J Mater Sci (2009) 44:477–482
DOI 10.1007/s10853-008-3095-y

Novel nanostructured PCC fillers

**Kimmo Koivunen · Ilpo Niskanen · Kai-Erik Peiponen ·
Hannu Paulapuro**

Received: 20 August 2008 / Accepted: 29 October 2008 / Published online: 23 November 2008

Abstract New filler and pigment technologies are needed to improve the optical properties of paper. Filler contents in different paper grades are approaching the maximum levels achievable with current papermaking practices. Much work has been done to maximize the light scattering potential of fillers and pigments by modifying their particle size distribution or specific surface area. The refractive index (RI) is an optical constant of pigment, and less attention has been paid to the possibility of increasing this parameter. In the present study, a novel nanostructured filler-grade precipitated calcium carbonate (PCC) pigment was synthesized. Zinc-based nanostructures, physically contacted with the host PCC material, increase the differences in RI between filler-fiber and filler-air interfaces, yielding increased light scattering. The effective RI of the novel filler was measured using a method which combines a multi-function spectrometer with the immersion liquid method. This method enables effective RI measurement from pigment suspensions, irrespective of the shape, size, and nanostructures occurring on the host pigments. When compared to conventional PCC, the results gained with the nanostructured PCCs suggest an increase in the effective RI. When used as filler in paper, nanostructured PCC yields improved light scattering, i.e., better opacity.

Introduction

In papermaking, mineral fillers are added to the stock to improve the appearance of paper expressed in terms of measured values, such as brightness, opacity, and formation. Fillers enhance printability by optimizing the pore structure for controlled ink absorption, reduce print-through, and increase the contrast between printed and blank areas of the paper surface. Moreover, fillers bring cost savings by replacing more expensive fibers.

The need for more efficient use of materials often means a shift to lower-basis-weight paper grades. With lower basis weights, the number of optical solid–air interfaces is reduced, and opacity becomes critical. In paper, fillers and pigments improve light scattering by increasing the number of such interfaces and hence improve opacity. Filler loading levels have increased in recent years, being highest in uncoated fine and wood-containing grades at around 30% relative to the base paper's weight [1]. Filler contents are approaching the highest levels achievable with current papermaking practices. The negative effects of filler on paper properties and the papermaking process impose a limit on the use of higher loadings. In paper, fillers prevent fiber-to-fiber bonding, which is observed as reduced paper strength. Fillers also reduce bending stiffness. Negative process effects include low retention, with consequent loading of circulation and waste waters, increased size consumption, abrasion of wires, foaming, and deposit problems [2–5].

Besides the amount of filler, the properties of individual filler particles also affect opacity. Light scattering is

K. Koivunen (✉) · H. Paulapuro
Department of Forest Products Technology, Paper and Printing Technology, Helsinki University of Technology TKK,
P.O. Box 6300, 02150 Espoo, Finland
e-mail: kimmo.koivunen@tkk.fi

I. Niskanen
Measurement and Sensor Laboratory, University of Oulu,
Technology Park 127, 87400 Kajaani, Finland

K.-E. Peiponen
Department of Physics and Mathematics, University of Joensuu,
P.O. Box 111, 80101 Joensuu, Finland

dependent on the particle size distribution (PSD), specific surface area (SSA), and morphology of the filler. The ability of the filler to create pores is important in this respect. However, much work has been done to optimize these particle properties. Alternative solutions are needed. In this study, nanostructured precipitated calcium carbonate (PCC) with an enhanced effective refractive index (RI) is discussed.

The RI of a medium [6] is a fundamental material parameter, an optical constant, affecting the intensity of scattered light. It is a coefficient related to the retardation of light when it enters the material from vacuum. The RI does not belong to the group of traditional control variables in the production of pigments. Titanium dioxide, TiO_2, has a significantly higher RI compared to other materials used in paper, but it is far more expensive than fibers.

Light scattering takes place only on interfaces that manifest a difference in refractive indices. In reducing the basis weight, opacity can be kept at an acceptable level by more effective utilization of remaining interfaces, both solid–solid and solid–air. In current paper grades, the majority of solid–solid interfaces does not contribute to light scattering. Refractive indices for cellulose and lignin are 1.56 and 1.61, respectively [7, 8]. Most traditional fillers also have refractive indices close to 1.6.

In both filling and coating applications, pigment blends are used to optimize paper properties. In these blends, specialty pigments are sometimes used together with high-volume pigment. By using a composite pigment instead of a blend, advantages related to materials handling and process flows can be achieved. Furthermore, the statistical distribution of the pigment components increases the probability of maximum pigment–light interaction. According to Gane et al., attachment of two different pigments to each other can be utilized to obtain better properties than what can be achieved with simple blends of corresponding pigments [9]. This is important especially in filling applications where interface synergy characteristics of composites are not easily achieved with simple blends. This phenomenon can also be observed in coating applications where separation of particle morphologies may occur. Traditionally, simple blends of high-brightness spherically symmetrical blocky pigment—such as rhombohedral or scalenohedral calcium carbonate—and lower brightness but good physical-coverage platey pigment—such as talc—have been used to achieve a combination of high brightness and opacity. With this kind of blend, blocky particles can be lost in the voids of the base paper surface, leading to a loss of interface synergy between particles. Instead, by using composite pigments, such as those developed by Gane et al., both high brightness and good coverage can be achieved. An example of such a structure is a composite of fine high-brightness calcium carbonate and platey talc [9].

Lattaud et al. enhanced the RI of calcium carbonate particles by coating their surfaces with a thin layer of zinc carbonate (RI 1.62–1.85) [10]. Zinc carbonate was used since its atoms perform an isostructural arrangement with calcium carbonate, facilitating its even introduction. Zinc carbonate-coated calcium carbonate particles yielded an increased RI and a higher light scattering coefficient than pure calcium carbonate particles, as light scattering was measured from coatings applied on synthetic paper.

Based on the results of theoretical model studies conducted by Penttilä et al., it can be concluded that RI enhancement could be a potential approach to increase light scattering in paper. Results calculated from modeled coatings using computational wave-optical methods suggest that light scattering could be notably increased by reasonable enhancement of the RI of pigment [11].

The RI of a material is essentially determined by its chemical composition. Different functional groups have different effects on the RI [12]. However, even within the same chemical composition, atoms can be arranged energetically in different modes, i.e., they can be differently coordinated. The electron structure controls the chemical nature of the material and, hence, the probability of different coordination modes. On the specific density level, the nature of chemical bonding, viz., ionic or covalent, significantly affects the RI [13]. The average refractive indices of calcite- and aragonite-type calcium carbonates are known to be 1.58 and 1.63, respectively. The difference is related to their atomic structure. In aragonite, atoms are arranged in a denser configuration in which the aragonitic calcium atom is coordinated by nine oxygen atoms, compared to calcite in which coordination with six oxygen atoms occurs [14].

This article describes the fabrication of a novel nanostructured PCC filler, its characterization by several standard methods, and a procedure for measuring the effective RI by a novel multi-function spectrophotometer. In addition, data are presented on light scattering coefficients measured from filled handsheets.

Materials and methods

Nanostructured PCC samples consisting of zinc-based nanostructures contacted with scalenohedral host particles were prepared with a laboratory-scale cylindrical carbonation reactor (volume 5 dm^3). The reactor is equipped with a centrifugal impeller mixer with rotation speed control, thermo-element casings, a gas feed system with rotameters for carbon dioxide and nitrogen, and pH/temperature sensors. The reactor is illustrated in Fig. 1.

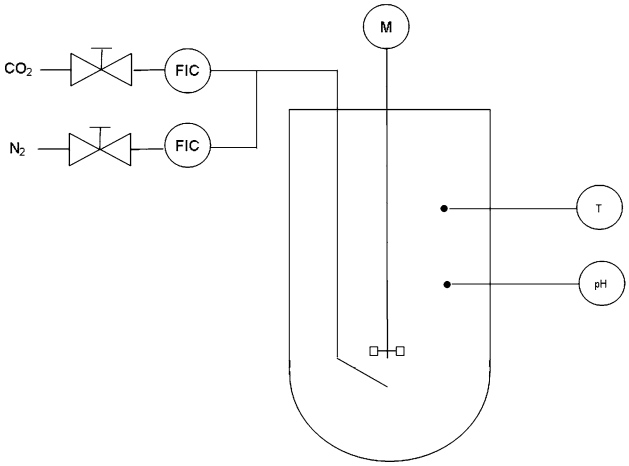

Fig. 1 The laboratory reactor

A slurry was prepared by mixing calcium hydroxide (50 g) in deionized water (2.0 dm^3, 25 °C) in the reactor. For nanostructure formation, a zinc compound was dissolved in deionized water (100 cm^3) and added to the slurry. Zn/Ca ratios of 0.1 and 0.25 were used to obtain nanostructured samples. The starting temperature of carbonation was 60 °C. Carbon dioxide gas was lead into the slurry during vigorous stirring, until the pH of the slurry dropped to 7. The pigment was filtered with a glass filter, thoroughly washed with deionized water, and dried. The fabrication conditions of the samples are listed in Table 1.

For morphology and particle size information, micrographs were taken with a Hitachi S-3400N VP-SEM (Variable Pressure SEM). A trace of the pigment sample was placed on the sample base and subsequently coated with a thin layer of gold. The accelerating voltage of the SEM was 15.0 kV**.** Both secondary electron images and backscattered electron images were taken.

The SSA of the samples was measured with a Micromeritics FlowSorp II 2300 analyzer. The measurements were made in accordance with the BET theory developed by Brunauer et al. in 1938 [15] covering adsorption of gas molecules on a solid surface. Specific surface areas of the samples were calculated by measuring the amount of nitrogen adsorbed on and desorbed from the samples in the temperature of liquid nitrogen. Before the measurements the samples were dried at 200 °C for 30 min.

Quantitative energy dispersive X-ray spectroscopy (EDS) analysis was used to determine the realized average zinc content of the PCC samples. This was done using the NSS202E-EDS system (Thermo Electron) with the SEM. For EDS analysis, the samples were coated with carbon. In addition, a spot EDS analysis was performed to detect local Zn contents in selected nanostructure-free and nanostructure-rich areas of a sample.

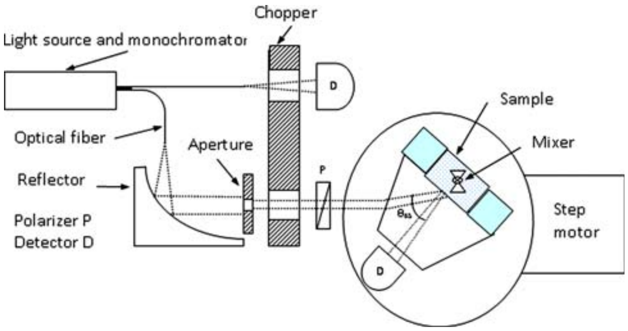

Fig. 2 Schematic diagram of the MFS. *D* detector, *P* polarizer

X-ray diffraction patterns were collected with a Philips PW1710 diffractometer using Cu K$_\alpha$ radiation.

Refractive indices of the samples were determined by measuring the backscattering signal from the pigment suspension using a multi-function spectrometer (MFS). A schematic diagram of the apparatus is shown in Fig. 2. The light source is a 150-W xenon lamp and a monochromator is used for the selection of the probe wavelength. The wavelength can be scanned over the spectral range of 270–800 nm. The probe light is guided into a bifurcated optical fiber. The output end of the fiber can be considered as a point source, and when it is set at the focal point of a parabolic reflector, a collimated light beam is generated. The linearly polarized light beam propagates toward the prism and the sample interface. The angle of backscattering was set at 29.4° by a step motor. A more detailed technical description of the MFS can be found in [16]. The whole system operates automatically. Using the MFS, the RI was measured both for the set of immersion liquids as well as the index of the samples. The samples were suspended in acetone–methylene iodide mixtures with refractive indices varying from 1.54 to 1.73 in steps of 0.05. The definition of the RI of the immersion liquid, n_1, is based on the measurement of the acetone and methylene iodide volumes V_a and V_m, and the measurement of the refractive indices n_a and n_m of these liquids by the multifunction spectrophotometer. Hence, n_1 can be calculated from the formula:

Table 1 Fabrication conditions of the PCC samples

ID	Target morphology	Starting temperature (°C)	Zn/Ca (mol/mol)
S-PCC	Scalenohedral PCC (reference)	60	0
Nano-S-PCC1	Nanostructured scalenohedral PCC	60	0.1
Nano-S-PCC2	Nanostructured scalenohedral PCC	60	0.25

$$n_1 = \frac{V_a n_a + V_m n_m}{V_a + V_m}. \quad (1)$$

The measurement wavelength and the temperature were 589.6 nm and 22 °C, respectively. The mass concentrations employed were 0.50 g (S-PCC, Nano-S-PCC1) and 0.40 g (Nano-S-PCC2) in the total sample volume of 15 mL.

Dried chemical pulp (70% birch, 30% pine) was beaten to a tensile strength index of 50 Nm/g and used as a furnish for the handsheets.

Handsheets were made using a conventional laboratory sheet mold in accordance with the standard SCAN C 26:76. First, water was added to the upper section of the mold, i.e., a stock container, to reach the mark at 350 mm above the wire screen. Pulp and filler were added, in the said order, and the container was filled with water according to the standard. Mixing was performed manually using a stirrer with a perforated plate, and the bottom valve of the mold was opened to drain the water through the wire. The formed wet sheet was couched with a couch roll. The target filler contents of the handsheets were around 10 and 20 wt%. The filler content was controlled by first making test sheets and determining the rise in the dry weight of the sheet due to the addition of filler. After reaching the target filler content with the test sheets, actual sheets for further analysis were prepared. Sheets were pressed under 490 kPa for 4 min and drum-dried at 60 °C for 2 h. The dried sheets were stored in a temperature- and humidity-controlled paper testing laboratory prior to measurements.

Kubelka-Munk light scattering coefficients were determined from the handsheets using reflectance values and grammage information with an L&W SE 070R Elrepho spectrophotometer.

Results and discussion

The SEM image in Fig. 3 shows the reference scalenohedral PCC, S-PCC, a typical clustered scalenohedral calcite. Figure 4 shows the Nano-S-PCC2 sample. Evaluations made from a collection of SEM images suggest that the size and aspect ratio of the host particles is approximately equal for the reference S-PCC and the nanostructured S-Nano-PCCs. However, clear morphological differences can be observed between the samples. In the nanostructured ones, irregularly shaped nanostructures, 100–500 nm in diameter, form a randomly distributed layer on the scalenohedral host particles. BET studies suggest that the surface area is increased by the nanostructures. Average zinc contents of 10 and 18 wt% were detected with EDS in the Nano-S-PCC1 and Nano-S-PCC2 samples, respectively. Figure 5 presents a backscattered electron image of

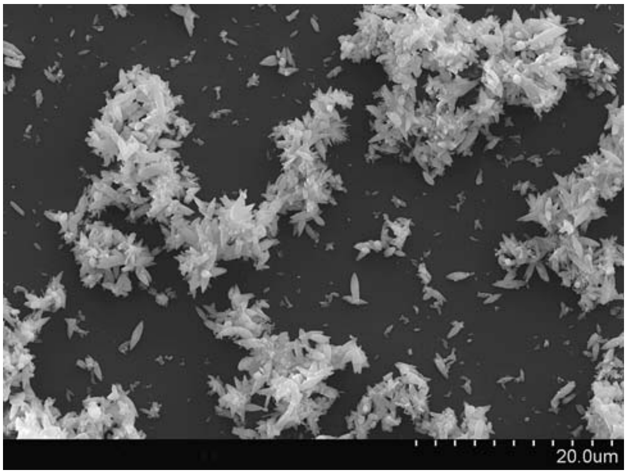

Fig. 3 Reference scalenohedral PCC (S-PCC)

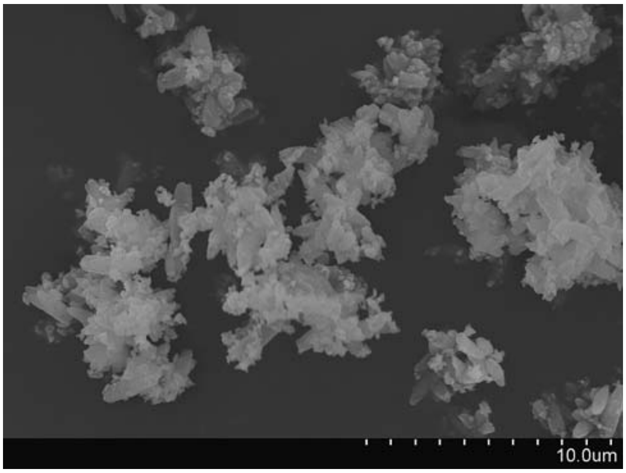

Fig. 4 Nanostructured scalenohedral PCC (Nano-S-PCC2)

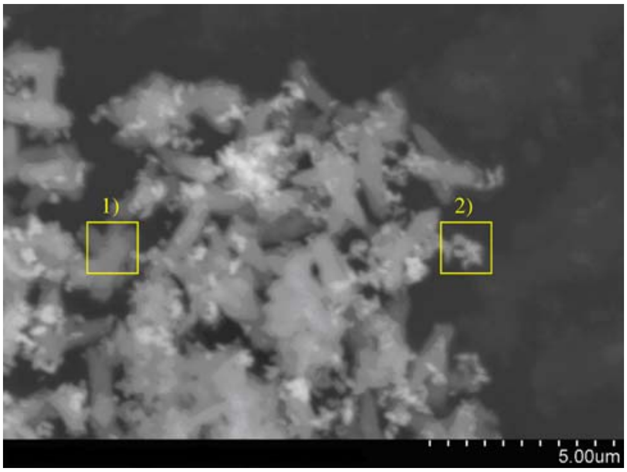

Fig. 5 Backscattered electron image of the Nano-S-PCC2 sample. (1) Nanostructure-free area, (2) nanostructure-rich area

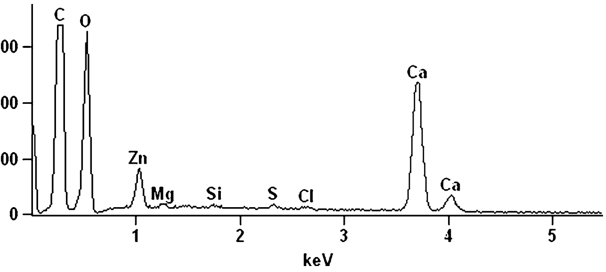

Fig. 6 Spot EDS analysis, Nano-S-PCC2, nanostructure-free area

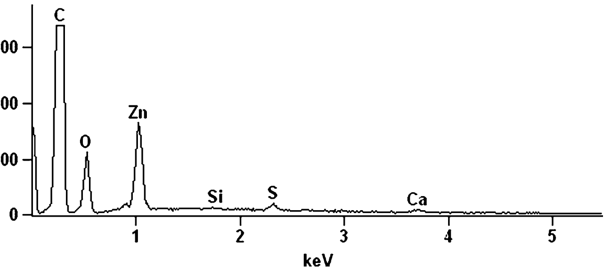

Fig. 7 Spot EDS analysis, Nano-S-PCC2, nanostructure-rich area

the Nano-S-PCC2 sample. In the figure, nanostructures appear whiter than the scalenohedral host particles, suggesting enrichment of zinc in the nanostructures. Spot EDS analysis spectra, presented in Figs. 6 and 7, support this assumption. The realized Zn/Ca ratio was significantly higher in the nanostructure-rich area than in nanostructure-free area. XRD studies indicated that zinc appears in the form of zinc oxide (zincite). Some zinc carbonate (smithsonite) was also detected. The main polymorph in the samples is calcite (host particles). Traces of aragonite were observed in Nano-S-PCC1.

Figure 8 shows light backscattering intensity data for some pigments measured with the multi-function spectrophotometer. The best match between the indices of the immersion liquid and the pigment is obtained, when the backscattering signal reaches the minimum value [17]. Since these are birefringent pigments, the minimum of the backscatter signal will never reach zero. As seen in the figure, the position of the scattering minimum changed when the pigment was modified by nanostructures. The effective RI for the reference calcium carbonate is 1.58, which corresponds well with the values given in the literature [18]. For the Nano-S-PCC1 and Nano-S-PCC2, the refractive indices were 1.62 and 1.67, respectively. Sample characteristics are summarized in Table 2.

Light scattering coefficients of the filled handsheets, as a function of filler content, are presented in Fig. 9. In general, the results indicate an increase in light scattering coefficient due to nanostructuring. It is clear that the increased effective RI has a positive effect in this respect.

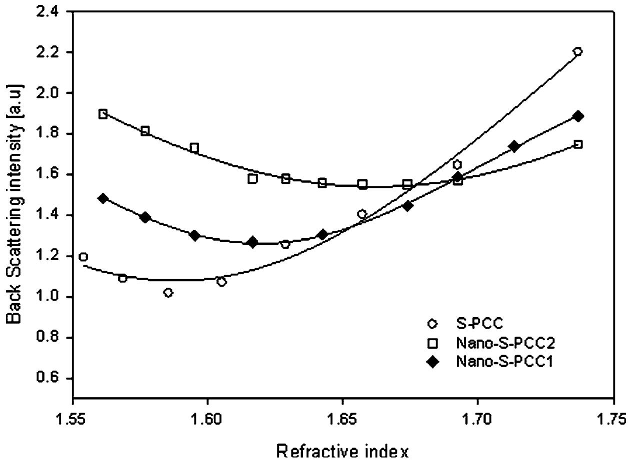

Fig. 8 Backscattering intensity curves of pigments as a function of the refractive index of the immersion liquid (*filled circles*). The *solid lines* represent Gaussian fitting for experimental data. The angle of backscattering was 29.4° and the wavelength of the light was 589.6 nm

However, the simultaneous change in other parameters, such as morphology and SSA of the pigment, must also be considered.

Conclusions

The objective of the present study was to develop paper fillers with an increased effective RI and light scattering potential. The study approach involved introducing zinc-based nanostructures on the PCC host material with scalenohedral particle morphology. Because of the nanostructures, the shape and SSA of the novel filler are different. Thus, to measure the realized RI of the novel filler, it is essential to have a method which is insensitive to changes in particle shape. The method used in this study combines an MFS with the immersion liquid method. This recently developed method decisively facilitated the work to develop the novel filler. A simple way to obtain a nanostructured PCC with effective refractive indices higher than 1.60 is to use a soluble zinc additive during the conventional carbonation process. Today, nearly all essential raw materials of paper have the same RI, about 1.60. However, light scattering and, hence, the opacity of paper are only improved by interfaces which manifest a difference in refractive indices. Modification of the RI has only recently attracted increased attention as a means to develop new fillers. Accordingly, the findings of this study can be considered important for the future development of paper fillers and pigments. Initial studies with filled handsheets suggest increased light scattering. In further studies, special emphasis will be put on exploring the effect of changing a single particle parameter at a time.

Table 2 Properties of the PCC samples

ID	Effective RI	Specific surface area (m^2/g)	Zn content (wt%), EDS	Detected crystal forms by XRD
S-PCC	1.58	5	–	Calcite
Nano-S-PCC1	1.63	9	10	Calcite, aragonite, zincite, smithsonite
Nano-S-PCC2	1.67	8	18	Calcite, zincite

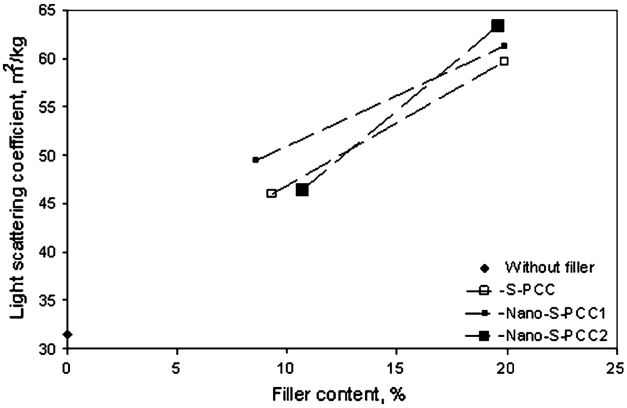

Fig. 9 Light scattering coefficient of handsheets as a function of filler content

Acknowledgements Financial support from Finnish Funding Agency for Technology and Innovation (Tekes), J.M. Huber Finland Oy, M-real Oyj, Omya Oy, and UPM-Kymmene Oyj is gratefully acknowledged.

References

1. Laufmann M (2006) Pigments as fillers. In: Holik H (ed) Handbook of paper and board. Wiley-VCH Verlag GmbH&Co, Weinheim, p 33
2. Krogerus B (1998) Fillers and pigments. In: Neimo L (ed) Papermaking chemistry. Fapet Oy, Jyväskylä
3. Laufmann M, Rapp HU (1995) Wire abrasion and its potential causes. In: 1995 Dyes, fillers & pigments short course, Chicago, 26–28 April 1995. TAPPI Press, Atlanta, p 49
4. Huuskonen J, Eiroma E (1983) In: Arjas A (ed) Paperin täyttö, Paperin valmistus, 2nd edn. Suomen Paperi-insinöörien yhdistys, Turku, p 271
5. Gill RA (1992) Precipitated calcium carbonate (PCC) fillers and the sizing of alkaline papers. In: 1992 Sizing short course, Nashville, 8–10 April 1992, TAPPI Press, Atlanta, p 75
6. Peiponen K-E, Vartiainen EM, Asakura T (1999) Dispersion, complex analysis and optical spectroscopy. Springer, Heidelberg
7. Scallan AM, Borch J (1972) An interpretation of paper reflectance based upon morphology, I. Initial considerations. Tappi 55(4):583
8. Giertz HW (1951) Opaciteten hos pappersmassor. Svensk Papperstidning 54(8):267
9. Gane PAC, Buri M, Blum R (1999) Pigment co-structuring: new opportunities for higher brightness coverage and print-surface design. In: Proceedings of the international symposium on paper covering coverage, Helsinki, 1999
10. Lattaud K, Vilminot S, Hirlimann C, Parant H, Schoelkopf J, Gane P (2006) Index of refraction enhancement of calcite particles coated with zinc carbonate. Solid State Sci 8:1222
11. Penttilä A, Lumme K (2004) The effect of particle shape on scattering—a study with a collection with axisymmetric particles and sphere clusters. J Quant Spectrosc Radiat Transf 89:303
12. Seferis CJ (1999) Refractive indices of polymers. In: Brandrup J (ed) Polymer handbook, 4th edn. Wiley, New York, p 571
13. Jaffe HW (1996) Crystal chemistry and refractivity, 2nd edn. Dover Publications, Mineola, 335 pp
14. Merrill L, Bassett WA (1975) The crystal structure of $CaCO_3$ (II), a high-pressure metastable phase of calcium carbonate. Acta Crystallogr B31:343
15. Brunauer S, Emmet PH, Teller E (1938) J Am Chem Soc 60:309
16. Niskanen I, Räty J, Peiponen K-E (2006) A multifunction spectrophotometer for measurement of optical properties of transparent and turbid liquids. Meas Sci Technol 17:N87
17. Niskanen I, Räty J, Peiponen K-E (2008) Estimation of effective refractive index of birefringent particles using a combination of the immersion liquid method and light scattering. Appl Spectrosc 62:399
18. Palik ED (ed) (1998) Handbook of optical constants of solids II & III. Academic Press, San Diego