas, A. and White, D. (2011): Methods and compositions for papermaking. US Patent 7,964,063 B2.

Fairchild, G.H. (1995): Treatment of inorganic filler material for paper with polysaccharides. US Patent 5,458,679.

Fairchild, G.H. (2008): Treatment of inorganic pigments with carboxymethylcellulose compounds. European Patent 0731826 B2.

Fan, H.M., Wang, D.X., Bai, W.R. and Liu, J.N. (2012): Starch-sodium stearate complex modified PCC filler and its application in papermaking, Bioresources 7 (3), 3317-3326.

Gamelas, J.A.F., Lourenço, A.F. and Ferreira, P.J. (2011): New modified filler obtained by silica formed by sol-gel method on calcium carbonate, J Sol-Gel Sci Technol. 59, 25-31.

Gamelas, J.A.F., Evtyugina, M.G., Portugal, I. and Evtuguin, D.V. (2012): New polyoxometalate-functionalized cellulosic fibre/silica hybrids for environmental applications, RSC Advances 2, 831-839.

Gamelas, J.A.F., Lourenço, A.F., Xavier M. and Ferreira, P.J. (2014): Modification of precipitated calcium carbonate with cellulose esters and use as filler in papermaking, Chem. Eng. Res. Des. http://dx.doi.org/10.1016/j.cherd.2014.02.003

Gill, R.A. (1991): Cationic polymer-modified filler material, process for its preparation and method. Canada Patent, 2037525.

Huang, X., Shen, J. and Qian, X. (2013): Filler modification for papermaking with starch/oleic acid complexes with the aid of calcium ions. Carbohydr. Polym. 98, 931-935.

Hubbe, M., Pawlak, J. and Koukoulas, A. (2008): Paper's Appearance: A Review, BioResources 3(2), 627-665.

Jaakkola, P. and Manner, H. (2001): Comparison of methods for stabilization of PCC against dissolution at acid papermaking conditions, Nord. Pulp Paper Res. J. 16 (2), 113-117.

Laleg, M., Collins, R., Gagne, D. and Middleton, S. (2008): Latex-treated filler slurries for use in papermaking. WO Patent 148204.

Lourenço, A.F., Gamelas, J.A.F., Zscherneck, C. and Ferreira, P.J. (2013): Evaluation of silica-coated PCC as new modified filler for papermaking, Ind. Eng. Chem. Res. 52 (14), 5095-5099.

Myllymaki, V., Aksela, R., Sundquist A. and Karvinen, S.M. (2006): New composite materials, method for their preparation and use in paper and board manufacturing. WO Patent 097571.

Nelson, K. and Deng, Y. (2008): Enhanced bondability between inorganic particles and a polysaccharide substrate by encapsulation with regenerated cellulose, J Appl. Polym. Sci. 107, 2830-2836.

Passaretti, J.D. (1991): Acid-stabilized calcium carbonate, process for its production and method for its use in the manufacture of acidic paper. US Patent 5,043,017.

Raymond, L., Turcotte, R. and Gratton, R. (2004): The challenges of increasing filler in fine paper, Paper Technol. July, 34-40.

Saraiva, M.S., Gamelas, J.A.F., de Sousa A.P.M., Reis, B.M, Amaral, J.L. and Ferreira, P.J. (2010): A new approach for the modification of paper surface properties using polyoxometalates, Materials 3, 201-215.

Shen, J., Song, Z.Q., Qian, X.R. and Song, C.J. (2008): Chitosan-coated papermaking grade PCC filler prepared by alkali precipitation: properties and application, Proceedings from the 2nd International papermaking and Environment Conference, Books A and B, Tianjin, China, 659-664.

Shen, J., Song, Z., Qian, X. and Liu, W. (2009a): Modification of papermaking grade fillers: a brief review, Bioresources, 4 (3), 1190-1209.

Shen, J., Song, Z., Qian, X. and Liu, W. (2009b): A preliminary investigation into the use of acid-tolerant precipitated calcium carbonate fillers in papermaking of deinked pulp derived from recycled newspaper, Bioresources 4 (3), 1178-1189.

Shen, J., Song, Z., Qian, X. and Liu, W. (2009c): 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 (4), 1498-1519.

Shen, J., Song, Z., Qian, X. Liu W. and Yang, F. (2010a): Filler engineering for papermaking: comparison with fiber engineering and some important research topics. Bioresources 5, 510-513.

Shen, J., Song, Z., Qian, X. and Yang, F. (2010b): Carboxymethyl cellulose/alum modified precipitated calcium carbonate fillers: preparation and their use in papermaking, Carbohydr. Polym. 81, 545-553.

Snowden, K.J., Wu, K.T. and Rodriguez, J.M. (2000): Stabilized calcium carbonate composition using sodium silicate and one or more weak acids or alum and uses therefor. US Patent 6,083,317.

Thorp, B. (2005): Engineered fillers: an agenda 2020 goal, Solutions People, Processes Pap. May, 45-48.

Tokarz, M., Jaras, S. and Sikkar, R. (1991): Process for the preparation of an acid-resistant coating on filler particles. US Patent 5,000,791.

Wu, K.T. (1997): Acid resistant calcium carbonate composition and uses therefor. US Patent 5,593,488.

Van Der Horst, P.M., Sanne, E., Andersson, K.R., Garcia-Lindgren, C., Wallberg, M. and Wannstrom, S. (2005): Filler for papermaking process. WO Patent, 061793.

Zhao, Y., Hu, Z., Ragauskas, A. and Deng, Y. (2005): Improvement of paper properties using starch-modified precipitated calcium carbonate filler, Tappi J. 4(2), 3-7.

Manuscript received October 24, 2013
Accepted January 21, 2014