Complementary microscopy techniques for surface characterisation of uncoated and mineral pigment coated paper

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The quantification of surface structure is of major importance for several industry sectors. For the paper industry, the surface topography is essentially important for securing a good print quality of various paper grades. The surface affects various print quality parameters such as ink transfer, ink distribution, gloss and missing dots. It is thus important to have a detailed assessment of surface topography to be able to understand its influence on paper and print characteristics. In this study, several complementary characterisation techniques are reviewed and demonstrated, including scanners, optical microscopy, laser profilometry, scanning electron microscopy and atomic force microscopy. The techniques prove to be complementary and adequate for structural quantification at various scales, from the millimetre to the nanometre levels.

Keywords Laser profilometry, scanning electron microscopy, atomic force microscopy, electron microscopy, computerized image analysis.

1. Introduction

The quantification of surface topography is of major importance for several industry sectors. For the paper industry, the surface topography is essentially important for printing paper grades. It affects several paper and print properties like ink transfer, ink distribution, gloss and missing dots. It is thus important to have a detailed assessment of surface topography to be able to understand its influence on the paper and print characteristic details.

Printing paper includes uncoated and coated paper grades such as newsprints, supercalendered (SC) and light-weight coated (LWC) paper. In newsprints and supercalendered paper the mineral fillers and fibre material are mixed. In LWC paper a relatively rough basepaper, composed of fibres and fillers, is coated with a layer of fine mineral particles, thus creating a smooth surface structure.

The quality of a given paper grade is commonly characterised by the quantification of its roughness. Although there are several roughness parameters available, see [1]-[4], the root-mean-square is the most used roughness descriptor. The surface roughness may be divided into several scales, each scale affecting a given paper or print property. A proper description of a given surface structure requires reliable image acquisition devices. This is most important as the quality of a given surface representation determines or limits the extraction of valuable numerical data, which may describe a given surface. During the last two decades several methods have been proposed for assessing the surface structure of paper. This includes stylus profilometry [5]-[8], laser profilometry (LP) [9]-[11], a photometric stereo method [12], confocal laser scanning microscopy (CLSM) [13], scanning electron microscopy (SEM) [14],[15] and atomic force microscopy (AFM) [16]. This chapter will give examples of various complementary image acquisition techniques and how they are applied to paper and print analyses, i.e. scanners, optical microscopy, laser profilometry, SEM and AFM. The mentioned characterization methods are complementary and cover a wide range of scales, including the micrometre and nanometre levels.

2. Paper and print applications

2.1 Laser profilometry

During the last years LP has been used for assessing the surface topography of several paper grades, including newsprints, SC and LWC paper (Fig. 1a). The method is fast, fully automated, non-contact, non-destructive and capable of assessing large areas [17]. However, LP has some limitations with respect to the detection and description of steep gradients. Such limitation causes noise on the digital images, especially along coarse surface fibres. On the other side, covering the surface with a layer of gold before image acquisition seems to reduce internal reflections and reduces the amount of error height values [4].

Suontausta [10] applied LP for assessing the effect of coating and calendering on the surface structure of paper. The study demonstrated one of the major advantages of profilometer devices, i.e. a topographical map may be decomposed into several scales of roughness. This gives the opportunity of assessing the effect of a given scale of roughness on a specific response. Wavelength analysis was thus used for exploring the development of the surface structure depending on a given coating composition and calendering configuration. Using LP, Holmstad et al. [18] studied the effect of temperature gradient calendering on the surface structure of pilot calendered paper. According to the authors, the
Calendering conditions used in the study had a major effect on the uppermost surface structure, being the temperature the variable having the major impact on the reduction of the surface roughness and thus on increasing the paper gloss. LP has been applied for studying the effect of the surface structure of SC and LWC paper on gloss \cite{10,11,17,18}. Gloss is one of the most important paper and print quality parameters of magazine paper. It may be affected by the surface roughness and the corresponding refractive index \cite{5}. For the same roughness, clay yields usually higher gloss compared to ground calcium carbonate (GCC), see e.g. \cite{19}. In addition, it has been demonstrated that the amount of fillers in the surface layers explains part of the gloss development of commercial SC papers \cite{20}. Compared to SC paper, LWC paper has commonly higher gloss levels due to the smoothing effect of the coating layer (Fig. 2). In addition, when SC paper is in contact with water a roughening phenomenon occurs due to the swelling of the fibre material. The roughening is less in coated paper \cite{21}. Contrary to water application that causes roughening, a layer of printing ink usually smoothens a given surface structure (Fig. 1, Fig. 2).

For a detailed understanding of the characteristics of a surface structure, a surface representation can be decomposed into gradients. In this context, a gradient is considered a small facet having a given angle relative to the paper plane. A gradient analysis of surface topography images can be performed with the SurfCharJ plugin for ImageJ, which is freely available in the Internet \cite{4}. For exemplification purposes, a gradient analysis has been performed on the image in Fig. 1a. Compared to the gradient image of the same area before printing (Fig. 1b), the gradient image of the printed sample (Fig. 1c) has a lower fraction of large polar angles. A lower fraction of large polar angles indicates that the surface has been smoothened due to the printing ink \cite{21}. Consequently, the printed surface (Fig. 1c) will thus have a higher gloss than the unprinted surface. This exemplifies one of the benefits of using a non-destructive surface assessment device in combination with appropriate image analysis, i.e. samples can be characterized before and after a given surface treatment.

![Fig. 1. Laser profilometry analysis. a) Surface representation of an unprinted sample. b) Facet orientation analysis of the unprinted sample in a). c) Facet orientation analysis of the same area after printing. Each facet in b) and c) corresponds to an angle relative to the paper plane. Note the facet orientation that decreases after printing due to the smoothening ink layer. The calibration bar in a) is given in micrometres. The calibration bars in b) and c) are given in degrees.](image)

Based on a LP concept, Sung and Keller \cite{22} reported on a new method defined as twin laser profilometry (TLP). The instrument consists of two laser sensors, placed on each side of a sample holder. This configuration makes it possible to acquire surface profiles from each side of a paper sample. The profiles are thus combined to generate a thickness map with a resolution of 1 μm. According to the authors, the TLP method yields the intrinsic thickness of a given sample, thus eliminating the overestimation of thickness that is characteristic of standard caliper methods.

### 2.2 SEM

The scanning electron microscope (SEM) is a versatile device for exploring surface structures. Images can be acquired at several magnifications and with a resolution unattainable by other techniques. Images can be acquired in backscatter electron imaging (BEI) mode (Fig. 2) and secondary electron imaging (SEI) mode (Fig. 3). Due to its extensive capabilities, SEM has been one of the most widely used devices for assessing the structure of paper and prints, see e.g. \cite{18,23,26}.

An ideal paper surface should be smooth with optimal structure to improve e.g. gloss and keep a good interaction between the paper surface and the applied inks during printing (Fig. 2). Imperfections and irregularities on the paper surface structure such as coarse fibres (Fig. 3) should be avoided. SEM has, without doubt, been a most valuable tool for assessing paper structures and their components. Such capability has facilitated the development of improved paper grades and advanced our understanding of how a given structure is affected by specific process variables.
As stated above, the SEM is a powerful tool for assessing different characteristics of the surface structure of paper. In SEI mode the SEM gives a clear 3D impression of the topography of a given surface. This capability has been used for exploring e.g. the surface development due to calendering, the consolidation of coating layers and the smoothening effect of printing inks. The SEM can also be used for reconstructing surface structures (Fig. 3). The method is based on stereo imaging and parallax, see e.g. [27]. Such surface reconstruction makes it possible to perform a quantitative assessment of the surface topography [28]. Another approach has been introduced by Suganuma [29] and applied to paper surface analysis by Enomae et al. [14]. The authors used a SEM having two secondary electron detectors. Images were acquired from each side of the vacuum chamber and a topographical height map was reconstructed. Such approach facilitates the quantification of roughness based on high-resolution SEM images.

The surface coverage by a layer of coating/fillers is an important characteristic of printing paper. Coverage may determine some paper and print properties. SEM-BEI mode yields contrast depending on the average atomic number of a given local area. Mineral fillers such as clay and CaCO₃ may appear lighter than the matrix of darker fibres (Fig. 2a, Fig. 7b). SEM-BEI mode images with appropriate image segmentation and analysis procedures make this technique suitable for quantification of coverage and related characteristics. Such capability has been used for quantifying the coverage of the coating layer on coated papers (see e.g. [30]-[32]) and the coverage of fillers on SC paper surfaces [4]. Coverage is defined as the ratio of areas covered with a coating layer to the whole imaged area. Kaartovara[30] quantified several statistics of uncovered areas, such as percentage, average size and number of uncoated areas. The author found a reduction of uncoated areas as the coat weight was increased from approximately 8 to 20 g/m². However, care must be taken when using the SEM-BEI mode for quantification of coverage, as the amount of uncovered areas depends on the accelerating voltage used during image acquisition in the SEM-BEI mode. It is recommended to use low accelerating voltage in order to assess only the uppermost layers of the paper surface. An acceleration voltage of 5 kV seems to be appropriate in this respect.

In addition to surface assessment, the SEM is a powerful tool for quantification of cross-sectional details of paper structure [33]-[36]. Such quantification may be used for describing the porosity, fibre and pore cross-sectional dimensions, filler distribution, fines distribution, the interaction between coating layers and base papers and the structural details of mineral pigment layers on paper.
2.3 AFM

According to Niemi et al. [19] AFM has three major advantages compared to other microscopy techniques, i.e. i) no or little preparation, ii) high-resolution and three-dimensional surface information and iii) the microscope can be used in environments inaccessible with other techniques.

In addition to extracting 3D topographic information (Fig. 4), AFM can be used in phase mode to distinguish different components in a coating structure, such as pigment particles and latex [16]. The AFM is thus a suitable method for assessing the structure of calendered coated paper (Fig. 4). Rougher surfaces have to be analysed with care due to limitations in the movement in the z-direction (height). Local areas of fibre surfaces may also be assessed thus giving a detailed description of pulp fibres, including the different layers of the fibre walls with their characteristic arrangements of microfibrils [16].

Using AFM, the structures of coating surfaces have been studied in detail [37]-[39]. In addition, AFM has also been suggested for assessing the coating layer cross-sectional structure including the pore structure and binder distribution [40],[41]. Using the versatility of AFMs, adhesion mapping for discriminating pigments from the binder material in coating layers has been proposed [41]. The proposed method may be an alternative to SEM cross-sectional analysis of osmium tetroxide (OsO4) stained samples [42]. OsO4 reacts with C=C double bonds, which are present in latex used to bind pigment particles in coating structures (Fig. 2b) [35]. However, in AFM cross-sectional analysis of coating layers, the preparation and image acquisition steps seem to be time-consuming and demanding.

2.4 Field-emission SEM

Several studies have demonstrated the potential of modern microscopy techniques such as the field-emission SEM (FESEM). FESEM offers high-resolution, which makes it possible to visualize and explore structures unattainable with conventional microscopy techniques. FESEM combined with modern methods for preparation of cross-sections have been most suitable for the understanding of coating layer composition and structural distribution [43],[44]. Dahlström et al. [44] applied OsO4 to stain the latex binders in mineral coating layers on paper (see Fig. 2). Argon ion milling was introduced as a preparation method for acquiring high-resolution FESEM images, which were most suitable for image analysis. Based on this modern microscopy technique the authors provided clear evidence about the binder distribution in coating structures. Contrary to relatively large pores, small pores in coating structures are filled by latex. Poor homogeneity of latex distribution has been suggested as a factor affecting print quality defects. It is thus important to have adequate methods for assessing latex distribution in order to understand the causes of print quality defects. Applying a similar method Ström et al. [43] performed a detailed characterisation of coating layers. The high-resolution of FESEM equipped with an in-lens detector provided a good differentiation of the latex from the pores. This is most valuable as staining with OsO4 was avoided. The sizes of pores in the assessed coating layers were reported to be roughly between 0.4 and 1 μm [43]. It is worth to mention that such pore sizes are usually underestimated by mercury porosimetry [45]-[47], which is also an indirect method for assessing the pore structure in coated paper. This is due to the irregular shape of pores in coating layers (Fig. 2b). Mercury porosimetry measures the void entry radii while microscopy and image analysis assess the void themselves.

Recently, FESEM has also become a powerful technique for assessing paper structures containing cellulose nanofibrils [48]. Cellulose nanofibrils have been proposed as a most valuable nano-component in potential
upgraded paper qualities with improved mechanical properties and higher loading of fillers [49],[50]. A larger fraction of fillers (e.g. GCC) improves the optical properties and also increases the dewatering ability of a given furnish. Higher dewatering during paper forming and pressing implies a higher dry content after pressing and thus lower energy consumption for drying [50], which is obviously a major economical and environmental benefit in a paper production process. Nanoﬁbrils in e.g. newsprints with relatively high ﬁller content, bind the ﬁller material in a 3D network in the paper ([50], Fig. 5). Such surface structural reinforcement may contribute to reducing linting. Linting is a major print quality challenge in coldset printing, which is used for printing newspapers.

Worth to mention, cellulose nanoﬁbrils have proven to be a most promising material for several applications within for example packaging, composite materials, potential medical applications, emulsions, to name a few [51]-[54]. Cellulose nanoﬁbrils can also be the main components in novel paper concepts, i.e. nanopaper with superior strength, oxygen barrier, transparent and smooth. Importantly, such materials could be optimal substrates for printing functional structures, which could be used in various high-tech applications.

### 3. Assessing print defects in magazine paper

A clear example of the suitability of the described techniques is the assessment of missing dots in gravure printing. Gravure printing offers significant advantages relative to other printing processes for medium and long runs, producing high quality printing. In SC paper, which is used in glossy magazines, gloss, missing dots and whiskering are critical parameters that may determine the quality of a given gravure-printed paper. In addition to surface roughness and compressibility, missing dots can be caused by surface details like coarse ﬁbres, ﬁller material and the corresponding topography, formed by the surface components [55]-[59]. This means that surface valleys may reduce the contact between the paper surface and the printing gravure cylinder. Poor contact reduces the ink transfer and thus is a major cause of missing dots (Fig. 6 and Fig. 7). Such mechanism can be revealed by the complementary capabilities of various microscopy methods, such as optical scanners, light microscopy, laser profiometry and SEM (Fig. 6 and Fig. 7).

The number of missing dots can be simply and effectively quantiﬁed based on scanner images (Fig. 6a). As an example, the local characteristics of the surface structure causing missing dots can be revealed by a combination of LP, light microscopy and SEM. LP revealed in this case local surface depressions deeper than 2 μm, which seem to have caused the occurrence of missing dots (Fig. 6b). Martorana et al. [59] reported results with respect to the size of the surface cavities affecting the missing dots occurrence, on gravure printed samples. Cavities having a depth of 2-5 μm and diameter of 50-250 μm caused missing dots [59]. In addition to deep surface valleys, the fraction of ﬁller (Fig. 7b), have been reported to affect the missing dots occurrence [57]. It is worth to mention that in addition to microscopy methods for assessing the surface structure and composition, potential methods for quantification of surface topography details under pressure may be most valuable for estimating ink transfer during printing.

![Assessment of missing dots after gravure printing of a magazine paper](image-url)

**Fig. 6.** Assessment of missing dots after gravure printing of a magazine paper. a) A large area exemplifying an unprinted area with occurrence of missing dots (dashed rectangle). b) the local area assessed by LP. Note the surface depressions, which limit the contact between the paper surface and the printing cylinder, thus causing missing dots.
In addition to the surface structure, the print quality of gravure-printed paper may be influenced by the paper’s electrical characteristics. In gravure printing, electrostatic assist (ESA) can be applied to increase the contact between the ink in the engraved cells in a hard printing cylinder and the relatively rough paper surface. ESA applies a charge to the impression roller, which causes an attraction of the ink from the gravure cylinder to the paper substrate [60]. Since its invention ESA has significantly improved the print quality of gravure printing. However, depending on the paper substrate, its composition and the humidity in the pressroom, ESA can cause a build-up of charge on the web, which in turn may cause a print defect denominated whiskering (Fig. 8).

Whiskering appears as hairlike structures expanding into non-image areas [61]. The degree of whiskering can be effectively assessed by using relatively simple, yet powerful image acquisition and analysis techniques. The image in Fig. 8 has been acquired with a desktop scanner in reflection mode (Fig. 8a). Automatic thresholding segments the printed area from the background. Applying a rolling circle with a suitable radius to the printed area segments the whiskering structures locally (Fig. 8b). The whiskering lengths can thus be quantified for each single structure (Fig. 8c). Such assessment yields effective and adequate information for following up the development of a given paper quality as a function of varying paper production parameters, which is most valuable.

4. Conclusion

This chapter has considered the characterisation of printing paper surfaces by complementary surface assessment methods, scanners, optical microscopy, laser profilometry, scanning electron microscopy and atomic force microscopy. A description of some practical applications has been given. The methods are suitable for assessing specific characteristics of paper surfaces and to some extent their interactions with printing inks. The structural assessment comprises scales from the millimetre (scanners) to the micrometre (LP, SEM) and to
the nanometre-levels (AFM, FESEM). The necessity of applying complementary surface assessment methods for giving a comprehensive description of a given structure has been emphasized. Proper information of paper structural details, in combination with additional chemical analyses, are necessary to understand relevant structures, their development upon finishing variables during the paper making process and their interactions with inks during printing. Such information is essential to improve paper quality and the corresponding printing performance. Finally, all the knowledge gained during the last decades about paper manufacturing, finishing and characterisation, will be essential to move paper forward as an effective information medium. New approaches to design paper structures suitable for advanced printing techniques such as inkjet printing will be most valuable for the next step of paper development, i.e. electronic paper. Probably not on conventional printing paper as we know it today, but printing electronics on novel cellulose-based substrates will most probably widen the possibilities of this wonderful biodegradable material and open for novel and advanced applications.

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References


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