

# Hydrogen and Chemical Quantification of an Organic Coating

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## Key Words

XPS, steel, carbon, thin films, surface modification, polymer coating

## Abstract

The Thermo Scientific™ Theta Probe was used to quantify the chemical composition and hydrogen concentration of an organic coating on a steel substrate.

## Introduction

Zinc-coated steel substrates often have an additional organic coating applied, protecting the steel surface or altering its appearance for decorative reasons. These organic coatings are expected to have long lifetimes and since they are often used outside, they must be durable and have good weathering properties. The characteristics which make a particular organic coating suitable for steel protection will depend on the elemental and chemical composition of the organic material.

X-ray Photoelectron Spectroscopy (XPS) is an analysis technique which provides chemical bonding information from the top few nanometres of a surface down to many microns in depth. It is the ideal technique, for example, for identifying the carbon functional groups in an organic coating. XPS cannot detect hydrogen, however, but the complementary technique of Reflection Electron Energy Loss Spectroscopy (REELS) is able to both detect and quantify hydrogen. REELS can also be used to discern between aliphatic and aromatic carbon.

The Thermo Scientific Theta Probe is a multi-technique surface analysis system which combines XPS and REELS and also provides the additional technique of Ion Scattering Spectroscopy (ISS) as standard.



## Experimental

The Theta Probe was used to analyse an organic coating on steel, yielding a full elemental and chemical quantification, including hydrogen concentration. The polyester-based coating was 25µm thick, with hexamethoxymethyl melamine (HMMM) used as a cross-linker (Figure 1). Ultra low angle microtomy (ULAM) was used to prepare a shallow-angle cross-section of the coating, enabling depth profiling of the organic layer by means of XPS and REELS linescans across the sample.

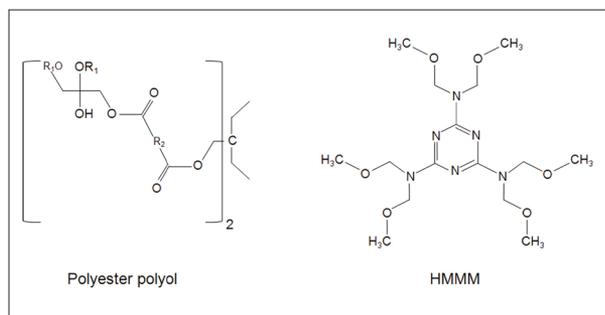


Figure 1: Structure of polyester polyol (R1 is an alkyl functional group and R2 are aromatic or alkyl groups) and HMMM cross-linker.

### XPS Elemental Quantification (Excluding H)

Wide scan XPS survey data acquired at each point on the linescan identified all elements present, from the surface of the organic coating, down through its 25 $\mu\text{m}$  thickness and finishing in the zinc-coated steel substrate. Quantification of the XPS data provided an elemental profile of the sample (excluding hydrogen) as a function of depth (Figure 2).

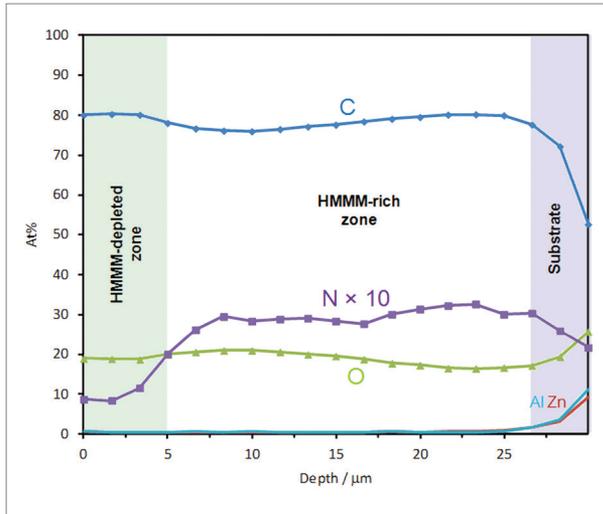


Figure 2: Elemental profile (excluding hydrogen).

Nitrogen observed in the organic coating is due only to the HMMM cross-linker. (The polyester polyol is nitrogen free.) The elemental profile indicates there is  $\sim 5\mu\text{m}$  region of the organic coating surface where the concentration of the HMMM is significantly depleted. The average nitrogen concentration in the bulk of the coating is 3.0 At%, corresponding to a polyester : HMMM Wt% ratio of 6.4 : 1.

### XPS Carbon Bonding Analysis

High energy resolution carbon spectra were acquired at each point along the linescan, allowing the carbon bonding as a function of depth to be determined. The XPS elemental analysis identified two distinct regions in the organic coating, which were HMMM-rich and HMMM-depleted. Carbon spectra from these two zones are shown in Figure 3.

Peak fitting of the C1s spectra (using the Thermo Scientific™ Avantage data system) indicated the presence of C-C/C-H, C-O, N-C-O and C=O bonding. The HMMM-rich zone was also found to have a significant aromatic carbon concentration. The binding energy of this carbon state was too low to be due to the aromatic ring in HMMM (expected at 288eV) and is instead assigned to increased aromaticity in the polyester material in the HMMM-rich zone.

The carbon bonding states were quantified as a function of depth (Figure 4), enabling the change in chemistry to be tracked as a function of depth. The profile of the N-C-O bonding state from the high resolution data matches the nitrogen elemental profile, confirming the increase in HMMM cross-linker concentration towards the metallic substrate.

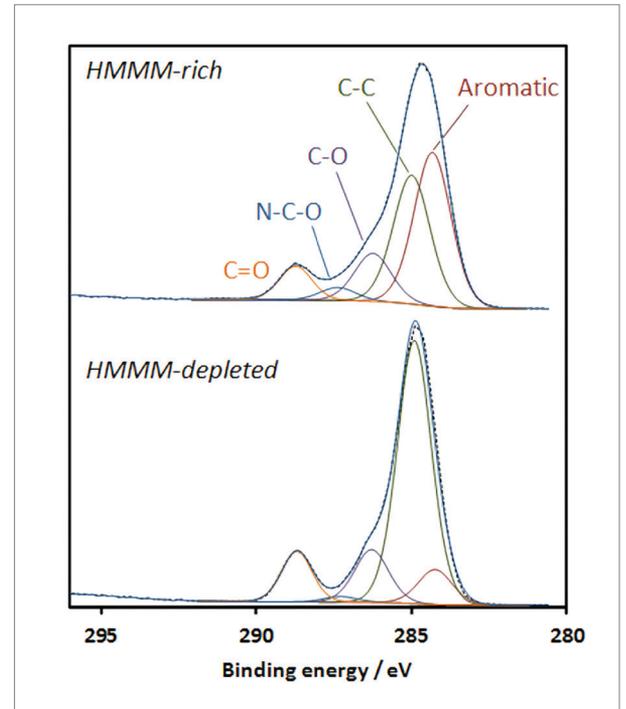


Figure 3: Carbon C1s spectra from HMMM-rich and HMMM-depleted zones.

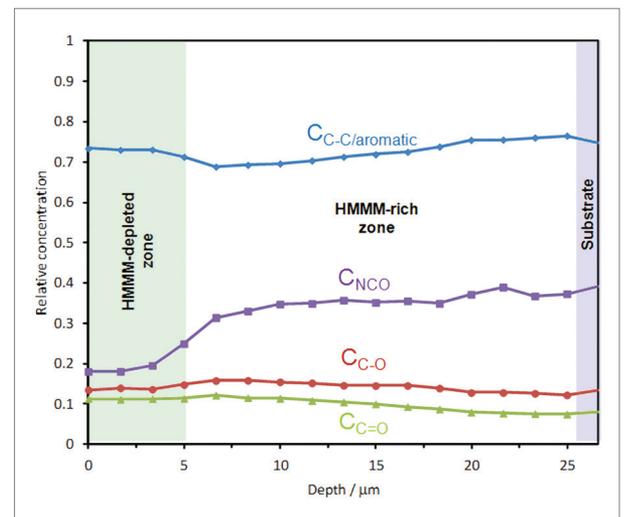


Figure 4: Quantification of carbon bonding states as a function of depth.

## Complementary REELS Analysis

A REELS linescan (Figure 5) was performed on the organic coating cross section, providing complementary information to the XPS analysis. REELS spectra were analysed in a straightforward manner, as described below, to quantify hydrogen and to investigate the change in aromaticity as a function of depth.

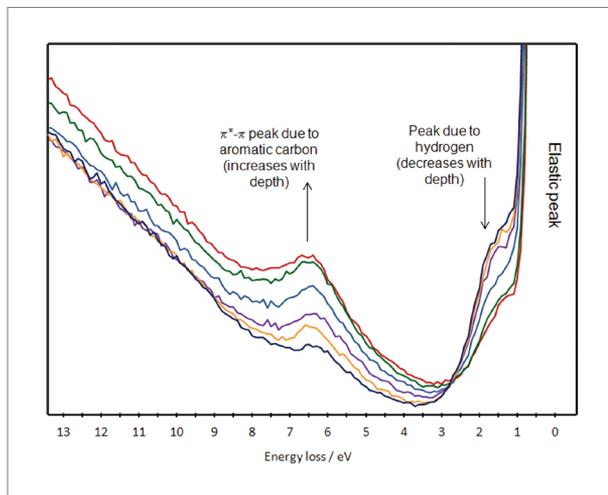


Figure 5: Data from REELS linescan showing features due to hydrogen and aromatic carbon.

## XPS/REELS Total Elemental Quantification

The strongest peak in a REELS spectrum is due to electrons elastically scattered from the sample. The small peak at the base of the elastic peak is due to electrons interacting with hydrogen atoms in the organic coating. Simple peak fitting of this shoulder versus the elastic peak enables quantification of the hydrogen versus all non-hydrogenic peaks. This data was combined with the XPS quantification to give a total elemental quantification throughout the coating (Figure 6).

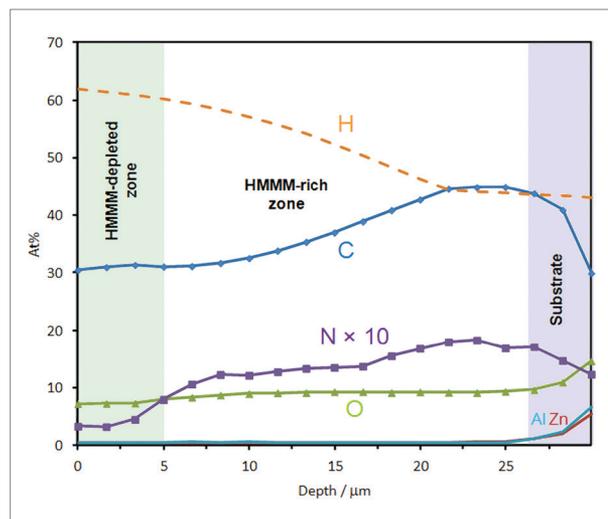


Figure 6: Total elemental quantification with XPS/REELS (including hydrogen).

The concentration of hydrogen decreases towards the metallic substrate, as the concentration of the HMMM cross-linker increases. (The methodology for hydrogen quantification was confirmed using a series of known polymer samples.)

## REELS Analysis of Carbon Aromaticity

Core electrons from the C1s level leaving the sample under the influence of X-rays can promote transitions in the aromatic bonding system of organic materials. These transitions (from the  $\pi$ -HOMO level to the  $\pi^*$ -LUMO) can result in weak, broad satellite features in XPS appearing several volts to higher binding energy of the main C1s peak. The same transitions are visible in REELS spectra, however, where they are typically stronger, sharper and easier to analyse.

The intensity of the  $\pi^*$ - $\pi$  feature in a REELS spectrum is related to the concentration of aromatic carbon in the sample and the energy of the same feature is diagnostic of the valence electronic structure of the polymer.

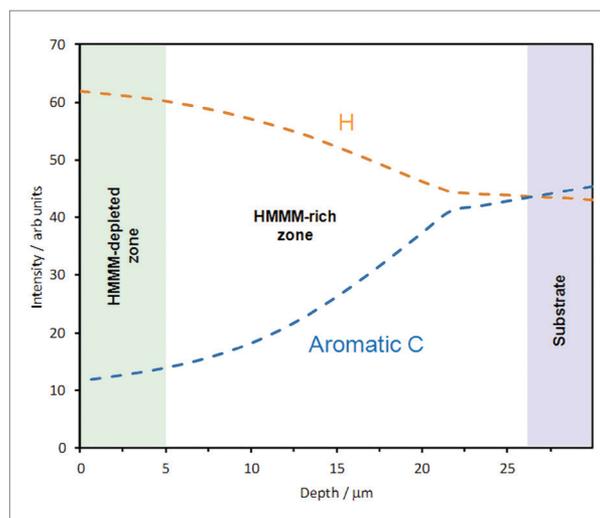


Figure 7: Profile showing hydrogen and aromatic carbon concentration as a function of depth

REELS data from the polyester/HMMM cross-linker sample shows a decrease in  $\pi^*$ - $\pi$  intensity towards the metallic substrate (Figure 7), indicating an increase in the concentration of aromatic carbon with depth.

High energy resolution XPS analysis of the carbon chemistry indicated that increased aromaticity in the HMMM-rich zone was not solely due to the HMMM cross-linker. REELS analysis of the organic coating confirmed this conclusion (Figure 8). The energy of the  $\pi^*-\pi$  peak observed in the REELS spectrum from the HMMM-rich zone is different to that of pure HMMM and is actually consistent with phenyl groups in a polyester material.

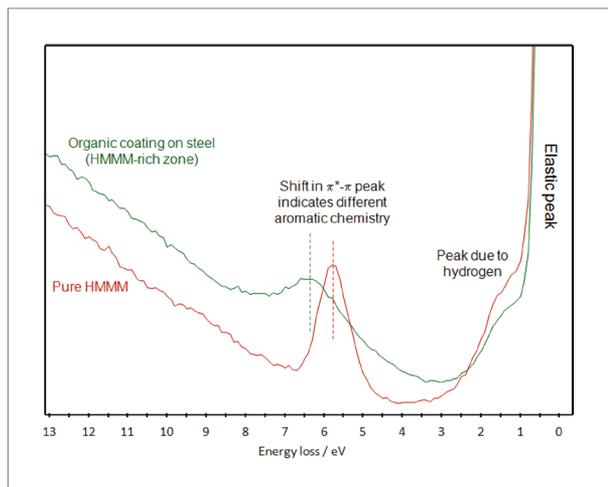


Figure 8: REELS spectra from pure HMMM and HMMM-rich zone of the organic coating on steel.

## Conclusion

A combined XPS/REELS analysis using the Thermo Scientific Theta Probe enabled a comprehensive analysis of an organic coating on steel. XPS data provided quantification of all non-hydrogenic elements and enabled study of the carbon bonding states. REELS completed the quantification, providing data about the hydrogen concentration. The variation in aromatic carbon concentration through the organic coating was also studied using REELS.

## Acknowledgements

Conclusions drawn in this application note are based on an experimental work performed at CDL-MS-MACH/ZONA, Johannes Kepler University (JKU) Linz. Thermo Fisher Scientific would like to thank Theresia Greunz and David Stifter (JKU Linz, Austria) and Bernhard Strauß (voestalpine Stahl GmbH, Linz, Austria) for providing these data (originally published as “Cryo-ultra-low-angle microtomy for XPS-depth profiling of organic coatings; Anal Bioanal Chem 405:7153-7160”.)

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