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ToF-SIMS imaging: a valuable chemical microscopy technique for paper and paper coatings

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Abstract

The distribution of papermaking chemicals on the surface of various uncoated and coated papers was investigated by ToF-SIMS, FE-SEM, EDS, and XPS. Four paper samples, two office papers, one matte-coated and one traditionally coated paperboard were investigated with the aim of evaluation of chemical microscopy methods for examination of morphological and chemical heterogeneities on paper surfaces. Distribution of fillers, pigment particles, size, optical brightener, latex and other paper and coating components was assessed. Application of Au–Pd treatment on paper and coating surfaces prior to ToF-SIMS imaging increased the secondary ion counts for the region of low intensity peaks and improved the chemical mapping of papermaking and coating chemicals. ToF-SIMS imaging is shown to be a valuable and promising technique for chemical microscopy of paper surfaces.

Keywords: Pulp fibres; Coating; Latex; Sizing; FE-SEM; XPS; EDS; ToF-SIMS

1. Introduction

Paper and paper coatings are complex materials with remarkable heterogeneity in chemistry and morphology. Fibre surfaces are modified during papermaking, and interactions with fillers, starch, polyelectrolytes and other paper chemicals affect the paper performance [1]. Different treatments, either mechanical such as calendering or chemical such as coating, are applied to the paper surfaces to improve printability, optical properties, and strength. A multitude of surface phenomena are also involved during the preparation and application of coating color and printing [2–4]. Most of the surface interactions in papermaking and coating are not very well understood. As a consequence, many paper and coating formulations are designed through an empirical trial-and-error approach. Where are the additives attached to the fibres or fillers? How inhomogeneous is a coating layer? These questions are difficult to answer without application of analytical methods with proper molecular sensitivity and suitable spatial resolution.

Chemical microscopy methods ideally combine information about morphology and chemical composition. A great number of techniques can be used for this purpose [5], although techniques with the best

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spatial resolution usually give limited information about chemical composition, and vice versa. Among the techniques chosen in this investigation, field emission-scanning electron microscopy (FE-SEM) has a lateral resolution as high as 2 nm, but no chemical information is obtained. Energy dispersive X-ray spectrometry (EDS) is suitable for elemental analysis at a surface depth of 1 μm and distribution with a lateral resolution in the order of 1 μm. X-ray photoelectron spectroscopy (XPS) can give both elemental and oxidation state distributions with a lateral resolution as poor as 10 μm in addition to the surface depth of 5–10 nm. Time-of-flight-secondary ion mass spectrometry (ToF-SIMS) is the technique that is most close to the ideal of chemical microscopy, once that detailed chemical information in form a surface mass spectrum at depths lower than 1 nm can be obtained simultaneously with surface distribution of secondary ions at a lateral resolution of 200 nm. In spite of that, ToF-SIMS suffers from drawbacks, such as topographic and contamination effects which may lead to artifacts. The same problems can also disturb in XPS, but in a lower extent in EDS. XPS and ToF-SIMS also have problems regarding raster size, but that is not the case for FE-SEM and EDS.

Applications of SIMS imaging for paper and paper coating have been reported to study the distribution of surfactants [6], sizing [7–9] and de-sizing [10] agents, starch penetration [11], location of ink-components after printing [12], and binding of dyes in ink jet media [13]. Additionally, SIMS imaging was used for investigation of surface defects in papers [14,15]. XPS imaging was applied for distribution of sizing agent on paper [16], while SEM has been traditionally used for investigation of surface morphology of papers and coating layers [17–19]. In this investigation, we show the advantages of ToF-SIMS imaging over FE-SEM, EDS and XPS as a chemical microscopy method for paper and coated paper samples. A strategy to improve ToF-SIMS imaging is also presented.

2. Experimental

2.1. Paper samples

Two office paper samples (multipurpose, 75 g/m^2; standard office copying and printing, 80 g/m^2), one matte-coated (80 g/m^2) and one traditionally coated paperboard (180 g/m^2) were used in this study. The composition of uncoated and coated papers was intentionally unknown. Our strategy was to investigate the capability of different techniques in giving surface chemical information about paper samples in similar method used in paper industry for benchmarking and competitors analysis. Five sheets randomly chosen in a pad of 500 sheets purchased in a paper shop were taken for investigation. Sheets were wrapped in aluminium foil of ultra-high-vacuum grade. Test pieces were taken from different regions on the same sheet. At least three different sheets were analysed by each technique.

2.2. FE-SEM and EDS

Surface morphology was studied using a JEOL JSM-6335 FE-SEM microscope. Samples were previously coated with Au–Pd for 10 s using an AGAR scientific coater. The proximate coating thickness was 10–20 nm. The accelerating voltages were 5 kV and the microscope working distance was 16 mm. The EDS spectra and elemental distribution were obtained using an INCA energy microanalysis system coupled to the microscope. The accelerating voltage was 20 kV and the acquisition time 100 s. At least three different spots were analysed on each paper sheet.

2.3. XPS (ESCA)

The XPS spectra and images were recorded using a Physical Electronics Quantum 2000 ESCA instrument. The pass energies for low- and high-resolution spectral acquisition were 117.4 and 23.3 eV, respectively. The acquisition times were 10 and 20 min for low- and high-resolution XPS, respectively. The raster size was 500 μm × 400 μm. Images were taken using 187 eV pass energy and 30 min acquisition time. At least three spots were analysed on each paper sheet.

2.4. ToF-SIMS

Secondary ion spectra and images were recorded using a Physical Electronics ToF-SIMS TRIFT II spectrometer using a $^{69}Ga^+$ primary ion beam on a raster size of 200 μm × 200 μm. At least three different spots were analysed on each paper sheet.