Synchrotron X-ray Microtomography: A New Tool to Characterize the Interaction Between Paper and Toner[1]

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Abstract. *The interaction between paper and toner depends on paper properties (roughness, paper surface, and tension) and toner properties (granulometry and chemical composition). Deepening the knowledge on fixation and adhesion of toner onto the paper substrate is crucial to improve the end-use properties of paper dedicated to electrophotographic printing. The aim of this article is to introduce and describe a new tool to visualize and analyze this interaction. Three-dimensional (3D) imaging is a key tool used to investigate such a phenomenon. For this reason, synchrotron x-ray microtomography (SXRM) was applied to characterize the toner-paper interaction in a noninvasive and nondestructive manner. To validate the feasibility of such means in a 3D context, the obtained data are compared to those obtained by traditional two-dimensional (2D) imaging systems such as optical profilometry and environmental scanning electron microscopy. SXRM emerges as a crucial tool to get a detailed characterization of the ink layer and of the ink-paper interaction. This is a powerful technique to complete studies carried out by classical means.* © 2008 Society for Imaging Science and Technology.
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INTRODUCTION

Electrophotographic printing technology has became increasingly widespread since the early 1980's. Today, this technique competes with conventional printing methods in

terms of quality and price. In order to reach the increasing demands on quality, electrophotographic paper properties need to be constantly improved. One of the steps in laser printing is to create a toner layer on the paper surface. During the process, solid toner particles are heated and pressed onto the paper substrate. The thickness of this toner layer can typically reach 20 μm. The toner/paper adhesion process involves many parameters[1] such as the paper structure, surface roughness[5] and surface energy,[2] the toner rheological properties,[3] and the temperature field reached in the nip of the printer.[4] In such a context, this article investigates a new tool to characterize the paper/toner interaction. Paper samples dedicated to electrophotography were printed with varying black halftone coverage according to a given chart. The samples were imaged by three different techniques. The surfaces of the printed samples were characterized by an optical profilometer that provides information on the topography of the surface.

Classically, paper structure is imaged by an environmental scanning electron microscope (ESEM). This method gives access to the paper thickness and allows a partial characterization of the structure. During the last decade, paper structure has been imaged using synchrotron x-ray microtomography (SXRM).[7] This technique provides relevant information on the three-dimensional (3D) structure of the samples in a noninvasive and nondestructive way.[6] It is advantageous to combine this information with that obtained by the two previous techniques. What information

Table I. Properties of the two studied papers before the printing process.

	Grammage (g/m^2)	Thickness (μm)	Bendtsen roughness (ml/min)
Paper Q+	103	116	67.2
Paper Q−	82	103	137

can this technique provide for the case of an ink/paper interaction study? This article is therefore organized as follows. First, the samples and the characterization techniques are described. Then the results obtained by SXRM are compared to those obtained by optical profilometry and by ESEM to validate the feasibility of the study. The last part presents the benefits of using SXRM to investigate the ink/paper interaction. Conclusions and perspectives will end this article.

MATERIALS AND METHOD
Samples
We chose two common electrophotographic papers: Q+ and Q−. Q+ is assumed to be of better quality than Q−. One may recall that paper is a complex network of pores, fibers, and fillers. Fillers are mineral constituents that are added to the cellulosic network to improve, for example, optical properties. The main properties of the two papers studied (basis weight, thickness, and Bendtsen roughness) are reported in Table I.

Papers Q+ and Q− were printed with different halftoning according to a chart. The printer used is a Gestetner 3532 (Ricoh). In this article, attention is focused on four halftone coverages: 100%, 56%, 17%, and 0%. The samples are referred to Q+ or Q− completed by the corresponding halftoning coverage. For example, Q+_56% is the high quality paper printed with a 56% of coverage. These eight samples were analyzed using the three following methods: optical profilometry, ESEM, and SXRM.

Characterization Techniques
In our research, paper and printed paper surfaces were characterized by optical profilometry (Altisurf® apparatus). This system consists of a white light source, lens, spectrophotometer, and signal processing system, coupled with a motorized stage and appropriate image analysis software (Altimap® expert). The analyzed surface was a 2 mm × 2 mm square, with a measurement spacing of 1 μm. The vertical resolution is below 0.01 μm.

It is not possible to extract relevant information from the raw images. Consequently, data treatments must be applied first. The following protocol was applied for the entire set of samples considered in this study. We applied a central rectification, which ensures the flatness of the surface. To maximize the contrast, a threshold operation is performed. This technique allows getting relevant information on surface properties such as roughness. The root mean square roughness parameter, Sq, is deduced from the altitude mapping. This standard parameter is classically used as a quality indicator. Let us recall that a small value of Sq is characteristic of a smooth surface whereas a high one refers to a rougher surface topology.

For scanning electron microscopy investigation, an ESEM quanta 200 (FEI) was used. It is equipped with a backscattered and secondary electron detector. The vacuum in the chamber reaches 2660 Pa. The image resolution is 3584 × 3094 pixels, coded in 16 bits. This device has the advantage of very high resolution making it possible to distinguish features with a size of 200 nm. Cross sections of the samples were prepared in order to visualize the toner layer conformation on the paper. Samples were sliced using a razor blade and put on a stage with an adhesive. The optical contrast between the different phases is sufficient for a correct selection.

The third technique is SXRM. All the data presented in this work were acquired at the European Synchrotron Radiation Facility in Grenoble, France. The main goal of this imaging tool is to obtain a thorough description of the inner structure of the studied samples,[6] in a noninvasive and "nondestructive" manner. SXRM has already been successfully applied to paper.[7,8] According to the main paper constituents a pixel size of 0.7 μm was chosen, leading to an imaged volume of (1.4 mm × 1.4 mm × paper_thickness). During data acquisition, a parallel and monochromatic beam irradiates the sample. The transmitted beam forms radiographs, which are recorded for different angular positions. A filtered back-projection algorithm is applied to the radiographs to reconstruct the 3D structures.[6] When performing SRXM, the data obtained represent a 3D map of the coefficient of absorption of the sample's constituents. The values of the absorption coefficient are represented as gray level. The gray levels on these pictures are therefore indicative of the paper constituents. In the case of paper samples, dark gray refers to the pores, the gray to the fibers, and the brighter part to the fillers. This technique is sensitive to the sample preparation; the samples often appear to be tilted. Therefore the volumes extracted to obtain the 3D views will never appear as perfectly flat.

FEASIBILITY OF SYNCHROTRON X-RAY MICROTOMOGRAPHY FOR THE STUDY OF THE INTERACTION BETWEEN PAPER AND TONER, AS A COMPLEMENTARY TECHNIQUE
To our knowledge, SXRM has not yet been applied to characterize the 3D structure of the toner layer and its interaction with the paper. However, this technique was used to characterize in detail the coating layers by Turpeinen.[9] In this section, images obtained with SXRM are shown. In order to facilitate the understanding of the data, marks are added to the figures to point out the most relevant parts. Furthermore, these images are compared to the two other imaging techniques.

Surface Characterization
Examples of 3D views obtained with SXRM are presented in Figure 1 for the high quality paper (Q+). Similar results are obtained in the case of the low quality paper Q−. In the particular case of the black ink used, the coefficients of absorption of the fibers and of the ink are so close that we cannot distinguish these two phases using the gray levels.

(a)

(b)

(c)
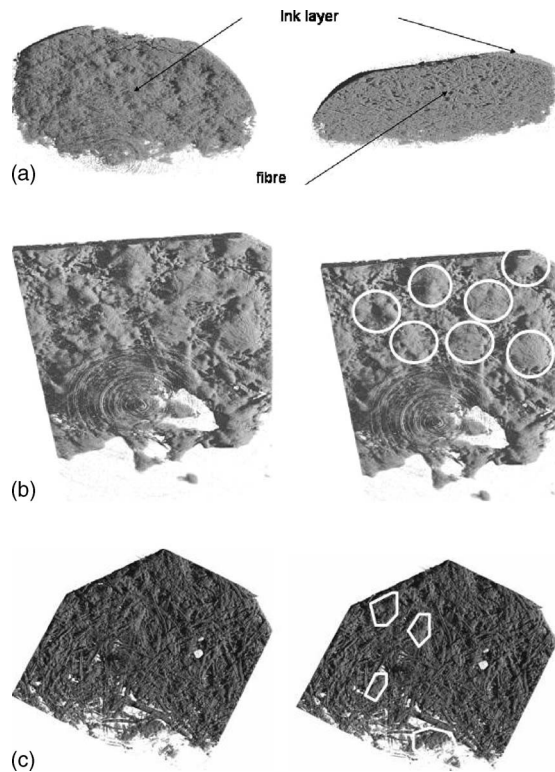
Figure 1. 3D view (about 1 mm×0.7 mm×35 μm) of the high quality printed papers obtained by SXRM. The two pictures in (a) correspond to the Q+100% sample. These two pictures are the same volume seen from two opposite points of views. On the left image, the ink layer can be observed whereas on the right one the paper structure can be analyzed. The two pictures in (b) correspond to Q+56% and the bottom one to Q+17%. For the two last samples, the two same pictures are presented. The left one is the original one and circles are added around the toner dots to more easily observe them on the right one.

Marks are therefore added to the SXRM data to give an indication on the ink layer boundary, on the fiber phase and on the pores localizations. The ink layer was visually defined using texture information. On these 3D views, the halftoning screens can be observed: dots are present on the paper sur-

faces. [Fig. 1(b)]. Moreover, we can also note that the surface appears rougher in the case of the 56% of coverage than in the case of 100% of coverage.

Figure 2 shows a cross section extracted from the 3D SXRM volume. We can observe the fibers, fillers, and pores. They are extracted from paper Q− covered with different halftoning levels. We can also notice a homogeneous layer, which represents the ink.

These cross sections permit the investigation of the surface roughness. For the solid print the ink layer interface with the air is smooth and continuous; the toner layer's thickness seems to be even along the sample. As expected, the layer is smaller and part of the paper is toner free as the coverage decreases. The surface seems rougher for 56% and 17% of halftoning. Finally, we can notice that the virgin paper surface appears almost as smooth as the one with solid print.

These observations made on SXRM images are qualitatively consistent with the Sq evaluation obtained by the optical profilometry. The obtained results are reported in Table II for the samples studied.

In this table, results confirm the expectations: the paper Q+ has a lower Sq value than Q−, which is coherent with the fact that paper smoothness influences printing quality. But for both paper qualities, the Sq value in case of solid prints is higher than the Sq value for a non-printed paper value. This indicates that the paper surface directly influences the final solid toner topology. Moreover, the comparison between surface measurements made with profilometry and observations made by microtomography shows the same visual appearance for the toner layer surface. We may therefore infer that SXRM is suitable to study qualitatively the toner layer shapes and should be considered in future quantitative measurements.

Surface Properties/Bulk Properties

The next step is to relate these surface properties to the bulk properties. Therefore, imaging the structure is a crucial

(a)

(b)

(c)

(d)
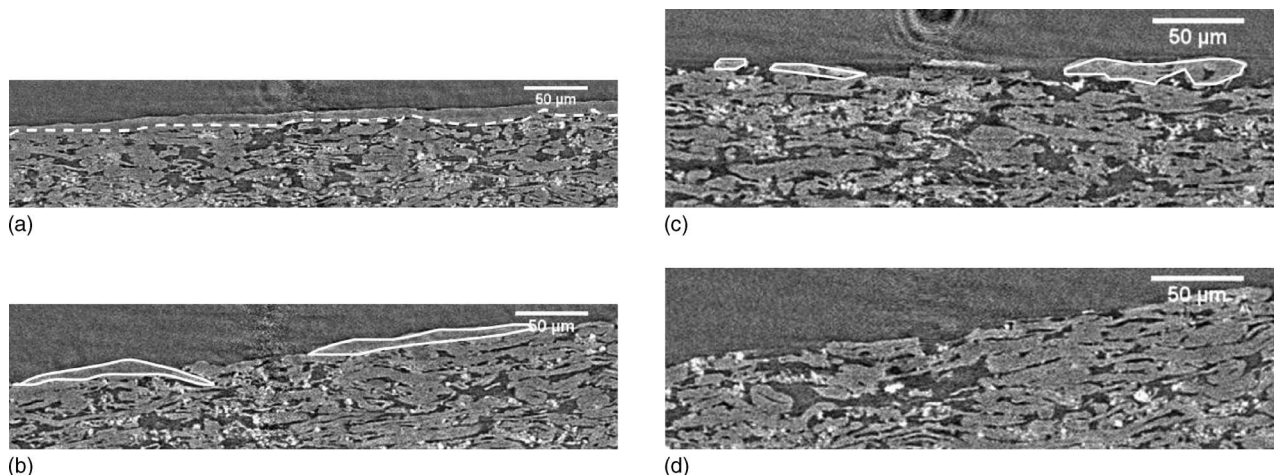
Figure 2. Cross section in the thickness direction of the paper Q− extracted from the synchrotron x-ray microtomographies for the four studied halftone coverages 100%, 56%, 10%, and 0%. The ink parts are isolated from the paper.

**Table II.** Values of the surface parameter Sq for the 10 different samples. Q+ and Q− refer to the virgin paper.

Sample	Sq (μm)
Q+ _0%	3.02
Q+ _17%	3.36
Q+ _56%	3.99
Q+ _100%	3.42
Q+	2.99
Q− _0%	5.37
Q− _17%	6.04
Q− _56%	5.61
Q− _100%	5.83
Q−	5.12

point and was first performed by ESEM. The obtained results are presented in Figure 3. We can observe the fillers, pores, fibers, and ink. Nevertheless, there are few precautions to be taken while analyzing samples obtained with this method. This is a destructive analysis in the sense that cutting the sample with the blade could damage the structure of the paper.

For example, particles of the upper layers could contaminate the lower layer, as illustrated by the arrows in Fig. 3(a). The visual perspective problem must also be considered. During the measurement, the sample is just set on an adhesive: there is no way to control precisely its angle compared to the horizontal axis. On Fig. 3(b), measuring the thickness of the toner layer may be difficult considering the separation of the thickness contribution to the surface contribution. We thus need to apply a nondestructive technique to overcome these drawbacks. That is why SXRM was used and the obtained results are presented Figure 4. For a better comparison, the same sizes of images are shown for ESEM and SXRM.

ESEM and SXRM data exhibit differences. For example, ESEM data show ink contamination for one of the two samples, which might be understood as a penetration of the ink into the paper. However, the ink part on the SXRM images is easily distinguishable and does not penetrate into the fiber substrates. It is well known that the penetration into the paper during the electrophographic process is negligible.[10] Furthermore, the porosity and the pore size distribution also seem to depend on the imaging techniques and the sample preparation. Samples imaged by SXRM present higher porosity than the samples imaged with ESEM. This visual comparison demonstrates the value of a nondestructive method to analyze the ink/paper interaction.

To summarize this section, on one hand the observations made on microtomograms are consistent with the results obtained by optical profilometry and on the other hand with the observations and models found in the literature. The volumes imaged by SXRM are small (about 1.4 mm × 1.4 mm × paper thickness) compared to the ones used in
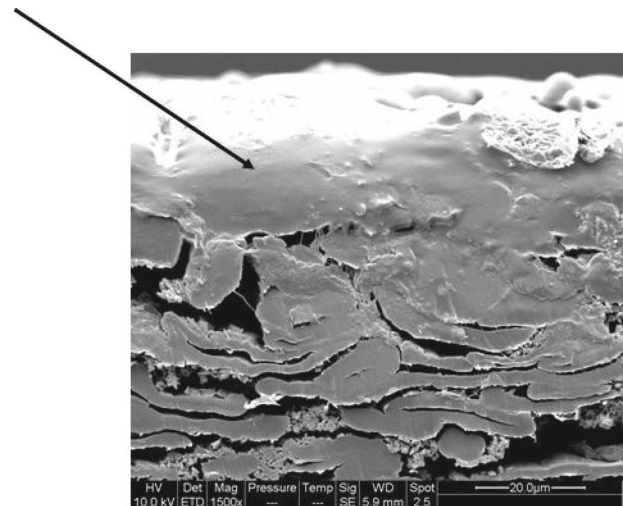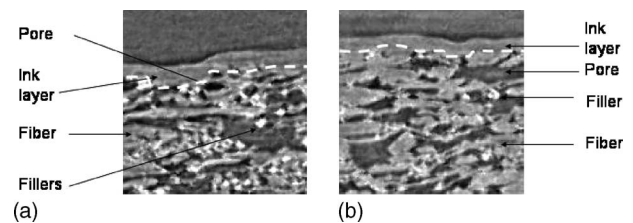

(a)
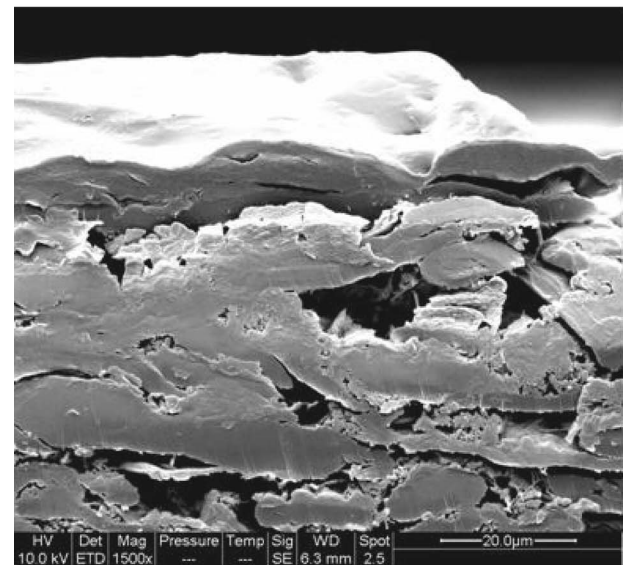
(b)

Figure 3. Cross sections obtained from ESEM acquisitions of the two paper qualities printed with 100% coverage. The arrow presented in picture (a) illustrates the contamination problem.

(a)   (b)

Figure 4. Tomography cross section (90 μm × 90 μm) of two printed samples. These samples are the same as the ones presented in Fig. 3.

most of the standards. However, it was demonstrated that such a volume was sufficient for a microstructural characterization.[11] We can therefore conclude that SXRM is suitable to study the interaction between papers and toner layers.
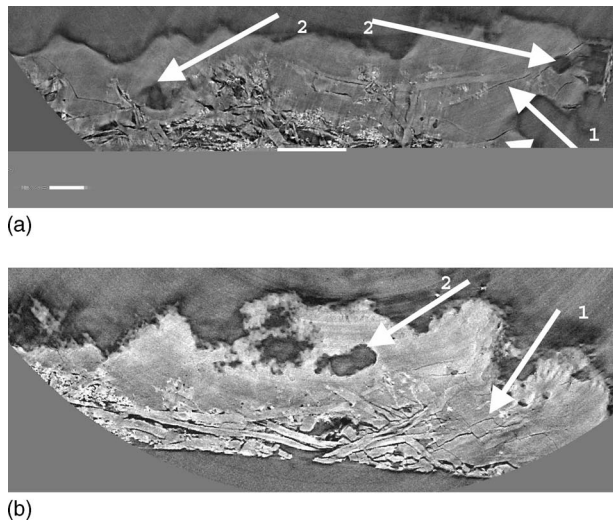
Figure 5. Cross sections of the ink layer extracted from the SXRM data (a) represents the low quality paper and (b) the high quality one. Both samples were printed with 100% coverage. On these pictures arrows are added to indicate the most interesting features: cracks are labeled with "1", pores in the ink layer with "2."

CONTRIBUTION OF THE SYNCHROTRON X-RAY MICROTOMOGRAPHY TECHNIQUE TO ANALYZE THE INTERACTION BETWEEN THE PAPER AND THE TONER

Figure 5 illustrates the following observations.

Ink-Paper Interaction

Let us first consider the interaction between the paper and the toner layer. A careful visual inspection of the slices in different directions of the 3D volume shows the presence of cracks. Cracks have never been observed using classical tools (e.g., the images from the ESEM presented Fig. 3) or with indirect measurement such as Raman spectroscopy.[12] These cracks are due to an incomplete interaction between fibers and the toner at the observation scale. However, we can observe a complete interaction between fillers and toner.

Toner Layer

Let us now focus our attention on the ink layer. One may recall that the information obtained about the structure is the absorption coefficient of the elements present when dealing with microtomography in absorption mode. Therefore, relevant information on the ink layer may be deduced. The ink layers have always been considered as homogeneous and continuous.[12] Nevertheless, we can notice some variations in the gray level within the toner layer, which are characteristic of a nonhomogeneous structure, and which might be related to the surface properties of papers. Moreover, even in the toner layer, we can notice the presence of small pores in the toner layer, regardless of the paper quality. We have considered whether these pores were created during the scan owing to modification of environmental conditions. As paper is a hygroscopic material, its structure can be dried by the beam during the scan. These structural modifications induce artifacts, such as two objects that seem to overlap or edges that are only partially defined. We can observe that the borders of the pores located in the ink layer are sharp: the pores are closed and no blur appears along the edges. We may therefore consider that no swelling occurred during data acquisition that could have modified the paper structure.[13] We may conclude that these pores were present in the ink layer prior to data acquisition.

The visual inspection of the 3D structure brings to light two types of porosity: the effective porosity, which refers to the fraction of the total volume in which fluid flow may effectively take place, and the nonconnected cavities (also called closed porosity). It seems that there is a gradient of the effective porosity whose maximum is located close to the border of the ink layer. Different hypotheses may explain the location of the maximum of the porosity gradient close to the toner/air interface. A delamination of the upper part of the layer due to the action of the roller in the nip could lead to structural alteration. On the other hand, the roughness of the hot roller itself could also be responsible for this effective porosity.

The pores belonging to the region of so-called closed porosity are smaller than the ones close to the interface. During the formation of the toner film, part of the air is captured in the structure due to the porosity of the toner accumulation.[12] This phenomenon does not seem to depend on the paper quality. Indeed, both Q− and Q+ papers reveal air cavities in their ink layer, whatever the surface coverage may be. Nevertheless, the values of these two types of porosity are low. We can estimate it to be around 5% of the ink volume.

CONCLUSIONS

This study was focused on the characterization of the interaction between the paper and the toner of the ink layer. Investigations with conventional imaging methods such as optical profilometry and ESEM show the influence of the substrate on most of the printing characteristics. The results were compared to ones obtained by SXRM to validate the feasibility of the study. The benefit of the SXRM as a complementary technique to study the relation between the paper substrate and the toner layer property was shown. The 3D structure of the toner layer and its interaction with paper was thoroughly described. The following observations can be made regardless of paper quality and level of coverage. (1) The interaction between fibers and ink is not total, whereas it appears that it is between fillers and ink. (2) It also appears that this toner layer presents two types of porosity: an open and a closed one.

The next step would be to obtain quantitative parameters on the ink layer characteristics. Therefore a segmentation method must be developed to separate the toner layer from the paper constituents. In such a case, quantitative measurements can be carried out on the two types of porosities found. This will allow characterizing the induced defects (particle migration) and also the barrier properties of the ink layer in food packaging. Moreover it seems realistic that in the near future,[14] electronic device printing may be

achieved by means of electrophotography. In this case, homogeneity of the layer would be the key parameter to control the quality of the printed electronic devices.

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