Characterization of thin pigment coating layers produced by foam coating

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ABSTRACT: Foam coating is a promising method for applying a thin pigment layer of nanoparticles on a paper web. The interest in applying a low coat-weight coating layer arises from the need to create new functional surfaces using small amounts of new, typically expensive nanoparticles. The characterization of thin pigment layer properties is more demanding than analyzing traditional pigmented coatings layers because of the low coat weight (0.3-2.0 g/m^2) and a corresponding low layer thickness of 1 μm or less. This characterization requires surface-sensitive measuring techniques and a combination of different microscopic and spectroscopic surface analyses. In this study, the pigment layer structure and chemical properties of nanosilica-coated paper were analyzed. The results were used in the development of the foam coating process.

Application: Relatively fast spectroscopic and microscopic characterization methods might be used to analyze thin pigment-coated paper surfaces produced by foam coating. The combination of measurements is needed to obtain a comprehensive picture of the properties and structure of foam-coated paper samples.

Foam coating is an established technology in the textile and nonwoven industries [1-3], and a well-known technique in plastic film production. A dye or finishing agent is applied to the textile material in the form of foam containing a gaseous propellant, a water liquid containing a dyestuff or finishing agent, and a surfactant. The foam layer applied to the surface of textile material is collapsed and the material is subjected to fixing the dyestuff or finishing agent. By using air as an additional diluent in the coating, foam coatings may be applied to a surface at much lower coat weights than traditional water-based coatings. Thus, the foam application method reduces the problems caused by large amounts of liquid medium used in the conventional textile fabric treatment [4]. The technique has been one of many used in the textile industry over the past 10 years, but currently, because of demands for energy savings and for optimizing the use of costly chemicals, its importance is growing.

Beyond a few paper applications, however, foam coating technology has so far failed to gain ground in the paper industry. Coating of compositions containing microcapsules with natural foaming agents, gelatin, casein, and soybean extract has been applied as foam to a paper web [5]. By using foam in the manufacture of surface-sized paper, significant wetting of paper is obviated. Foam produced from a protein foaming agent was found to be the most suitable for various purposes in the manufacture of paper [6]. However, foam coating is an attractive technology and could be used in paper mills to convert small paper machines to production of specialty products.

In the foam coating process, foam is used as a carrier phase for the coating material. The liquid, containing coating solids and foaming agents, is mixed with air in a foam generator. The foam normally contains 90%-95% air. This means, for example, that instead of a 1 μm layer of liquid, a 10 μm layer of foam is spread, which makes it possible to spread a small amount of nanoparticles evenly. The coating nanomaterial is located in "bubble pockets" (vortices), preventing flocculation of the nanoparticles [7]. The advantage of using nanoparticles is that they achieve adhesion and cohesion via surface forces, which means that binders are not needed.

EXPERIMENTAL

Foam coating

Silica pigment water dispersion and foaming agent were mixed with pressurized air in a separate foam generator. The foam was produced with a rotor-stator mixing head to an air content of 80%-95%; the corresponding densities being 200 g/L down to 50 g/L. Depending on silica solutions, the foaming agents used were anionic or cationic surface active agents, added in amounts of 0.03-0.3 w-%. With anionic surface active agents, polyethylene glycol was used as a foam stabilizer. The silica foam was pumped from the generator to a narrow slot-type applicator for application to the moving paper web. On the web, the foam bubbles collapse as the liquid is absorbed into the uncoated paper, leaving the coating material on the web surface. Drying after foam application was performed with infrared (IR) dryers. The amount of pigment applied on the paper depends on the silica pigment con-

Coating	Pigment	Silica Content of Pigment Dispersion, w-%	Silica Particle Size,[1] nm	Calculated Coat Weight, g/m²
Silica A, trial 1	Bindzil CC40	40	7-12	2.4
Silica B, trial 2	Bindzil 50/80	20	20-100	4.7
Silica C, trial 3	Bindzil NH_3/80	10	40	0.9

[1] Measured by pigment supplier.

I. Silica pigments in foam coating trials

tent of the aqueous dispersion, the air content of the foam, and the pumping speed. **Table I** lists silica pigments and calculated coat weights.

Foam application is a non-contact method, which is important when coating with highly adhesive particles such as nanoparticles. Coating speeds of 100-400 m/min were tested with the pilot coater. The base paper for the tests was an uncalendered fine paper (78 g/m²) with calcium carbonate filler. The paper was produced in a Finnish paper mill. Silica pigments in the foam coating trials were commercial Bindzil (Eka Chemicals AB; Bohus, Sweden) water-based colloidal solutions in which the main component is silicon dioxide. The chosen silica products have mean pigment particle diameters of 10-80 nanometers. The silica dispersions were anionic, except for one cationic product (Bindzil CAT 80). The silica content of the pigment dispersion was adjusted to obtain coat weights of 1-4.5 g/m².

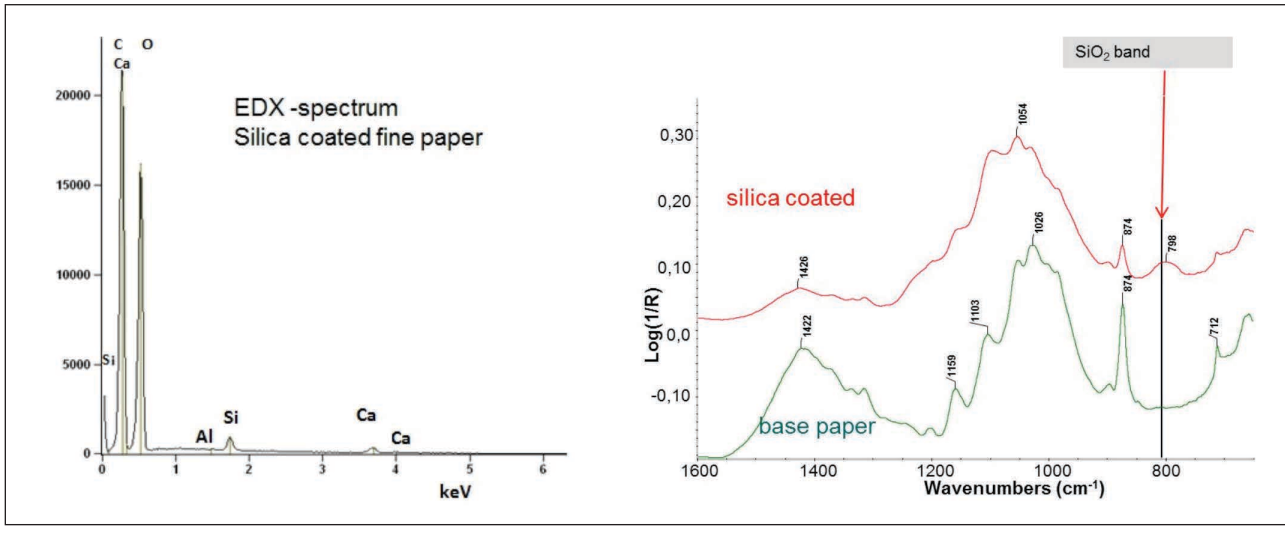
Characterization methods

Combinations of different methods were used to characterize the surface layer and paper of the nanosilica foam-coated paper samples. The aim of characterization was to measure the surface layer chemical composition and coating structure, and to identify how a thin silica layer affects paper standard properties (roughness and gloss) and wetting.

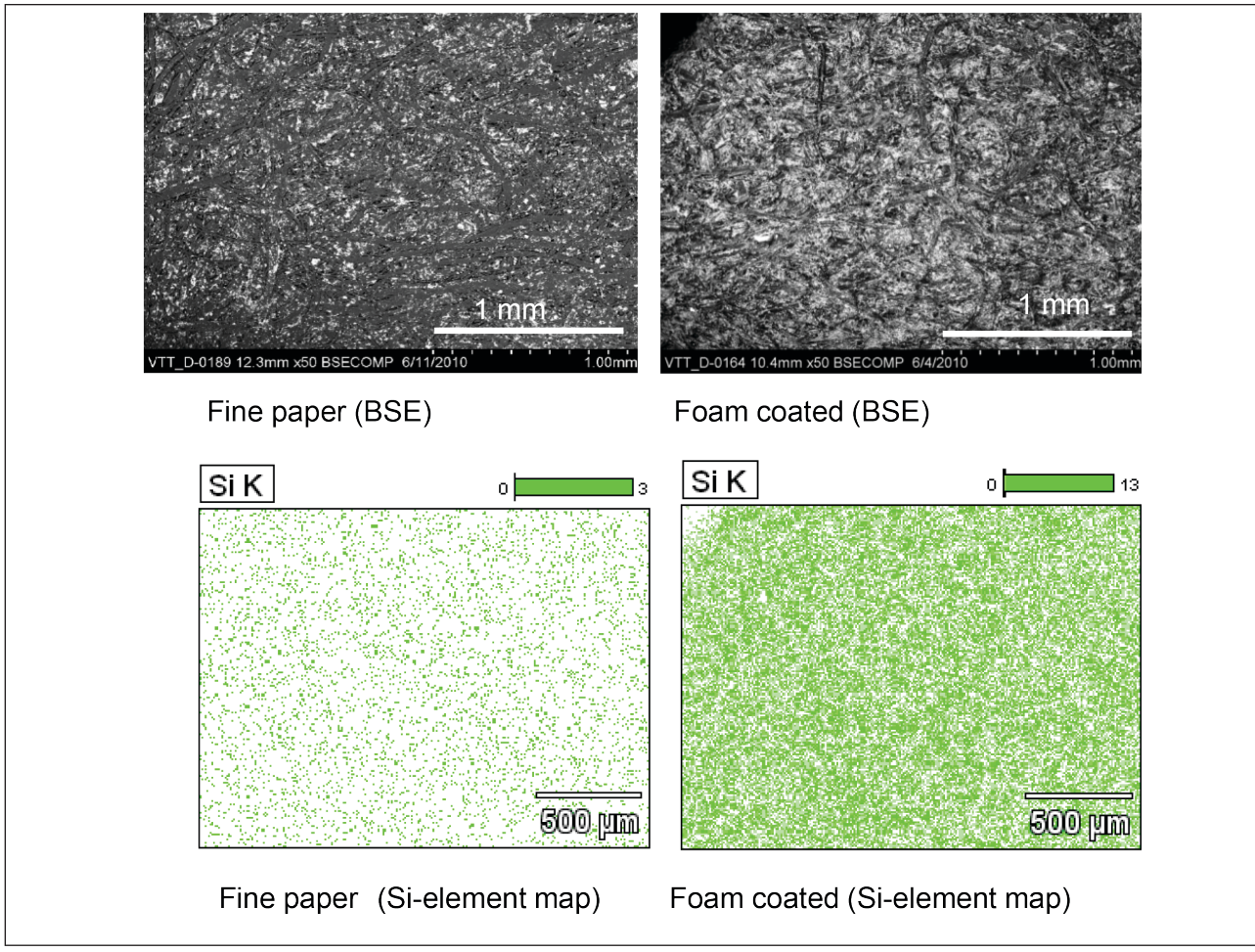
The element composition of silica pigment, pigment-coated paper surfaces, and base paper surface were determined semi-quantitatively with energy dispersive X-ray (EDX) spectra using a Noran System Six EDX spectrometer (Thermo Scientific; Watham, MA, USA). The main chemical compounds of the paper surface were determined measuring the IR spectra of the surface with the diamond crystal attenuated total reflectance (ATR) technique using a Nicolet Nexus 870 Fourier transform-infrared (FT-IR) spectrometer (Thermo Scientific).

An S-3400N scanning electron microscope (SEM) (Hitachi; Tokyo, Japan) and Noran System Six EDX spectrometer were used to perform qualitative microscopic analyses of paper surfaces. The surfaces were examined under SEM with a back-scattered electron (BSE) image mode revealing topography variations and elemental contrast variation of the pigment layer on the surface base paper. Paper sample surfaces were coated with a thin carbon layer before imaging. The accelerating voltage used was 7 kV. At 50× magnification, the SEM image shows an area of 1.5 mm × 2.2 mm. Three adjacent images were taken to obtain a representative overview of the sample surface.

Elemental distribution uniformity of silicon over the silica-coated paper was studied using SEM-EDX silicon-element mapping analysis. EDX mapping analysis is a qualitative technique



1. Scanning electron microscope (SEM)-energy dispersive X-ray (EDX) spectrum of silica foam-coated paper (left) and attenuated total reflectance (ATR)-infrared (IR) spectra of silica-coated paper and base paper (right).



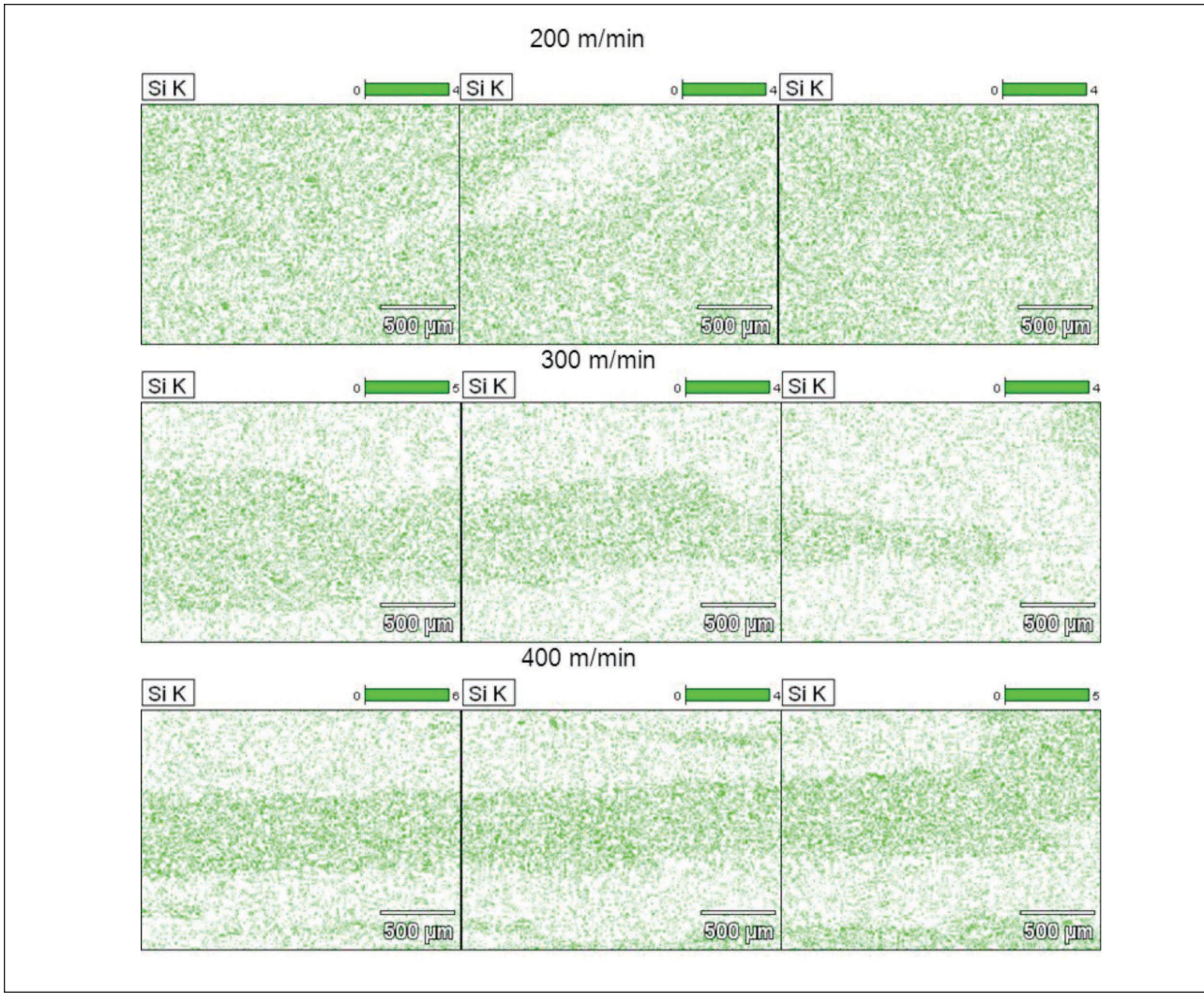
2. SEM-back scattered electron (BSE) image of 50× magnification and silicon (Si)-element map of base paper (left) and silica foam-coated paper (right).

in which the intensity of the X-ray energy characteristic of the element from which it is emitted is measured relative to its lateral position on the sample. Element mapping is used to determine element distribution across a studied area in samples such as paintings, plant tissue, or bone samples [8-10]. In the silica coating EDX mapping, the element images were collected from the same areas as those examined with the SEM BSE image mode. The silicon element map of foam-coated paper is able to show the variation of the amount of silica on surface. In the image, a higher intensity color represents those areas with higher amounts of silica.

A more detailed surface analysis of the silica pigment location on paper surfaces was carried out using a DSM 982 Gemini high-resolution scanning electron microscope (HR-SEM) (LEO; Oberkochen, Germany) with a secondary electron detector (SE-detector) and 2000× magnification. The EDX mapping analysis of silicon and calcium with HR-SEM was performed on the same areas from which the SE-images were obtained. The accelerating voltage was 8 kV. The paper surface was treated with platinum sputtering before HR-SEM imaging.

Silica distribution in the z-direction of the paper samples was studied quantitatively by comparing the relative ratio of silicon and calcium amounts determined in weight percentage units on the paper surface to the ratio in the whole paper. Silicon originates from silica foam coating and calcium originates from base paper filler pigment. The base paper had no substances that contained silicon. The silicon/calcium ratio of the paper surface was determined with EDX element analysis from the coated paper surface. EDX measurement is able to detect carbon and elements heavier than carbon and penetrates to a depth of about 1 μm. The silicon-to-calcium ratio of the whole paper was measured with a PW2404 X-ray fluorescence (XRF) spectrometer (Philips; Amsterdam, the Netherlands) from homogenized coated paper samples. The homogenized paper sample was prepared by grinding and subsequently forming a tablet from the ground sample. XRF measurement is able to determine fluorine and elements heavier than fluorine. The calcium and silicon percentages were calculated using SemiQ semi-quantitative software (Philips).

The contact angle of water used to describe the wetting of silica-coated paper was measured with a CAM 200 device (KSV Instruments; Monroe, CT, USA). Measurement was car-



3. Si-element map of silica foam-coated paper coating speed of 200 m/min (upper), 300 m/min (middle), and 400 m/min (bottom).

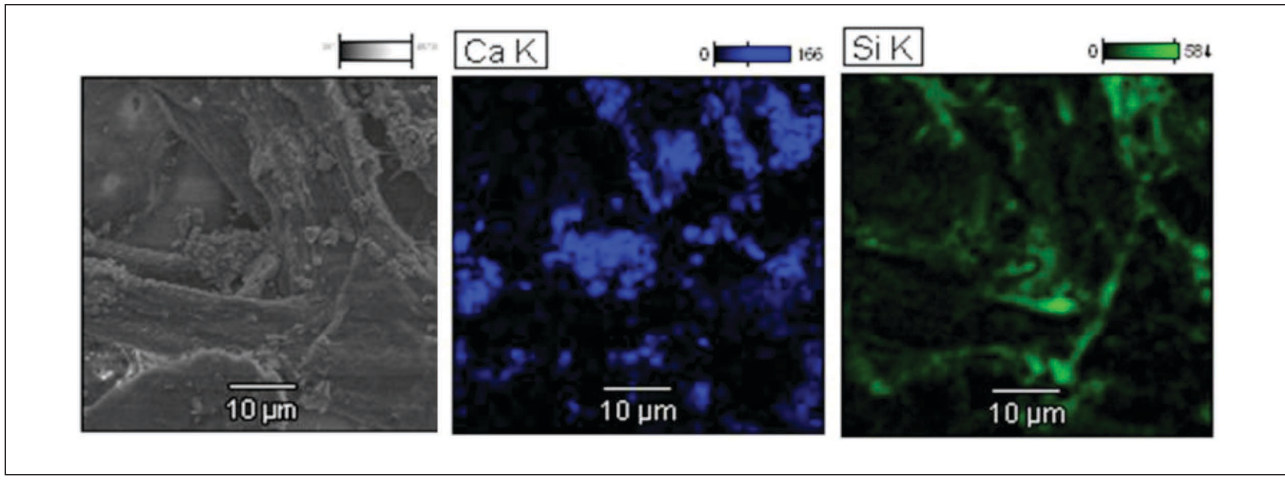
ried out after laboratory calendering of foam-coated papers. Paper gloss at 75° and Parker Print Surf (PPS) S10 roughness were also measured from laboratory calendered samples.

RESULTS AND DISCUSSION

The chemical composition of silica-coated sample surfaces was determined by measuring the EDX and ATR-IR spectra. The thin silica coating can be seen as weak silicon signals in the EDX spectra of the paper surface and as weak or medium IR bands of silicon dioxide in surface IR spectra (**Fig. 1**). Elements of base paper fibers (carbon and oxygen) and filler calcium carbonate pigment (calcium and oxygen) have strong signals in the EDX spectra. Strong or medium bands of cellulose and carbonate are seen in the surface IR spectra. It is obvious that EDX and ATR measurement penetrates through the thin silica coating into the base paper, as cellulose has strong signals in the measured surface spectra. The measurement depth is estimated for EDX measurements to be about 1 μm and for ATR-IR about 1-3 μm in the IR region studied.

The silica foam coating layer uniformity was determined with SEM-BSE images and silicon element maps. **Figure 2** shows examples of a base paper and silica-coated surface BSE image and a silicon-element map. In the base paper surface BSE images, the grey areas are fibers and the white areas are calcium carbonate filler particles. In the silica-coated paper surface BSE images, the grey areas are fibers, but it is difficult to differentiate the white silica pigment coating from the white calcium carbonate filler particles. Silicon distribution on the coated surface is detectable from X-ray silicon element maps. The base paper silicon-element map has only weak signs of silicon distribution. This weak sign originates mainly from the background noise of the EDX detector. The foam-coated paper silicon-element map has clear signs of silicon, and the silicon map indicates that silica pigment is evenly distributed on the coated paper surface.

Foam coating speed was a dominating factor in coating uniformity. On the pilot paper coating machine, greater uniformity of coating coverage was obtained using a lower coat-



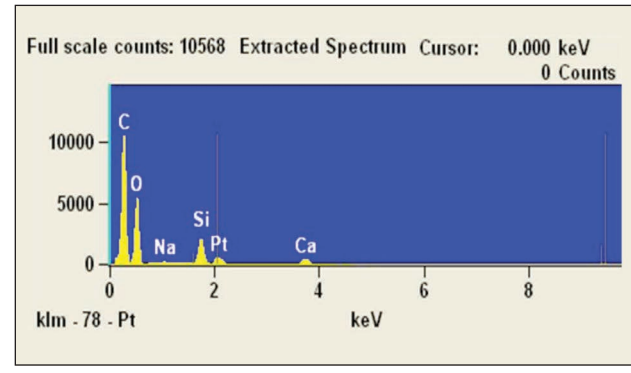
4. A high-resolution SEM-secondary electron (SE) image of 2000× magnification (left); a calcium (Ca)-element map of silica foam-coated surface (middle); and Si-element map of silica foam-coated paper (right).

ing speed of 100 m/min or 200 m/min. When the machine speed was higher, the silica coating formed a striped pattern on the paper surface. The silica coating stripes became sharper as the coating speed was increased to 300 m/min and further to 400 m/min, as represented in the silicon-element maps of silica-coated paper in **Fig. 3**.

The unevenness of the coating layer (stripes) was caused by the air coming with the paper web. One technical solution to improve the coating quality is an air knife, as used in curtain coating. The thin air layer from the paper surface is removed by an air knife so that it does not disturb the curtain between the web and the applicator. Unfortunately, this technique was not available in our trials.

A more detailed analysis of the silica pigment location on the uppermost surface layer of the foam-coated paper was carried out with the HR-SEM-SE images. This technique gives topographic information of the silica coating on the fiber network with filler pigments. **Figure 4** (left) shows fibers and pigment particle clusters in a high-resolution SE image of 2000× magnification, but it is difficult to differentiate silica pigment coating from calcium carbonate fillers in the SE image. Element mapping carried out by EDX analysis shows the position of pigments on the paper surface. The pigment clusters are mainly calcium carbonate filler pigment; the calcium-element map has high intensity in those positions (Fig. 4, center). According to the silicon-element map, silica has enriched at the fiber edges (Fig. 4, right). The silicon-element image suggests that silica pigment has a more film-like structure than particle clusters, because the highest silica intensity in the silicon map is seen in those areas where the SE image shows a uniform, smooth surface structure.

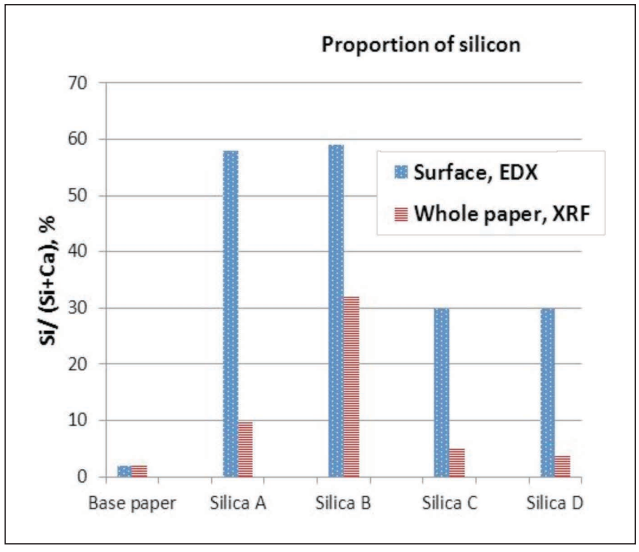
The SEM-EDX spectrum measured from the same position confirms that there is clearly silicon on the surface and some calcium carbonate (**Fig. 5**). Cellulose fibers are seen as carbon and oxygen in the EDX spectrum, and platinum originates from the sample surface sputtering before HS-SEM measurement.



5. SEM-EDX spectrum of a foam-coated paper surface.

One important quality that needs to be identified in making thin foam coatings is whether the silica pigment has attached to the surface of the paper or whether it has penetrated deeper into the paper structure. The z-directional silica pigment distribution was evaluated by comparing the results of two measurements to determine the relative proportions of silicon and calcium on the surface to whole paper ratio. The relative silicon and calcium weight percentages were scaled to 100%, calculated as the ratio of silicon to silicon plus calcium. The base paper contained calcium carbonate filler and had no silicon-containing substance. The surface proportions of calcium and silicon were measured with EDX and whole paper proportions from a homogenized paper sample using X-ray fluorescence analysis.

On the surface, the proportion of silicon was clearly higher than in the whole paper (**Fig. 6**). This confirms that silica pigment has attached mainly to the surface of the paper. The higher silicon amount detected on the surface of samples coated with silica A and B is in accordance with the higher amount of silica foam applied in coating trials 1 and 2. The proportion of silicon in the whole paper is exceptionally high in the sample coated with silica B, in which the amount of applied silica foam was highest (4.8 g/m^2). The reason for the higher pro-



6. Surface and whole paper Si:Ca ratio, SEM-EDX, and X-ray fluorescence (XRF) analysis.

portion of silicon in the whole paper could be that when the amount of silica applied is too high, only a portion of that amount is able to attach to the surface and form a surface layer. The rest of the silica penetrates into and attaches onto the base sheet fiber structure.

Silica pigment is hydrophilic and, accordingly, the silica-coated samples had a lower contact angle with water than the base paper (**Table II**). The thin silica coating made the paper surface more hydrophilic. Silica pigment coating decreased paper gloss somewhat, and roughness was the same or slightly higher.

CONCLUSIONS

The foam coating technique is able to create a thin pigment layer on paper. The characterization of a thin silica layer requires a combination of different microscopic and spectroscopic analyses because of the small amount of pigment material on the surface.

SEM-EDX and ATR-IR spectra can be used to detect the existence of the coating material. The ATR-IR and SEM-EDX analysis results showed that the measured surface layer contained silica coating and base paper. It is obvious that these measurements were not surface sensitive enough but penetrated partly to the base paper under the silica coating. Because of the low surface sensitivity of the ATR-IR and SEM-EDX measurements, it was not possible using these techniques to detect whether the coating material is only on the surface or partly in the bulk of paper. These measurements have good properties in terms of the short measurement time and no special sample preparation is needed.

SEM-EDX element mapping is a powerful qualitative tool for detecting uniformity of the pigment coating surface. Possible uncoated areas can be seen clearly on the element maps; even with some amount of coated substrate on the bulk structure, the intensity variations reveal uncoated areas. The samples that had a silica coating on fine paper with calcium carbonate filler had a beneficial element composition so that calcium could be used as a marker of base paper in element analyses based on X-ray techniques. The combination of SEM, EDX, and XRF methods can be used to study how well the coated particles remain on the surface. By comparing signals, the surface-to-bulk ratio of coated material can be measured.

The results presented in this paper clearly show that even a small amount of nanoparticles can change surface properties. Nanosilica particles increased paper hydrophilicity and slightly decreased paper gloss. By using more advanced nanoparticles, more interesting surface property changes can be obtained, and with the foam coating method, a small amount of material can be applied. By choosing proper characterization methods, the structure and uniformity of these surface modifications can be measured. **TJ**

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Coating	Contact Angle Water, 0.5 s, °	Gloss, 75° %	Roughness, PPS S10 µm
Base paper, trial 1	45	8.8	3.4
Silica A, trial 1	21	7.1	3.9
Base paper, trial 2	37	7.4	4.0
Silica B, trial 2	9	5.4	4.7
Base paper, trial 3	34	9.2	3.6
Silica C, trial 3	22	9.1	3.6
Silica D, trial 3	26	9.0	3.6

II. Contact angle, gloss, and roughness of the paper.

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ABOUT THE AUTHORS

Surface treatment of paper surface is the research area where we are working, and we wanted to study a technique that would be able to produce thin coating layers. Kenttä has been studying and analyzing pigment coatings produced with traditional coating techniques like blade and film coating. This research complements that previous work.

The most difficult aspect of this study was to find a good combination of characterization methods for determination of thin coating layers. An interesting finding was that by using the chosen combination of different measurements we obtained versatile and quite detailed information about the silica pigment coated surfaces.

The findings from this research will help mills to choose appropriate methods for thin-pigment layer characterization. For future studies, we will use different types of nanomaterials to prepare and study foam-coated paper.

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