Papermaking potential of novel structured PCC fillers with enhanced refractive index

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ABSTRACT: While much effort has been focused on optical properties imparted by particle size distribution, shape, and packing of inorganic particles, the refractive index contrasts within the paper matrix have received less attention. PCC fillers can be used as tools for increasing the refractive index contrast, which further improves paper optical properties. We studied the papermaking potential of novel PCC fillers with an enhanced refractive index. PCC samples were fabricated by conventional carbonation method in the presence of refractive-index enhancing additives. We had previously found that introduction of ZnO as fine spots, including nano-sized structures, on host PCC surfaces improved the effective refractive index and optical performance of PCC. Now, we have studied the papermaking potential of this approach in experiments with handsheets using moderate Zn modification. In addition to Zn, we studied the effect of Sr as an additive and found that Sr inclusion alters the host particle morphology and crystal structure. We report effects of such modifications on light scattering coefficient, brightness, opacity, tensile strength, bulk, and porosity of paper, both before and after calendering. Our results suggest beneficial optical properties, as well as combination of light scattering with strength properties, especially in the case of Sr modified filler. Zn modified fillers opened the sheet structure, while Sr structuring closed the sheets. Calendering resulted in reduced bulk with all fillers, while optical properties were maintained with the Sr modified PCC, but reduced benefit was observed in the combination of light scattering and strength. Calendering conditions should therefore be optimized for these fillers. A higher modification degree of the fillers should also be considered to achieve a more significant refractive index contrast.

Application: We found a practical method to introduce refractive index contrasts on PCC filler particle surfaces. This can be utilized to improve paper optical properties.

Light scattering occurs both in the fibrous base paper and in the coating layer matrices. One of the main functions of fillers and coating pigments is to boost light scattering of the matrices. Light scattering from filler and coating pigments depends on the particle size distribution, specific surface area (SSA), flocculation, and refractive indices of the particles. The resulting pore size distribution of the surrounding media is also important. The floc structure, influenced by the particle shape, affects the number and size of the pores [1].

Introduction of filler into paper usually takes place by mixing the filler with the fibrous stock prior to the forming stage. In a paper web produced by such a typical process, filler pigments affect light scattering through two mechanisms: by increasing the specific surface area of the matrix, and by preventing bonding between fibers. These effects were suggested by Hemstock [2], Alince and Lepoutre [3], who have further demonstrated the separation of these effects, and proposed that the role of fiber debonding in light scattering decreases as the refractive index of the filler increases.

Fillers can be located either on the free fiber surfaces or in the pores formed by the surrounding fibers without significant effects on the structure of the fibrous network itself [4]. Fillers can also be located at the crossings of adjacent fibers [4], which causes debonding and significantly reduced tensile strength.

Proper particle size of fillers and pigments is essential for achieving optimum light scattering. As suggested by Bown [5], particle size should be considered together with size distribution, density, and aggregate properties. The effective particle size is about half a wavelength of light and the particles should have narrow size distribution around this size class. The same is true for the pore size distribution [6], which is also affected by properties of filler or pigment particles. Work done by Alince et. al [7], suggests that when porosity provided only by such optimal pores is examined, and all particles display similar refractive indices, linear dependence between light scattering and porosity can be found. Work completed by Silenius [8] demonstrates how certain filler-fiber composites ("SuperFill" technology) can be utilized to boost the light scattering effect of filled sheets. This technology is thought to contribute to light scattering by providing less flocculated distribution of filler and by its ability to yield advantageous paper pore structure.

A low degree of particle flocculation contributes to light scattering but increases sheet debonding. Particulate retention requires controlled flocculation. Flocs can be formed among filler particles alone through homoflocculation [9, 10], or together with fines through heteroflocculation [11]. Low retention of fillers negatively affects papermaking, for example, by increasing sizing agent consumption. Therefore, to ensure development of paper's mechanical properties and

paper machine runnability, fillers may be introduced to paper as flocs. However, this approach reduces light scattering, as has been extensively documented in the literature. For example, according to Holm [9], preflocculation leads to improved sheet strength at the expense of optical properties.

It is possible to improve optical properties without sacrificing sheet strength by increasing the filler content in paper. A study conducted by Subramanian, et al., [12] suggests that filler contents up to 50%-60% can be achieved using fiber-filler composites in which PCC particles have been introduced on fine cellulosic material. Progress in micro- and nanocellulose technologies may provide new opportunities for papermakers to use such fillers.

In contrast to changing the particle size, specific surface area, or filler content, refractive index manipulation has not been exhaustively investigated. There are limits on decreasing particle size or increasing specific surface area beyond which light scattering starts to decrease. This applies to pore size as well. Further, retention sets another limit for reducing particle size. Filler effects on mechanical properties of paper and runnability of paper machine limit the filler contents. Such limits, however, do not concern refractive index. If other parameters are fixed, increasing the refractive index differences of optical interfaces always increases light scattering in a sheet. As the refractive index of most of the current papermaking materials is close to 1.6, significant improvement in light scattering can be achieved with refractive index values of around 2.0 by utilizing innovative colorless composite structures. This is an issue for investigation, as the lack of refractive index differences on the solid-solid interfaces of paper characterizes the majority of paper grades of the day. In a typical fibrous paper matrix, light scattering takes place mainly on solid-air interfaces.

In ray optics, effect of refractive index on the interaction between a light beam and transparent material (**Fig. 1)** can be described by Snell's law according to Equation (1),

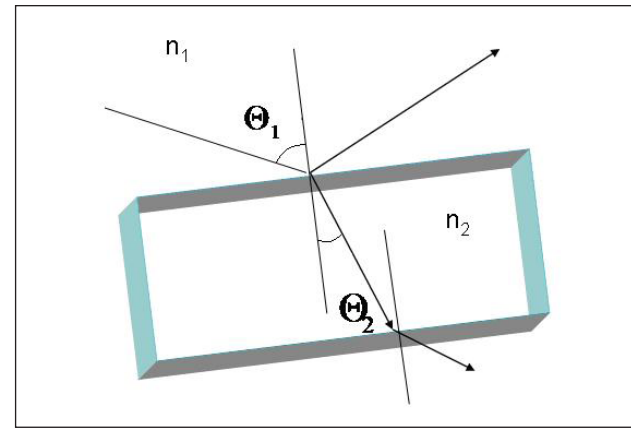
$$n_1 \sin \Theta_1 = n_2 \sin \Theta_2 \quad (1)$$

where n_1 and n_2 represent the refractive indices of the two media.

Furthermore the degree of bending of light, refractive index affects the intensity of the reflected light beam. The importance of refractive index differences on optical interfaces on this reflection can be understood from Fresnel equations,

$$R_s = \left[\frac{n_1 \cos(\Theta_1) - n_2 \cos(\Theta_2)}{n_1 \cos(\Theta_1) + n_2 \cos(\Theta_2)}\right]^2 \quad (2)$$

$$R_p = \left[\frac{n_1 \cos(\Theta_2) - n_2 \cos(\Theta_1)}{n_1 \cos(\Theta_2) + n_2 \cos(\Theta_1)}\right]^2$$



1. Interaction between light and transparent material.

where R_s and R_p are reflection coefficients for light polarized in two planes. The Fresnel equations are valid only for even surfaces. They show the effect of the refractive index of material on the intensity of specular reflection or gloss. In practice, the occurrence of micro-roughness reduces specular reflection and increases diffuse light scattering. On particle distances that are in the order of magnitude of wavelength of light, such as in a coating matrix, a wave optical approach, based directly on Maxwell's equations, should be used instead of the ray optical description [13].

The refractive index of material depends on its molecular constitution. Refractive indices of organic materials, including cellulose, are usually around 1.5-1.6 [14]. The nature of chemical bonding has an important role for development of refractive index. Chemical bonding in high volume fillers and pigments, such as carbonates and silicates, are characterized by low degree of covalence, and consequently low degree of specific refractivity [15]. Covalence of bonding affects the electron density, which is a major contributor for refractive index of a material, as equation (3) indicates [16],

$$n = 1 + \frac{N q_e^{\,2}}{2\varepsilon_0 m\left(\omega_0^{\,2} - \omega^2\right)} \quad (3)$$

with these values:

n	refractive index
N	number of charges per unit volume
q_e	charge of electron
ε_0	permittivity of vacuum
m	mass of electron
ω	angular frequency of radiation
ω_0	resonant frequency of electron

More specific descriptions on refractive indices of media can be found in the literature [17]. Combinations of high-volume pigments and specialty pigments are often replaced with modified high-volume pigments to boost paper performance [1, 18].

The industry is actively investigating the beneficial effect provided by nanotechnology. For example, a modified calcium carbonate with nano features has a positive effect on pigment-ink interaction [19]. As shown by Schoelkopf et al. [20, 21], Gane et al. [22] and Ridgway et al. [23], a discrete pore structure, provided by the modified calcium carbonate, contributes to rapid liquid absorption and high liquid uptake. This can be further utilized in printing paper applications. The fraction of GCC in GCC-clay coatings may be raised due to continually increasing demand for high brightness. The surface structure of GCC pigments can be modified to enable sufficient coating structuring with GCC alone [24]. A recent study by Koivunen et al. [25] introduces a novel ZnO-nanostructured PCC with an increased refractive index, birefringence, and light scattering potential. In this study we have examined the papermaking potential of PCC with moderate ZnO and $SrCO_3$ modifications.

Materials and methods

We fabricated PCC samples in laboratory by carbonation, i. e., feeding carbon dioxide gas into slurry of slaked milk of lime. In this process we fabricated (a) a reference PCC, referred to as "S-PCC", with clustered scalenohedral (rosette-like) particle morphology, and (b) three structured PCC samples (Nano-S-PCC): (b1) two PCC with light Zn based, and (b2) a PCC with a Sr-based modification. Formation of calcium carbonate takes place according to equation (4):

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (4)$$

PCC fabrication by carbonation has been thoroughly explained, for instance, by Silenius [8]. To form light scattering structures displaying refractive index contrasts on the PCC surface, soluble Zn and Sr compounds were used as additives during the reaction. A more detailed description of the structured PCC fabrication has been published elsewhere [25].

Samples were filtered, washed with deionized water, dried, and prepared for further analyses. One commercial scalenohedral PCC, referred to as "S-PCC (Com)," was also used as a reference. Particle size distributions of the fillers were determined with a Beckman Coulter LS 13 320 particle size analyzer.

To document the realized chemical composition of samples, we conducted thermal gravimetric analyses (TGA) using a Netzsch STA 449C device, combined with a capillary to Netzsch QMS 403C mass spectrometer. Sample size was about 10 mg, and helium was used as a protective gas. The flow rate of the protective gas was 70 mL/min. The testing samples were heated in Al_2O_3 crucibles up to 1,250 °C, with a heating rate of 10 K/min. Released gases were analyzed in the mass number range of 2-300.

The crystal structure of the Sr modified sample was analyzed by x-ray diffraction measurement. X-ray diffraction patterns were collected with a Philips PW1710 device using Cu K_α radiation. XRD analysis of zinc modified samples has been reported earlier [25]. The specific surface area (SSA) was measured with a Micrometrics FlowSorp II 2300 analyzer by determining the adsorbed and desorbed nitrogen, utilizing the BET (Brunauer, Emmet, and Teller) theory.

Component	Point of addition, s (after addition of the fibrous stock)	Dosage, mg/g
Starch	11	5
Filler	30	Determined by target filler content
Retention Aid	40	200

I. Addition of chemicals in handsheet preparation with MBF.

Dried birch and pine chemical pulp sheets from Finnish pulp mills were soaked in water and mixed to achieve 70/30 birch/pine fine paper furnish mix. The furnish was beaten with a Valley Hollander to °SR 18 in accordance with the Standard SCAN-C 25:76 and diluted to 3 g/l consistency for handsheet preparation. The pH and temperature of the stock were around 7 °C and 20 °C, respectively. Dry-strength starch (Raisamyl 50021) was cooked in 95 °C for 25 minutes prior to handsheet preparation. Fillers were dispersed with a Diaf mixer and then continuously stirred with a magnetic stirrer. Fennopol K 3400R was used as a retention agent. Handsheets of 80 g/m² were prepared with Moving Belt Former (MBF) drainage testing and sheet forming apparatus [26]. First, the fibrous stock was added in to the container of the MBF. Chemicals were then added in order as shown in **Table I**.

The procedure of chemical addition was intended to mimic the wet end operations of a typical paper machine environment. The stock in the container was continuously mixed with a propeller mixer. Target filler contents of the handsheets were 15 wt%, 25 wt%, and 35 wt%, with ±1.5 wt% unit deviation. Formed wet sheets were couched from the wire, wet-pressed and drum-dried. The sheets were then stored in accordance with the Standard SCAN-P 2:75 and finally tested with Standard Methods. Sheets were calendered through a single nip on an EP-210 laboratory calender using 70 kN/m line loads, 70°C hot roll surface temperature, and 35 m/min speed.

Micrographs were taken and elemental mapping was implemented for handsheets with SEM and EDS, respectively. The aim was to observe the presence of the structures carried by the host PCC particles in a paper web to verify that they had been retained. A piece of paper was attached on a sample base with two-sided tape and coated with gold, using a 15.0 kV accelerating voltage.

Sample	Cluster size, µm		SSA, m²/g	ZnO, w-%	$SrCO_3$, w-%	SrO, w-%	n_{eff}
	Mean	Median					
S-PCC	7.380	7.273	5.6	-	-	-	1.58
S-PCC (Com)	4.099	3.567	6.4	-	-	-	1.58
Nano-S-PCC 1	7.989	7.748	6.2	1	-	-	1.582
Nano-S-PCC 2	5.940	5.781	8	8	-	-	1.597
Nano-S-PCC 3	4.341	3.823	10.5	-	3.5	1	1.578*

** the value is based on the assumption that $CaCO_3$ is in the form of calcite. Presence of aragonite was later observed, and this effect is discussed below.*

II. Characterization of the fillers.

RESULTS AND DISCUSSION

Table II presents the average particle size: more precisely, cluster size, SSA, TGA (additive content), and calculated refractive index data from the PCC samples. The S-PCC reference together with the Nano-S-PCC 1 exhibited the coarsest cluster size. The Nano-S-PCC 3 occurred as finer clusters and is hence more comparable with the size of the other reference, S-PCC (Com). All structured samples were moderately modified. The chemical composition of the structured samples was assessed from the TGA measurements.

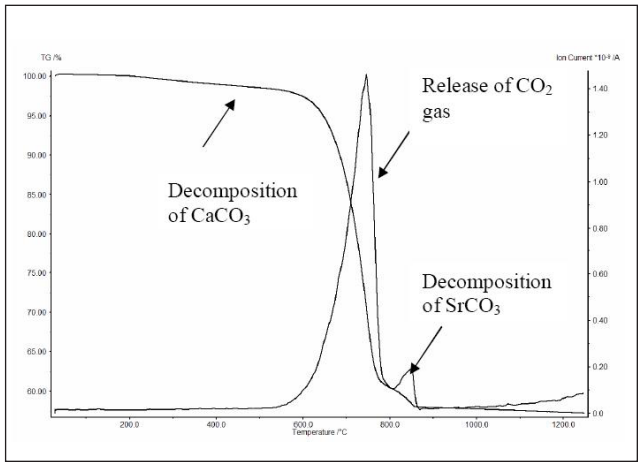
From TGA data, the effective refractive index (n_{eff}) of a composite pigment consisting of a host particle (h) and a coating layer of particles (c) can be approximated from the refractive indices (n) and the volume fractions (V) of the host and the particle layer, respectively, according to equation (5). The same formula has been used in immersion liquid-based measurements of refractive index of PCC, which have been described earlier [25]:

$$n_{eff} = \frac{V_h n_h + V_c n_c}{V_h + V_c} \quad (5)$$

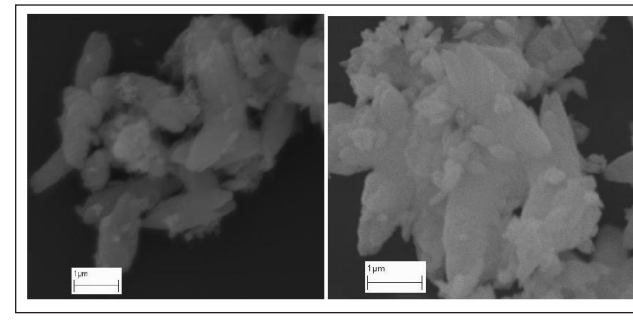
Using the densities and refractive indices of ZnO (5.606 g/cm³ and 2.0, respectively [27]), and $SrCO_3$ (3.7 g/cm³ and 1.516, respectively [27]), we have calculated the effective refractive indices accordingly (Table II). Density and refractive index of calcium carbonate (calcite) used in the calculation are around 2.71 g/cm³ and 1.58, respectively [27].

Figure 2 presents the TGA curve of the Nano-S-PCC 3 sample. The decomposition of $CaCO_3$ can be observed as steep weight loss around 600 °C – 700 °C. The minor loss occurring in 800 °C is due to decomposition of $SrCO_3$. Our assumption is based on the detected release of CO_2 gas. The remaining trace of strontium is expected to occur in the form of an oxide. Our XRD study indicated occurrence of aragonite together with calcite in the Nano-S-PCC 3 sample. The presence of aragonite (n=1.63) suggests that the refractive index must be higher than that calculated from Table II, in which the n value of 1.58 for calcite is used [27]. Because precise fractions of calcite and aragonite in the sample remained unclear, we decided to use the estimate $1.58 \leq n_{\text{Nano-S-PCC3}} \leq 1.63$ for this sample.

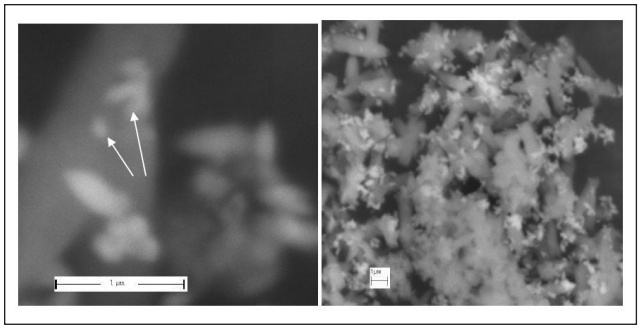
Figures 3-4 show micrographs of ZnO modified PCC samples. ZnO structures can be distinguished in the backscattering images (Fig. 4) as bright spots on the surface of PCC particles. For visualization, the structure contents in the samples presented in Fig. 3 are higher than examined elsewhere in this study. Figure 3 should be considered as a guide, illustrating the structured PCC concept. The reference PCC, typical scalenohedral calcite, is shown in **Fig. 5** (left). Effects of



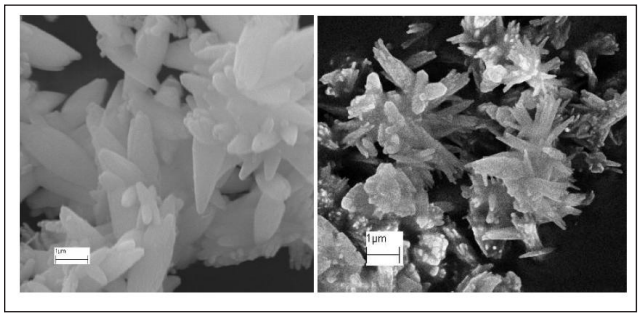
2. Thermal analysis of the Nano-S-PCC 3 sample.



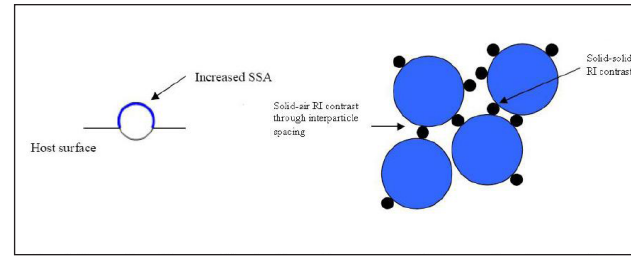
3. PCC samples with 10 w-% (left) and 18 w-% (right) Zn structure content.



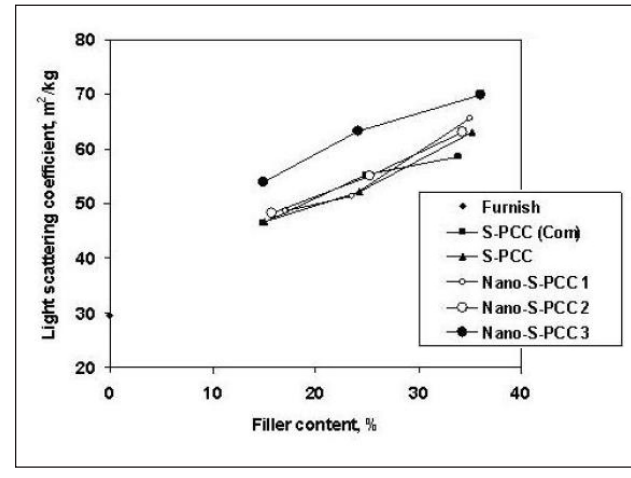
4. ZnO particles on the PCC surface. Backscattering images. Nano-sized structures (≤ 100 nm) are marked with arrows.



5. Reference PCC (left) and PCC with 3.5 w-% $SrCO_3$ content (right).



6. Schematic figure illustrating the suggested mechanisms of light scattering generation through the novel filler. Left: increased specific surface area due to the fine particle. Right: spacing effect and refractive index contrasts occurring in a filler aggregate.



7. Effect of filler type on the light scattering coefficient of the handsheets.

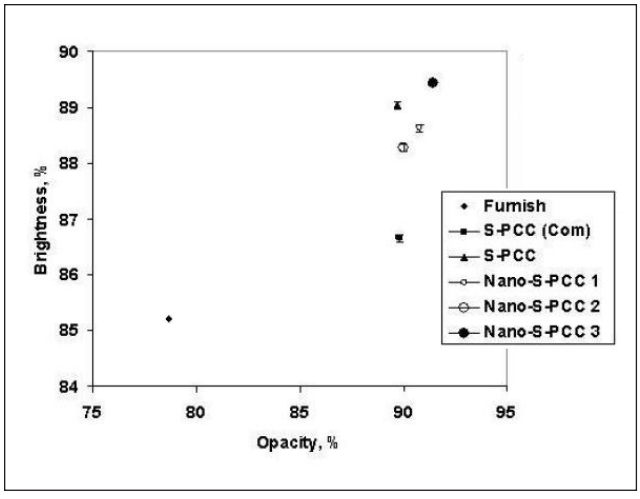
Sr can be observed both as bright spots and altered host particle morphologies (image on the right). EDS elemental mapping conducted for the sheets provided evidence that the Zn-based structures had been retained in the handsheets. Presence of these structures may affect both filler packing and refractive index contrasts present in the sheet. Therefore, in the following, we discuss such effects with respect to light scattering generation.

Packing of filler particles plays a critical role in the development of light scattering. The refractive index gamut associated with a filler system should be considered together with packing density. With the structure containing fine ZnO particles, illustrated in **Fig. 6**, our approach was to provide improved optical sheet performance, compared to conventional fillers, through the following distinctive mechanisms.

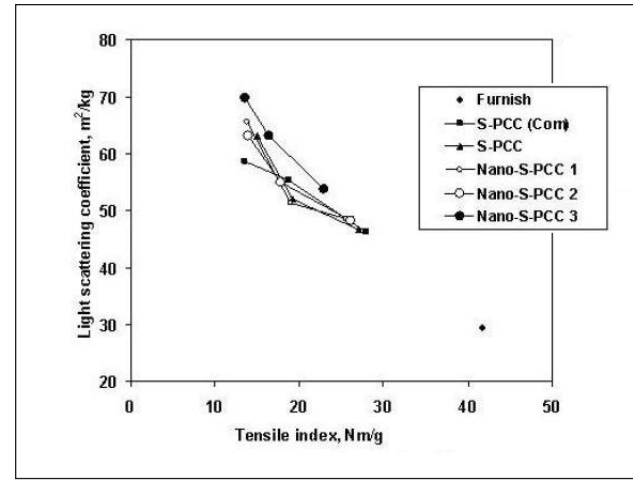
First of all, the Zn based nanostructures provide local refractive index contrast to the PCC host particles. As presented in Fig. 4, some of the structures are nano-sized (≤100 nm). Tailoring the refractive index of various nanocomposites has gained attention in the field of optical physics [28-34]. The light scattering provided by such nanoparticles has been discussed in an ellipsometric study completed by using our fillers and various nanoparticles [35]. The light scattering is boosted by local index mismatches introduced by such particles.

Second, in our case, particles with size class 100-500 nm are also present. Uneven surface topography of the structured fillers therefore can be expected to affect diffuse scattering. Incorporated particles raise the specific surface area, which consequently leads to an increase in interparticle spacing between host particles. In optics, interparticle spacing that displays no less than 200 nm distance between (host) particles makes the most significant contribution to light scattering. Packing should, therefore, be controlled to obtain effective interparticle pore size. Limited contact between particles is most attractive and attention to pore size distribution is critical.

The importance of spacing of high-refractive-index pigments has also been recently presented by Holm [36], while spacing technology through fine particles in GCC coatings has been presented by Gane [24]. When packing density increases throughout a sheet of paper; e.g., by calendering or locally by filler particle flocculation [9, 10], a high number of interparticle contacts form and, consequently, solid-solid interfaces replace solid-air interfaces. This decreases refractive index contrasts and reduces light scattering [9]. As presented by Gavelin [11], similarly in heteroflocculation, fillers form flocs together with fines. From the optics viewpoint, formation of solid-solid contacts is similar, since fines and fillers have similar refractive indices. The light scattering effect decreases when particles are assembled in distances below 200 nm from each other. Flocculation and local close packing are necessary to achieve sufficient retention. Col-



8. Effect of filler type on optical properties of the handsheets. 80 g/m² grammage, 35 w-% filler content.



9. Light scattering coefficient against tensile index of handsheets.

lapsing of the particle structure may also occur upon calendering. Therefore, it is beneficial that not all particles in a floc display similar indices.

The fourth mechanism we suggest is related to the distribution of nanoparticles on host particles. When considering an ordinary blend consisting of typical filler particles and very fine additional particles, separation between two particle types may take place due to colloidal interactions within the fraction of fine particles. Segregation of two filler types with differing morphologies has been explained earlier in detail by Gane et al. [18]. When the particles are attached onto the host particles, such separation is prevented and the number of solid-solid contacts displaying refractive index contrast is maximized.

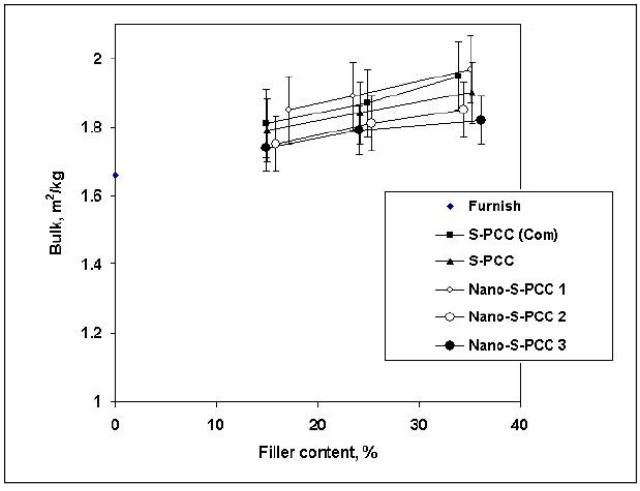
Fine structures, such as observed in the case of Zn based modification, are also present in the case of Sr modified PCC (Fig. 5). In addition, the host particles themselves display a different, needle-like, structure. Such a structure is characteristic of aragonite carbonates. This might be an indication of an additional Sr incorporation in the host particles. Such incorporation may have taken place through a substitution mechanism. According to V.M. Goldschmidt [15], substitution of ions in a crystal may take place if the size of the substitute does not differ from the size of the original ions by more than 15%. The size of Sr is close to that of calcium; hence such a mechanism could work. The presence of Sr has been observed to contribute to aragonite formation. In fact, strontium yields more stable aragonite than calcium [37].

Figure 7 shows the light scattering coefficient as a function of filler content with different fillers. Our samples display various cluster sizes, which obviously must be considered in this context. For instance, as presented in Table II, Nano-S-PCC 3 displays smaller cluster size than Nano-S-PCC 1 (or Nano-PCC-2) but is close to that of the commercial reference PCC. Nano-S-PCC 3 yields the highest light scattering of the fillers, including the reference, hence other parameters must also be considered. The shape of Nano-S-PCC 3 significantly differs from that of the other samples, and can be hence expected to result in different packing and pore structure of the sheet. These factors, together with different refractive indexes, may explain most of this behavior. The influence of crowding [3]; i.e., leveling of the light scattering with high filler content, can be envisioned in the case of Nano-S-PCC 3. This might be due to the high packing density. Nano-S-PCC 3 also yields the best combination of paper brightness and opacity, as shown in **Fig. 8**.

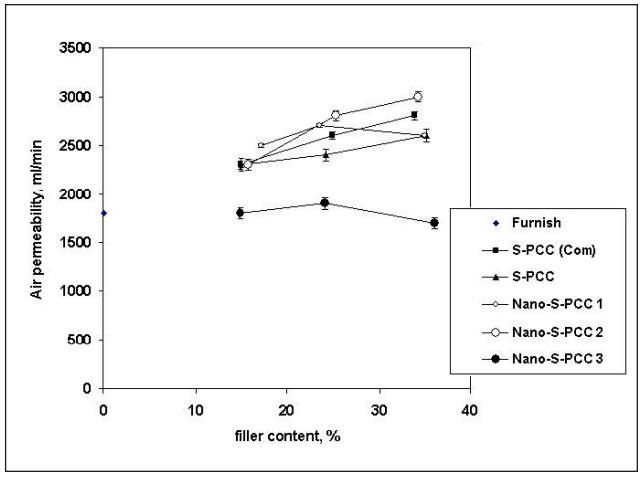
No benefits in optical properties were observed with Nano-S-PCC 1 or Nano-S-PCC 2. A probable reason for this is the very low content of ZnO particles. **Figure 9** suggests the contribution of the Nano-S-PCC 3 filler on both the light scattering coefficient and tensile index. Particle size affects both optical and strength properties and can influence combinations of the two. As suggested by Bown [5], small particles sized approximately 2 µm can yield better combinations than large particles (6 µm). If we assume that the cluster size has a similar effect in our case, this could explain results here, in addition to the effect discussed in the context of light scattering.

The refractive index contrast should be discussed together with packing density. As illustrated in **Figs. 10-11**, Nano-S-PCC1 and Nano-S-PCC2 yield increased bulk and especially air permeability, respectively, which might be an indication of the spacing effect discussed above. Nano-S-PCC3 yields low bulk and air permeability, suggesting high packing density. This could be expected due to the relative higher density and aspect ratio of aragonite. Differences however in the particle sizes between samples must also be considered.

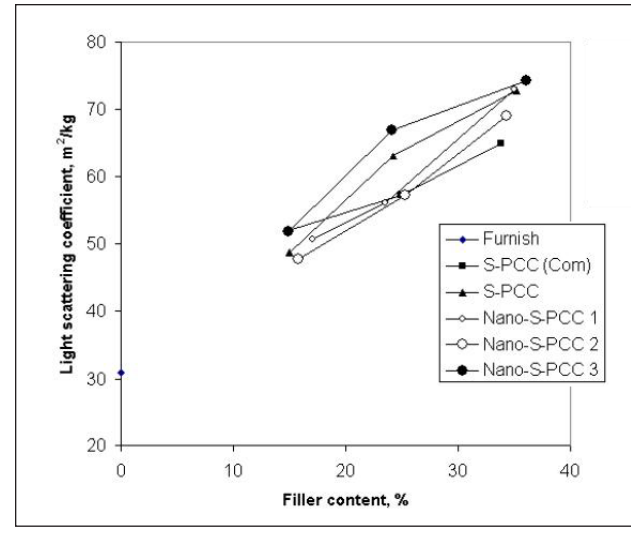
Figures 12-15 show the effect of calendering. Calendering typically reduces pore volume and can therefore affect light scattering. After calendering, Nano-S-PCC 3 maintains a competitive degree of light scattering. The advantage of light scattering and strength properties observed with uncalendered sheets has been reduced. Nano-S-PCC 3 provided the most closed sheet structure. The beneficial light scattering



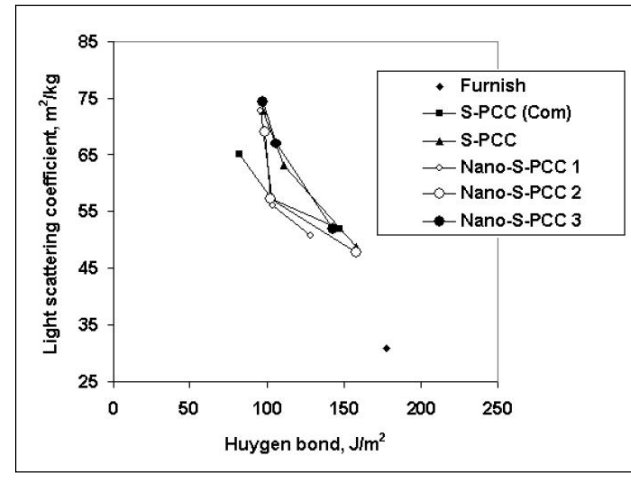
10. Bulk against filler content of the handsheets.



11. Air permeability against filler content of the handsheets.



12. Effect of filler type on the light scattering coefficient of the handsheets. Calendered sheets.



13. Light scattering coefficient against Huygen bond of the handsheets. Calendered sheets.

could be an indication that all pores which scatter light have not been totally collapsed. However, details of pores have not been examined and, accordingly, this is only a presumption.

CONCLUSIONS

The objective of this study was to test the papermaking potential of novel structured PCC fillers with enhanced refractive index. Considering the economic feasibility of such an approach, we examined only moderate structuring. Structuring comprised introduction of optically effective fine particles on conventional scalenohedral PCC host particles with or without host particles' shape modification. The nature of structuring was controlled by chemical modification. Zn was introduced in fine particles form only, while Sr was introduced by changing the host particles' shape to a more needle-like configuration.

Our results indicated acceptable optical properties and combination of optical-strength properties, especially in the case of Sr-based structuring. After calendering, beneficial light scattering was still observed, while property balance reduced the advantage. Introduction of Zn-based structures did not produce improved paper optical properties, probably due to the low structural content.

Our observations suggest easy processing and preparation of the modified fillers. These fillers can be introduced into paper in the wet-end and will yield competitive paper properties. The (nano)-structured fillers behave mostly as regular fillers without disturbances or adverse effects. Results complement our earlier findings and provide novel information regarding the good papermaking potential of (nano)-structured fillers. Modification of the fillers should, however, be high enough to realize beneficial paper optical properties. Optimization of calendering conditions must also be considered. **TJ**

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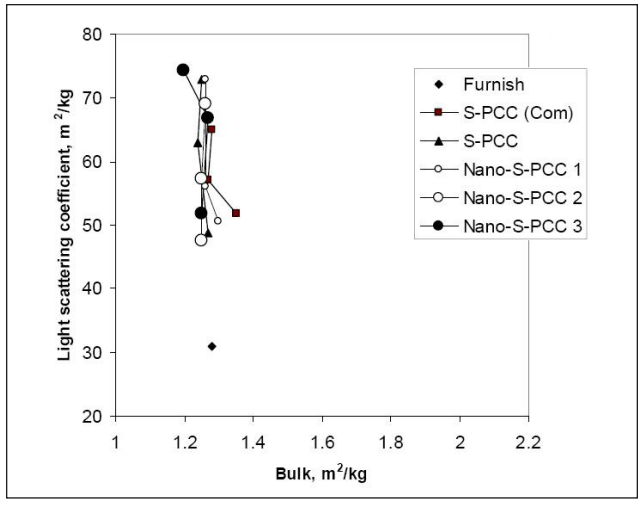
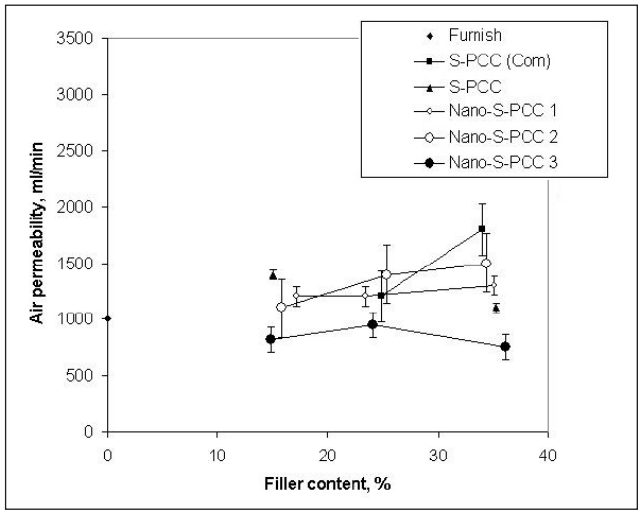


14. Light scattering coefficient against bulk. Calendered sheets.



15. Air permeability against filler content of the handsheets. Calendered sheets.

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INSIGHTS FROM THE AUTHORS

Fillers are added to paper stock to improve optical properties and to reduce costs, but they also have negative effects on paper properties, which limit their use. Accordingly, fillers must be optimized to achieve the best balance. This may be accomplished by changes in filler particle size, shape, specific surface area, or refractive index. The last of these possibilities has received the least attention.

We considered this topic of high relevance and, in 2006, launched a multidisciplinary three-year project called "Nanopap" together with our financiers and research partners. Our objective was to increase the refractive indices of various fillers and coating pigments by technically and economically feasible means, including nano-scale modifications.

In our studies, we have observed significantly increased refractive indices and improved optical performance, as well as beneficial combinations of optical and strength properties. Our findings may point to further potential for efficient use of materials. For example, PCC could be used as a platform to introduce refractive index contrasts in paper. The challenge is to introduce contrasts that can be realized in improved paper performance without excessive increase in material costs. An approach we present in this paper is attaching them to host filler particles. More research in the usability and economics of novel fillers is needed.

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