SERIAL SECTIONING OF COATED PAPER AS A NOVEL METHOD TO ANALYZE BINDER PENETRATION

PLASTNI RAZREZ VZORCEV PREMAZANEGA PAPIRJA KOT NOVA METODA ZA ANALIZO PENETRACIJE VEZIV

K. HOFER[1], A. ORTNER[2], G. S. NYANHONGO[2], H. WINTER[3], G. GÜßITZ[2], W. BAUER[1]

ABSTRACT

To understand and optimize mechanical and printing properties like e.g. picking resistance, information regarding the distribution of the coating binder and the penetration of the binder into the base paper is important. Especially water-soluble binders tend to follow the water phase into the base paper via drainage. Since these binders are used for pre-coatings these penetration phenomena play an important role. This work focuses on monitoring binder penetration of water-soluble coating binders into the base paper using serial sectioning combined with fluorescence microscopy (SSFM). This method allows a three-dimensional data analysis in an appropriate region of interest. Coating colors varying in their Abo Akademi Gravimetric Water Retention Value (AA-GWR value) were prepared to investigate differences in binder penetration depth into the base paper.

Key words: coated paper, binder penetration, serial sectioning, fluorescence microscopy

IZVLEČEK

Informacija o porazdelitvi veziva premaza in o penetraciji veziva v osnovni papir je pomembna za razumevanje mehanskih in tiskarskih lastnosti, kot je npr. površinska trdnost. Posebno vodotopna veziva sledijo vodni fazi v osnovni papir preko odvodnjavanja. Ker se ta veziva uporabljajo za predpremaze, igra penetracija pomembno vlogo. To delo je osredotočeno na spremljanje penetracije veziva vodotopne premazne mase v osnovni papir z metodo serijskega razreza v kombinaciji s fluorescenčno mikroskopijo (SSFM). Metoda omogoča tridimenzionalno analizo podatkov v izbranem območju. Premazne mase z različnimi AA-GWR vrednostmi (gravimetrična vrednost zadrževanja vode Åbo Akademi) so bile pripravljene, da bi raziskali kako globoko penetrira vezivo v osnovni papir.

Ključne besede: premazan papir, penetracija veziva, serijski razrez, fluorescenčna mikroskopija

1 INTRODUCTION

Binder migration/penetration and the distribution of binder within a coating layer play an important role regarding optical, mechanical and printing properties [1, 2]. Whalen-Shaw [3] defines binder penetration as the movement of binder towards base paper driven by drainage and binder migration as the movement of binder towards coating layer surface by evaporation. In this work the focus is on binder penetration.

Several methods to analyze binder penetration/migration and binder distribution are presented in the literature. These methods can be separated into two groups including two-dimensional measurements at the coating layer surface (binder migration) and three-dimensional measurements (binder penetration and binder distribution within the coating layer):

- Two-dimensional observation of the coating layer surface has been assessed via Raman Spectroscopy [4], Raman Microscopy [5], X-ray photoelectron spectroscopy (XPS) also known as electron spectroscopy for chemical analysis (ESCA) [1], Time-of-flight-secondary ion mass spectrometry (ToF-SIMS) and field-emission-scanning electron microscopy (FE-SEM) [6], and Atomic Force Microscopy (AFM) [7].
- Three-dimensional observation of the coating binder penetration and its distribution has been assessed via Confocal Raman Microscopy (CRS) [5, 8], argon ion beam milling in combination with FE-SEM [9], cross-section analysis with AFM [10] and Confocal Laser Scanning Microscopy (CLSM) [11, 12, 13].

To observe three-dimensional features of coating layers, our method combines serial sectioning with fluorescence microscopy. Wiltsche et al [14] developed an analysis routine for coating layer properties and fiber properties via serial sectioning in combination with light microscopy. To detect specific components of a coating color like binders, a second generation prototype (Figure 1) was developed and equipped with a fluorescent light source additionally to the visual light source [15]. It performs fully automated serial sectioning and microscopy of coated paper samples. Sample sizes of 6 mm in CD (cross direction), 2000 mm in MD (machine direction) and 2 mm in ZD (z-direction) at resolution down to (0.47 x 0.47 x 1) μm^3 can be analyzed.

Looking at the three-dimensional observation methods, advantages and disadvantages of our method (SSFM) need to be pointed out. Compared to CRS-analysis [5, 8], the possibility to observe images of each single cut is one big advantage of the presented method. However, no chemical information can be determined by SSFM. The selectivity regarding the detection of different binders is defined by the staining process. The area of interest in z-direction is limited to 10-30µm with CRS [8] compared to 2mm with our method. Also AFM [10] and FE-SEM [9] show smaller region of interest but higher resolution.

Starch can also be detected after the staining process with SSFM, compared to CRS. The similarity of CRS signal of cellulose and starch prohibits a distinction of those two components [8]. Compared to CLSM methods, SSFM is a destructive method and CLSM sample preparation is easier because of the fact that no embedding is necessary. However, SSFM is not limited in information in z-direction as CLSM regarding light penetration depth [12].

The aim of this work was the establishment of an analytical method to determine the binder penetration of coating colors into

Table 1: The three different coating colors, their AA-GWR value, coating composition and solid content
Preglednica 1: Tri različne premazne mešanice, njihove AA-GWR vrednosti, sestava premaza in vsebnost suhe snovi

Coating color with	AA-GWR value [g/m²]	Calcium Carbonate [%]	Binder [%]	Target Solid Content [%]
Binder A	95	100	10	70
Binder B	400	100	10	60
Binder C	970	100	10	60

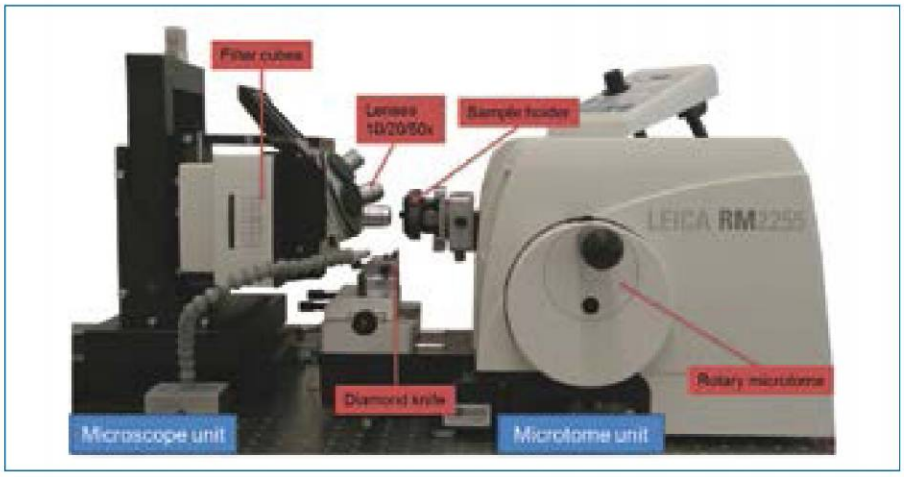

Figure 1: Second generation prototype (serial sectioning in combination with fluorescence microscopy, SSFM)
Slika 1: Prototip druge generacije (serijski razrez v kombinaciji s fluorescenčno mikroskopijo)

the base paper. Watanabe and Lepoutre [16] divide the consolidation of the coating layer during application and drying into three phases separated by the FCC (first critical concentration) and the SCC (second critical concentration). The first phase before reaching the FCC is interesting regarding the penetration of binder. Due to that fact we prepared three different coating colors varying in their AA-GWR value (Abo Akademi Gravimetric Water Retention Value) and determined the penetration depth of the binder into the base paper.

2 MATERIALS AND METHODS

2.1 Coating Color Preparation and Coating Process

Coating colors with calcium carbonate, binder, water (to set the target solid content) and sodium hydroxide (to set the pH of 9) were prepared (see Table 1). The aim was to create coating colors with three totally different AA-GWR values due to the fact that the ability of a coating color to retain the water during the coating process plays an important role with respect to binder penetration. In Table 1 the AA-GWR values and the solid contents are shown. The coating process was performed with a manual rod coater. As base paper, laboratory hand sheets with a grammage of 80 g/m² made out of short fiber sulfate pulp with a low Kappa number (free of fluorescence) were used.

2.2 Sample Preparation

Paper samples are cut into pieces of 8 mm x 25 mm and infiltrated with TechnoVit 7100 (cold curing embedding resin based on hydroxyethylmethacrylate). This solution has been stained with Sudan Black (Roth) (0,3 mass %) and stirred for 45 minutes. Staining is necessary to minimize out of focus light effects. Samples are infiltrated in a vacuum exsiccator, and a vacuum pump is switched on and off for 4 hours in intervals of 15 minutes. Infiltrated paper samples are embedded in gelatin capsules. Hardening time was 12 hours. Samples were then polished.

2.3 Microtomy, Image Creation and Analysis

Embedded samples were precut with a glass knife and then cut with a 4mm diamond knife (Diatome). The slice thickness was set to 4 µm and 300 cuts were performed. 100 automatically stitched and aligned images with a distance of 12 µm were created. The dimension of the images was 0,5 mm in ZD and 5,4 mm in CD. For fluorescence microscopy a GFP-filter was used. Images were transformed to binary images using ImageJ and penetration depth into the base paper was calculated (adapted method described by Wiltsche et al [14]). Furthermore the coating layer thickness was measured via image analysis with the method described in Wiltsche et al [14].

3 RESULTS AND DISCUSSION

The output of SSFM are images of the coated paper cross-sections and specific components can be detected. Figure 2 shows the visual light image (BF) and the UV light image (GFP) of the paper cross-sections of the three different coating colors.

The coating layer can be seen on the left side of the BF images in Figure 2. To visualize the binder penetration depth into the base paper the contour of the coating layer of the BF image was superimposed to the GFP image (white line). The green colored areas in the GFP images indicate the location of the binder after the coating and drying process. Figure 2 shows that Binder A has the lowest and Binder C the highest penetration depth into the base paper. Due to the fact that a lower water retention value leads to less binder penetrating into the base paper, the water retention value (see Table 1) correlates well with the analyzed microtome images. The coating color with Binder A has a higher solid content. As Watanabe and Lepoutre [16] pointed out, the FCC and thus the initial solid content has an influence on binder penetration.In case of Binders B and C there is a depletion of binder in the coating layer.

In the literature there is a contradiction regarding the amount of water-soluble binder (starch) in the surface near layers of the dry coating layer. Dappen [17] investigated the distribution of starch within the coating layer during drying and in dry coatings. Results showed that there is starch transported to the surface layers of the coating layer via evaporation. Du et al [1] found out that there is a depletion of starch at the coating surface when applying a coating color with a mixture of starch and latex as binder. During coating consolidation the starch cannot be deposited at the

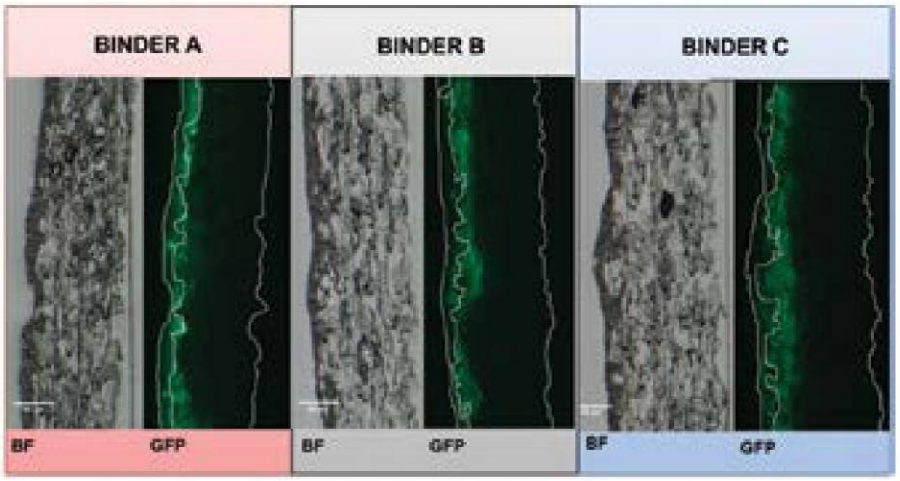

Figure 2: Cross-sections of coated papers (BF–VIS light microscope image, GFP–UV light microscope image) using binders with different AA-GWR
Slika 2: Prečni prerez premazanega papirja (mikroskopska slika: BF – s standardno svetlobno mikroskopijo, GFP – s fluorescenčno mikroskopijo) in uporabo veziv z različnimi AA-GWR vrednostmi

Table 2: Determination of coating layer thickness
Preglednica 2: Določitev debeline premaznega sloja

Coating color with	Coating layer thickness [µm]
Binder A	11,90
Binder B	15,56
Binder C	12,0

Table 3: 3D data analysis of binder penetration depth
Preglednica 3: 3D podatki analize globine penetracije veziva

Sample	Penetration depth into the base paper [µm]
Binder A	16,9
Binder B	21,0
Binder C	31,1

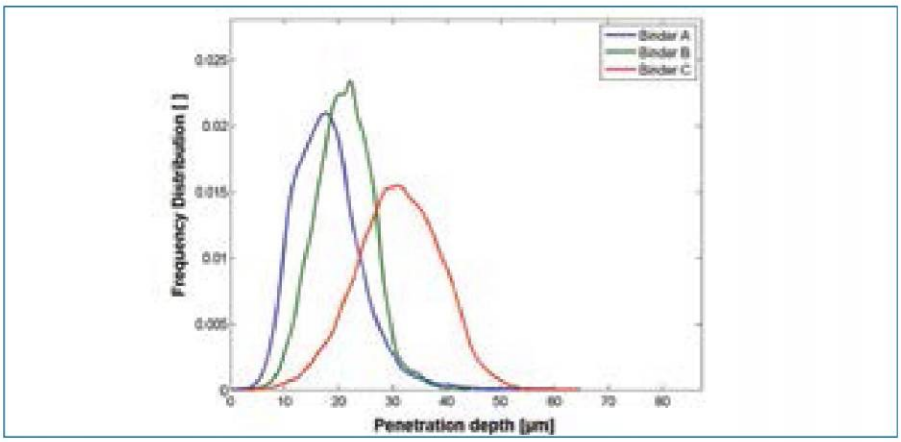

Figure 3: Distribution curves of binder penetration into the base paper
Slika 3: Porazdelitvene krivulje penetracije veziva v osnovni papir

coating surface, due to its water-solubility, but is enriched in the coating pores. Also Chattopadhyay et al [18] found out that there is no enrichment of starch at the top of the coating layer when applying a mixture of latex and starch in coating formulations.

The coating layer with Binder C is not fluorescent anymore because the binder completely penetrated into the base paper. This is an extreme case of binder penetration and this kind of binder cannot be used in conventional coating application.

To control the coat weight applied to the base paper, the coating layer thickness was determined. In Table 2 the results of the calculation of the coating layer thickness are shown. Coating layer thickness of coating color A and C are nearly the same and so they can be compared directly. Unfortunately, the coating layer thickness of the coating color B was a little bit higher. There were difficulties to control applied amount of coating with the manual rod coater.

In Table 3 the results of the 3D data analysis of an image stack (100 images) are presented. Binder A shows a penetration value of 16,9 µm compared to Binder C with 31,1 µm. The binder follows the water, which cannot be retained in the coating color, into the porous system of the base paper. The lower the water retention of the coating color, the deeper the binder penetrates into the base paper (see Binder C in Table 3).

Figure 3 shows the distribution curves of binder penetration into the base paper. Binder A and B show a narrow distribution and, in comparison, Binder C has a broad distribution.

4 CONCLUSION AND OUTLOOK

In conclusion serial sectioning of fluorescent coating layers (SSFM) is an appropriate method to obtain information about the binder penetration into the base paper. Cross-section images and 3D data analysis of an image stack can be correlated with water retention values of the coating colors. An important step regarding the establishment of this new binder penetration analysis method is the development of the staining process of each binder. So far, only water-soluble binders were analyzed. In the future, staining of latex, which is the most used conventional binder in coating, will be an important issue. Influences of coating application and drying method will also be investigated.

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[1]*Institute of Paper, Pulp and Fiber Technology, Graz University of Technology, Inffeldgasse 23, 8010 Graz, Austria*
[2]*University of Natural Resources and Life Sciences Vienna, Institute of Environmental Biotechnology, Konrad-Lorenz Str. 20, 3430 Tulln, Austria*
[3]*Sappi Paper Holding, BruckerStrasse 21, 8101 Gratkorn, Austria*

DI Karin Hofer, BSc
DI DI (FH) Andreas Ortner
Dr. Gibson S. Nyanhongo
DI Dr. Heribert Winter
Univ.-Prof. DI Dr. Georg Gübitz
Univ.-Prof. DI Dr. Wolfgang Bauer