Improving Paper Mechanical Properties Using Silica-modified Ground Calcium Carbonate as Filler

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The ability to increase the filler content of paper without significantly sacrificing its mechanical strength is of high interest for papermakers. In this work, three samples of ground calcium carbonate (GCC), differing in size and in brightness, modified with silica *via* the sol-gel method, were used as fillers in papermaking. Handsheets were produced using a *eucalyptus* kraft pulp furnish and with a filler amount near 20%. It was found that not only were the strength properties of the handsheets produced with the modified GCCs always significantly better than those obtained with the unmodified GCCs (*e.g.*, the tensile index exhibited improvements of 16 to 20%), but bulk also was increased (by 7 to 13%). Some decreases in the light scattering and opacity values were noted when using the modified GCC, but the brightness was roughly the same. The enhanced fiber-to-filler bonding may be attributed to the hydrogen bonding between the cellulosic fibers and the hydroxyl groups of the silica coating the calcium carbonate particles.

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

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INTRODUCTION

The importance of using mineral fillers in papermaking, especially in printing and writing grades, is so great that each year 13.6 million tons of filler are consumed (Laufmann and Gisella 2011). Precipitated and ground calcium carbonate (PCC and GCC, respectively), kaolin, talc, and titanium dioxide are the most important fillers. Their usefulness is not only economical (since they replace expensive cellulose fibers), but they also impart to paper important properties such as opacity, bulk, and smoothness that are crucial for paper quality. Moreover, they exert a positive influence on the papermaking process, runnability, and energy consumption. If it were possible to increase by 5% the filler content of a paper grade with, on average, a filler content of 30%, then for a paper mill producing 1800 tons/day, a considerable amount (90 tons/day) of fiber could be replaced.

GCC is a common filler used in the paper industry due to its high brightness, adequate rheology, and particle size versatility. However, as a calcium carbonate, it is intolerant to low pH values. In order to overcome this drawback, several studies have been developed: Passaretti (1991) modified GCC with a calcium chelating agent (sodium hexametaphosphate), while Chapnerkar *et al.* (1992) used sodium silicate and zinc chloride; Wu (1996) employed cationic and anionic salts, and Snowden *et al.* (1998) mixed GCC with sodium aluminate and a weak acid (*i.e.*, phosphoric acid) in order to produce acid-resistant GCCs. Despite its high degree of brightness, GCC does not compete with other fillers such as PCC and TiO_2, which confer optimal optical properties to paper. Nonetheless, the high price of the latter is a serious drawback for the industry. Therefore, some solutions have been proposed for granting good optical properties to GCC, namely, blending it with other fillers (Hubbe 2004; Santos and Velho 2004) or coating it with optically efficient fillers or other compounds (Wu 1996; Virtanen 2000).

Fillers can be 4 to 7 times less costly than kraft pulp, and the energy savings due to the incorporation of filler can reach values of 4% when 1% of the solids content is increased, since the sheets can be dried more quickly, consuming therefore a reduced amount of energy for water evaporation (Dong *et al.* 2008; Cheng *et al.* 2011). Nowadays, printing and writing papers can incorporate filler contents of about 20 to 40% (w/w) (mainly in the form of kaolin, PCC, GCC, and talc) (Cheng and Gray 2014). Even so, the main challenge in papermaking continues to be the deleterious influence of filler incorporation on the mechanical properties of paper. In fact, two drawbacks can be identified when aiming to increase the filler content: the reduction in mechanical properties and the additional problem of filler retention. Thus, there must be a compromise between degree of filler incorporation, retention, and paper properties.

A panoply of strategies is being employed to increase the filler content and performance and to improve the properties of paper containing filler in order to satisfy the industry demands. One of these strategies is based on the modification of the filler surface; to this end, techniques such as coating by spray, micro-encapsulation, or surface polymerization can be employed (Kim and Lee 2002; Shui 2003; Sasaki *et al.* 2011). 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 (Zhao *et al.* 2005; Shen *et al.* 2009; Huang *et al.* 2014).

An alternative to starch is cellulose and some of its derivatives. Coating filler particles with cellulose has the aim of 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, therefore improving 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. 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 (Shen *et al.* 2009). Gamelas *et al.* (2014) modified PCC with cellulose esters (cellulose acetate and cellulose acetate butyrate). The new hybrids, when applied as fillers, slightly enhanced the mechanical properties of paper without interfering with its optical properties.

Silica is a chemical compound commonly used in paper coating, especially in matte papers used in ink-jet printing. The silica-gel properties are very particular, namely high surface area, hydrophilicity, and internal porosity, allowing easy ink diffusion along the coating layer. Moreover, silica improves the brightness and opacity of paper. However, it is not applied as a filler in papermaking mainly due to its high production price (Hladnik and Muck 2002; Lee *et al.* 2005). Gamelas *et al.* (2011) modified PCC particles with silica synthesized *in situ* using the sol-gel method. The hydroxyl groups that are generated by this technique were proposed to establish strong interactions with cellulose fibers. Lourenço *et al.* (2013 and 2014) used PCC, modified by this process, as a filler in paper and compared the paper properties to those obtained when using unmodified PCC. They concluded that this new filler enhanced the mechanical properties of paper, *i.e.*, tensile and internal bonding, without affecting its roughness or brightness. The explanation was that the silica coating had enhanced the filler-fiber bonding. Compensating for the increased costs of this method were the increase in the filler level (by up to 5%) and also improvements in the mechanical properties (20% increase in the tensile index).

Considering the clear benefits of modifying the PCC surface with silica *via* the sol-gel method, and also considering the similarity in general characteristics between PCC and GCC, the question of whether the same approach could be used to increase the filler potential of GCC and its content in the paper matrix was posed. The main goal, therefore, of the present study was to analyze whether there could be found, on a lab scale, an improvement in the structural, mechanical, and optical properties of the paper sheets produced with GCC filler particles modified with silica using the sol-gel method.

EXPERIMENTAL

GCC and GCC Modification

Three commercial ground calcium carbonate (GCC) fillers were selected for use in the present study. The main characteristics of these fillers are listed in Table 1. GCC1 and GCC2 possessed the same brightness, while GCC2 and GCC3 were the same size. According to the technical information provided by the supplier, the particle size was determined following sedimentation in a Sedigraph 5100.

Table 1. Selected Properties of GCC Fillers*

	GCC1	GCC2	GCC3
$CaCO_3$ (%)	99	98	98
Average diameter (d_{50}) (µm)	1.7	0.8	0.8
% <2 µm	61	92	92
% <0.8 µm	25	49	54
Brightness R457 (%)	90	91	95

*Technical information obtained by Omya

The modification of GCC particles with silica followed the methodology developed by Gamelas *et al.* (2011). Water (38 mL), ethanol (356 mL), and NH_3 25% (9.5 mL) were mixed in a flask. Afterwards, 4.2 g of GCC followed by 19 mL of tetraethyl orthosilicate (TEOS) were added under moderate mechanical stirring to the resulting solution. The mixture was allowed to stand for 24 h under constant stirring at about 21 °C. Then it was centrifuged, and the resultant solid was washed with 84 mL of ethanol, centrifuged again, and dried at 40 °C over three days. The final dried product was gently milled in a mortar.

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 in Gamelas *et al.* (2011) and Lourenço *et al.* (2013).

Handsheets and Papermaking Properties

Eucalyptus globulus bleached kraft pulp refined up to 33 ºSR was used as the cellulosic fiber source. After disintegration, it was diluted to a consistency of 1% in demineralized water. Aqueous suspensions of the unmodified and silica-modified GCC containing 1 wt.% of filler were prepared by adding water to the filler and stirring, first by magnetic stirring (20 min), and then by sonication (15 min, 50 KHz), before use. A 3% starch suspension standing at 60 ºC was prepared (Saraiva *et al.* 2010). Industry-supplied alkenyl succinic anhydride (ASA, internal sizing agent) was added to the starch suspension. A 0.025% aqueous solution of a linear cationic polyacrylamide (C-PAM), used as retention agent, was also prepared by dissolving the solid in water.

Handsheets were produced in a batch laboratory sheet former (255/SA model, MAVIS) using a 120-mesh screen with formulations containing fiber, GCC (unmodified or modified with silica), ASA, starch, and the retention agent. The total contact time of the retention agent with the other components in the mixture was about 30 s. The aim was to achieve a basis weight of 80 g/m^2 and a target filler content per handsheet of 20%.

The sheets were collected from the web and pressed, dried, and conditioned in accordance with the ISO Standard 5269-1. The structural, mechanical and optical properties were measured following the corresponding ISO Standard Test Methods: basis weight (536:2012), bulk (534:2011), Gurley porosity (5636-5:2003), surface roughness (8791-2:2013), tensile index (1924-2:2008), tear index (1974:2012), burst index (2758:2001), light scattering (9416:2009), opacity (2471:2008) and brightness (2470-1:2009). Two series of handsheets (8 specimens each) were produced with each type of filler. The mean value of the two series and the pooled standard deviation was considered for the discussion of the results.

The handsheets were also analyzed by SEM-EDX using an X-ray spectrometer from Oxford Instruments (model X-Max). Before the EDX spectra acquisition, the samples were first sputter-coated with gold. Finally, the handsheets were also calcined at 525ºC for 16 h for a determination of the effective content of GCC and GCC-silica.

Filler Content

The effective filler content of the GCC and GCC-silica in the handsheets was calculated based on the TAPPI Standard T 211 om-93 for ash determination. The losses intrinsically due to the GCC and silica-coated GCC occurring during the thermal treatment at 525ºC were also accounted for, as a correction factor. For this task, experiments were carried out in the furnace using only the unmodified GCCs or the silica-coated GCC fillers, and correction factors, corresponding to the weight loss at 525 ºC, of 0.44, 1.4, and 3.1% for GCC1, GCC2, and GCC3, respectively, and of 8.9, 9.4, and 9.0% for the corresponding modified fillers were determined. The filler content (%) of the GCC (and GCC-silica) in the handsheets was then calculated as follows (Eq. 1).

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

RESULTS AND DISCUSSION

Characterization of Silica-Modified GCC Particles

The FTIR spectra of both the unmodified and the modified GCCs are shown in Fig. 1. The calcite characteristic bands (*) are clearly identified in all spectra: 1460 cm^{-1} (ν_3 (CO_3)), 872 cm^{-1} ($\nu_2(CO_3)$), and 713 cm^{-1} ($\nu_4(CO_3)$) (Ferreira *et al.* 2009). In the modified GCC samples it is possible to identify additional bands showing the presence of silica (+): 1210 cm^{-1} (sh), 1096 cm^{-1} (ν_{as}(Si-O-Si)), 957 cm^{-1}, 798 cm^{-1} (ν_s(Si-O-Si)), and 467 cm^{-1} (δ(Si-O-Si)) (Schroden *et al.* 2001). The calcite peaks are not as strong and defined in the modified GCCs spectra, which was due to the presence of silica, in accordance with Gamelas *et al.* (2011).

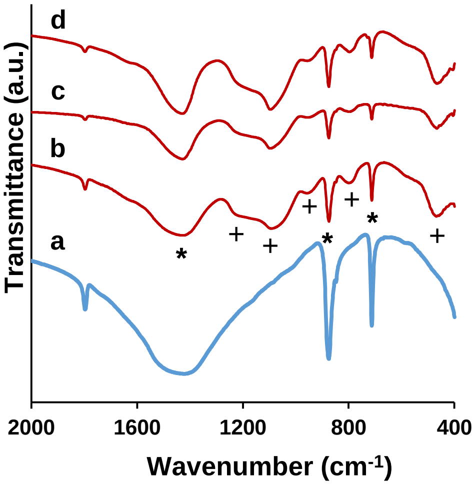
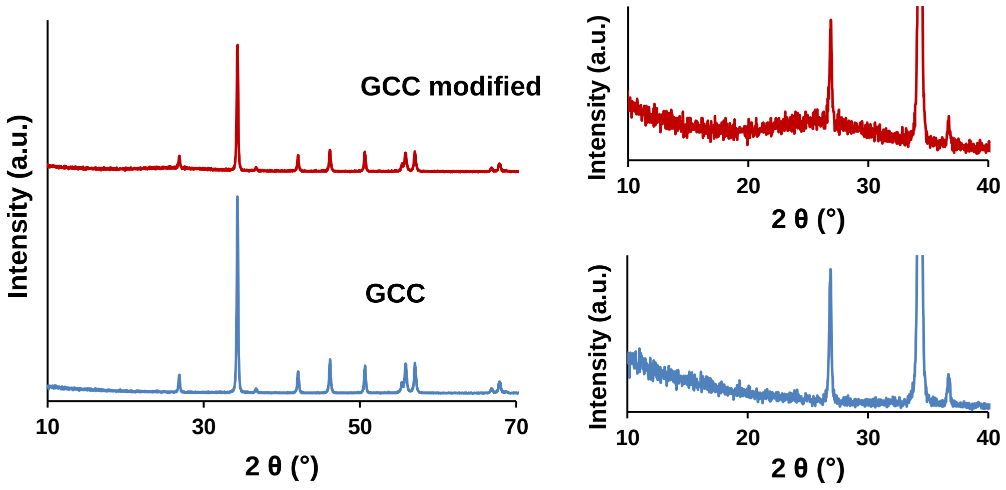


Fig. 1. FTIR spectra for unmodified GCC1 (a) and silica-modified GCC samples (b, c, and d stand for GCC1, GCC2, and GCC3, respectively). The spectra of the unmodified GCC2 and GCC3 samples are similar to that of GCC1. (*) and (+) denote bands due to calcium carbonate and silica, respectively.

The thermogravimetric analysis of the unmodified and modified GCC particles was performed in order to determine the amount of calcium carbonate and silica present in the materials, following the method explained in detail in two previous papers (Gamelas *et al.* 2011; Lourenço *et al.* 2013). Silica amounts of 41, 40, and 31 wt.% were obtained for modified GCC1, GCC2, and GCC3, respectively, while calcium carbonate represented 56, 56, and 64 wt.%, respectively, of the materials. The new materials contained also ca. 2-4% of adsorbed water and a minor amount of GCC impurities.

The X-ray diffractograms of the unmodified GCC1 and GCC2 showed the presence of only calcite (as visible in Fig. 2a for GCC1), whereas in the case of GCC3, minor amounts of dolomite were also detected. The modified GCC X-ray diffractograms were mostly similar to those of the unmodified GCC (Fig. 2a), except for the presence of an additional amorphous phase (see the halo in Fig. 2b), which can be related to the silica presence. The formation of amorphous silica under the sol-gel conditions used in the present paper was previously reported (Gamelas *et al*. 2011).

Due to the coating of the particle surface with silica, a modification of the particle size distribution and an increase in the median particle size, d_{50}, occurred, as evaluated by the laser diffraction spectroscopy (Fig. 3 and Table 2).



(a) (b)

Fig. 2. Powder X-ray diffractograms of the unmodified GCC1 and the corresponding silica-modified GCC. (b) shows a magnification of a selected region of the X-ray diffractograms presented in (a).

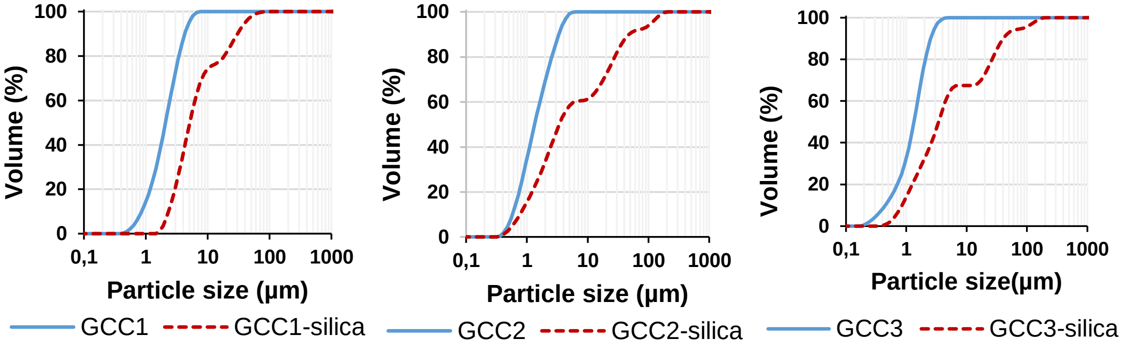


Fig. 3. Cumulative particle size distribution of unmodified and modified GCCs

The difference between the d_{50} values of the unmodified particles when comparing Table 1 and Table 2 resulted from the fact that the sizes were measured with different techniques: sedimentation (Table 1) versus light scattering (Table 2). It is well known that for non-spherical particles the equivalent dimensions measured by optical methods are larger than those measured by sedimentation methods (Barreiros *et al.* 1996).

Table 2. Influence of Silica Modification on the d_{50} and OPSD Parameters of GCC*

	GCC1	GCC2	GCC3
d_{50} (µm)			
Unmodified	2.1	1.3	1.3
Modified	5.1	3.7	3.4
OPSD			
Unmodified	0.39	0.53	0.44
Modified	0.67	2.74	2.83
* OPSD (open particle size distribution) was calculated as (d_{75}-d_{25})/(2.d_{50})			

With the modification, the average diameter increased about 2.5 times for all samples, and the size distribution became wider. This effect was explained by the presence of silica deposited on the GCC particles surface. These overall results are in accordance with those obtained by Gamelas *et al.* (2011), where the modification of PCC scalenohedral particles increased the average diameter from 4.0 µm (unmodified sample) to 6.3 µm (modified with about 25 wt.% of silica).

All SEM images corresponding to the unmodified samples (Fig. 4) show typical rhombohedral calcite particles along with smaller particles that are normal for GCC due to the milling process. From the SEM images of the modified samples (Fig. 5), the presence of silica particles on the calcite crystals is evident, and these particles somehow hide the typical rhombohedral shape. The presence of silica spheres around the calcite crystals was also observed.

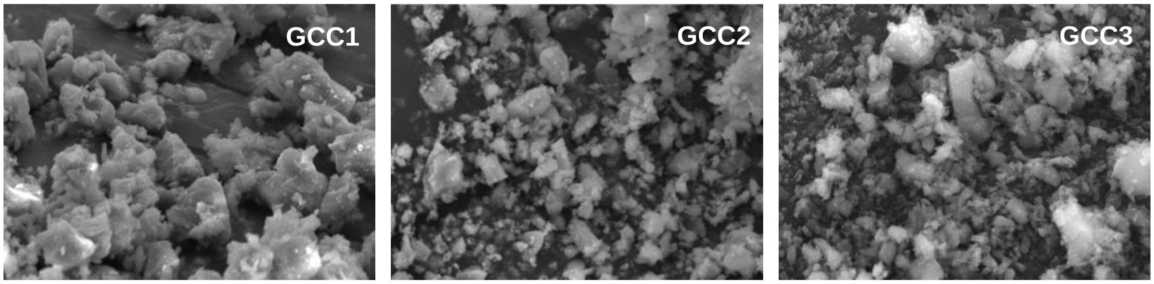


Fig. 4. SEM images obtained for the unmodified GCC samples (7500x)

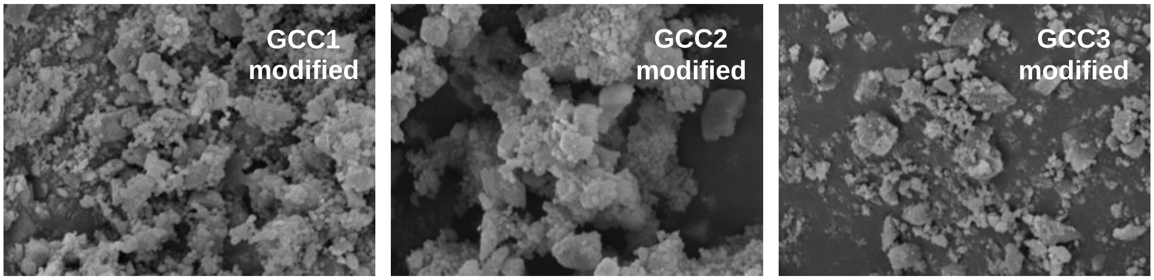


Fig. 5. SEM images obtained for the silica-modified GCC samples (7500x)

Table 3. Zeta Potential Results from Unmodified and Modified GCC Samples

	GCC1		GCC2		GCC3	
	Unmodified	Modified	Unmodified	Modified	Unmodified	Modified
Zeta potential (mV)	-29	-33	-29	-30	-28	-29
pH	8.1	8.3	8.4	8.4	8.2	8.2

The results of the zeta potential measurements are listed in Table 3. The surface charge of the unmodified GCC was negative, mainly due to the presence of anionic polyelectrolytes commonly used to stabilize the GCC dispersions (Vanerek *et al.* 2000). With the silica treatment, the GCC zeta potential did not change (only a slight increase was noted for GCC1). It should be mentioned that at the pH of the calcium carbonate suspensions (pH~8), the silica particles also had a negative charge (their isoelectric point is close to 2) (Franks 2002), and thus, negative values of the zeta potential were also obtained for the modified GCCs.

Regarding the effect of the filler surface charge in the filler retention, Lourenço *et al.* (2013), referring to PCC-modified particles, concluded that the retention of fillers with negative surface charge was not critical when a strong cationic polymer was added as retention agent, which was the case of the linear C-PAM with a high molecular weight used in this study.

Paper Properties

A SEM-EDX analysis of the handsheets was performed in order to confirm the presence of the filler particles, particularly of the silica-modified fillers. Carbon, oxygen, calcium, and silicon were detected in the handsheets prepared with the new silica-modified fillers (Fig. 6).

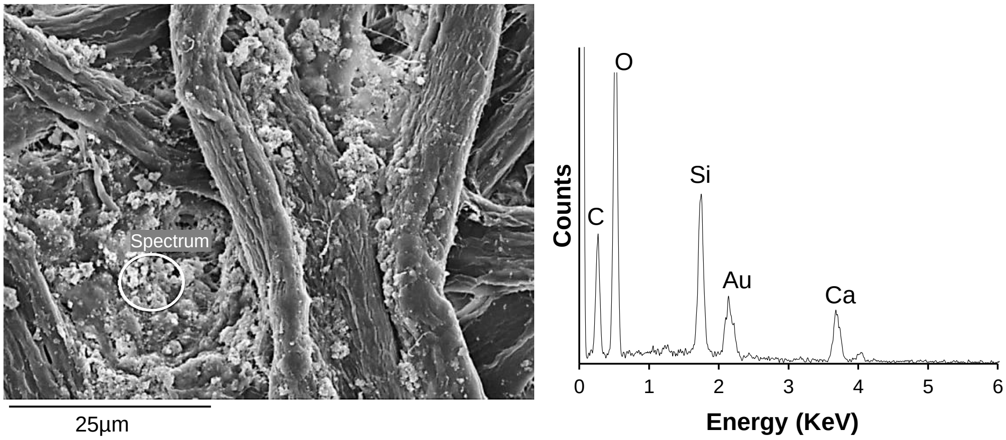


Fig. 6. SEM (left) and corresponding EDX spectrum (right) of handsheets produced with GCC modified with silica

Filler retention in the handsheets

Laboratory handsheets were produced with fiber, unmodified or modified GCC, starch, ASA, and C-PAM, as mentioned before. The corresponding filler retention results are presented in Table 4. Overall, the values are very high. However, by using the fillers modified with silica, retention decreased in comparison to that of the handsheets produced with the unmodified GCC (nevertheless, the results are similar to those obtained by Lourenço *et al.* (2013) for the PCC samples). This was most likely due to the excess of negative charge (Table 3) and the subsequent electrostatic repulsion of the silica particles, which do not bond and are partly lost during paper formation. In fact, some of the small silica particles, visible in the SEM images (Figs. 5 and 6), are free and not bond to GCC or to fibers, thus contributing to the smaller retention values.

Table 4. Filler Retention in the Produced Handsheets (%)

	GCC1	GCC2	GCC3
Unmodified GCC	91.6	92.1	88.2
Modified GCC	81.2	85.2	86.0

The same retention agent was added in the laboratory handsheets production both with the unmodified and with the modified GCC particles. Other polymers should be tested for the modified particles. However, Lourenço et al. (2013) showed that a linear high molecular weight cationic polyacrylamide, such as the one used in this study, is more efficient than a branched one for modified PCC particles with a negative charge.

Papermaking properties

The structural, mechanical, and optical properties of the papers produced with unmodified and modified GCC particles, and the corresponding filler contents, are listed in Table 5. Regarding the influence of the filler particle size, it is worth mentioning that the mechanical properties of GCCs with distinct median size or size distribution (Table 2 and Fig. 3) were not different, either between the 3 unmodified or the 3 modified GCCs. The size effect was only visible in the air permeability and roughness of the handsheets, mostly when using the unmodified particles. Moreover, despite the differences in brightness between GCC3 and the other two GCCs (Table 1), the brightness of the handsheets produced with the former GCC was only slightly higher (both with the unmodified or the modified filler), confirming that this property was much more determined by the dominant component: the fibers.

In general terms, by comparing the handsheets produced with unmodified and modified GCC fillers, the results showed an increase in sheet bulk, air permeability, surface roughness, burst and tensile indices, and a decrease in the light scattering coefficient. Opacity was also slightly decreased, whereas brightness remained roughly the same. The most relevant results were related to the significant improvements in the bulk and mechanical properties and the simultaneous decrease in the light scattering coefficient.

Table 5. Handsheets Properties*

	GCC1		GCC2		GCC3	
	Unmodified	Modified	Unmodified	Modified	Unmodified	Modified
Filler level (%)	18.3 (0.1)	16.2 (0.3)	18.5 (0.0)	17.0 (0.2)	17.6 (0.2)	17.5 (0.2)
Basis weight (g.m^{-2})	84.4 (0.5)	82.9 (1.5)	85.7 (0.8)	83.1 (1.0)	84.2 (0.8)	82.1 (0.3)
Sheet bulk(cm^3.g^{-1})	1.39 (0.03)	1.50 (0.02)	1.34 (0.02)	1.52 (0.02)	1.35 (0.02)	1.45 (0.01)
Air resistance (Gurley, 100 mL) (s)	4.6 (0.5)	3.7 (0.5)	7.0 (0.7)	4.2 (0.5)	6.9 (0.7)	3.9 (0.4)
Bendtsen roughness (mL.min^{-1})	196 (23)	412 (40)	144 (8)	342 (48)	150 (16)	396 (35)
Burst index (kPa.m^2.g^{-1})	1.9 (0.1)	2.3 (0.2)	2.1 (0.2)	2.2 (0.1)	2.1 (0.1)	2.4 (0.1)
Tensile Index (N.m.g^{-1})	35.9 (1.1)	43.0 (1.8)	35.6 (1.3)	42.0 (1.3)	37.8 (1.2)	43.7 (1.6)
Tear Index (mN.m^2.g^{-1})	5.7 (0.3)	5.6 (0.3)	5.3 (0.3)	5.3 (0.3)	5.5 (0.2)	5.4 (0.3)
Light scattering (m^2.kg^{-1})	48.1 (1.2)	43.6 (1.3)	49.6 (0.9)	45.7 (1.2)	49.1 (1.2)	46.5 (0.8)
Opacity (%)	88.1 (0.6)	86.1 (0.5)	88.5 (0.3)	86.7 (0.4)	87.8 (0.4)	86.2 (0.3)
Brightness R457 (%)	84.8 (0.3)	85.2 (0.1)	85.7 (0.2)	85.7 (0.1)	86.3 (0.5)	87.5 (0.0)

*Each value is the mean of two series. In each one, 8 specimens were produced and tested. The pooled standard deviation is presented in parenthesis.

For printing and writing paper grades, a high bulk is usually desirable for fiber savings, but it is usually accompanied by a loss in the inter-fiber bonding or by problems with dewatering after the wet-press (Hubbe *et al.* 2008). In the present study it was shown that by using GCC modified with silica a relevant increase in the handsheet bulk could be obtained, which was a positive achievement, since GCC is known to produce paper with lower bulk than that obtained with PCC and to lose bulk when the filler content is increased (Hubbe 2004). It must be stressed that this good result was not obtained with PCC modified with silica by the same sol-gel method (Lourenço *et al.* 2013; 2014). The bulk increase can be attributed to *i)* the agglomeration of the particles, which leads to higher particle size (Table 2), *ii)* the high amount of silica spherical particles (as visible by SEM, Fig. 5) and *iii)* the related increase in roughness which somehow may also affect the thickness measurement (by holding the caliper test platens further away). In the same way, the air permeability was increased, since more open spaces were formed due to the increase of the particle size.

The mechanical properties were normalized by basis weight, making it easier to compare the different samples. A 16 to 20% increase in the tensile index, in comparison to the unmodified GCC, was observed when the silica-modified GCC was used. The silica particles (attached to calcium carbonate or as isolated particles) are proposed to be responsible for the improvement in the mechanical properties. The hydroxyl groups of the silica (Gamelas *et al.* 2011) will promote not only a better bonding between the GCC and fibers (Lourenço *et al.* 2013) but also between the fibers themselves. Hydrogen bonding between the cellulosic fibers and the silica surface hydroxyl groups was reported before for cellulose-silica hybrids (Gamelas *et al.* 2012). An additional effect of the decrease in filler content on the improvement in mechanical properties may also be considered for samples GCC1 and GCC2. This was, however, a minor effect, since for the GCC3 the filler content was the same for the handsheets produced with the modified versus the unmodified GCC, even though the tensile index was significantly improved. Despite this, the tear index did not improve.

As for the light scattering, a decrease was observed when using the modified GCC despite the increase in the bulk and the presence of individualized silica particles. This decrease must be related to the smaller refractive index of silica and to the bigger filler particle size that leads to bigger pore diameters, thus having a greater negative influence in the light scattering. It is worth mentioning, however, that the decrease in light scattering was much less pronounced with the modified GCC than with the modified PCC (5 to 9% versus 20%, respectively) (Lourenço *et al.* 2013).

From the results it seemed that the silica formation on the surface of the GCC particles enhanced the filler-to-fiber bonding, which was reflected in an extraordinary improvement of the tensile index and simultaneously the considerable increase in bulk.

CONCLUSIONS

1. New silica-containing GCC particles were produced by means of the sol-gel method, using tetraethyl orthosilicate as precursor. A full characterization of the particles confirmed the presence of amorphous silica at the surface of GCC.
2. The modified GCCs were applied as fillers in papermaking at a filler content close to 20%. An increase in bulk and an improvement in the main paper strength properties (tensile and burst indices) were always found by using the GCC-silica hybrid as a filler.
3. The optical properties, such as light scattering and opacity, exhibited a minor decrease in their values, but the brightness was similar to that obtained for the handsheets produced with the unmodified GCC.

4. The differences in size and brightness between the distinct original GCCs were not translated into relevant differences in the corresponding handsheet properties, particularly after the modification of the particles with silica.
5. Therefore, it was concluded that the new GCC-silica materials effectively promoted the filler-to-fiber bonding and may therefore enable the production of paper with higher amounts of filler.

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