

Polymer analysis using femtosecond-laser-ablation depth profiling

Introduction

X-ray photoelectron spectroscopy (XPS) is an essential polymer characterization technique that can identify not just the elemental composition but also the chemical state of polymer samples. This allows the chemical bonding environment to be deduced and, as a result, the polymer species can be identified. This can all be achieved with minimal sample preparation thanks to the built-in charge-compensation systems found in XPS instruments, which simplify the analysis of insulating samples.

The introduction of gas cluster ion sources (GCIS), such as the Thermo Scientific™ MAGCIS Dual Mode Ion Source, marked a major step forward in polymer analysis. Unlike monatomic ion beams, GCIS are able to clean surface contamination, and etch away layers of sample material, without damaging the underlying chemistry of organic samples such as polymers. As a result, GCIS has allowed chemical-damage-free analysis to reach micrometers below the sample surface. This depth of analysis can be highly time consuming, however, and total experimental times can range from multiple hours to days.

The addition of femtosecond-laser-ablation (fs-LA) technology is alleviating this, allowing for XPS spectra to be collected from a depth of tens of μm into a sample in a matter of minutes. This is because the laser ablation occurs on the femtosecond timescale (i.e., nearly instantaneously), effectively eliminating the material removal time of the depth profile.

Additionally, unlike other material removal techniques such as atomic ion beam impact (where a collision cascade effect is induced to remove surface material) fs-LA is capable of removing material without chemical damage due to the ultra-short columbic explosion process used to eject the material. The resulting profile is therefore representative of the actual sample chemistry.

Damage-free depth profiling

One of the key concerns for XPS depth profiling is whether or not the chemistry of the sample is disrupted by the material removal process. For polymer samples, this can be monitored through the deconvolution of peaks found in the C1s spectrum.

To ascertain the impact of fs-LA material removal, 3 different polymers were examined by XPS before and after fs-laser ablation (Figure 1). In all three cases, there is no significant difference between the C1s spectrum following sample exposure to the laser, indicating that this method preserves the polymer stoichiometry of the sample. For instance, in the PET spectra (Figure 1a), the variation in FWHM of the ester peak (288.5 eV) is less than 0.1 eV before and after ablation.

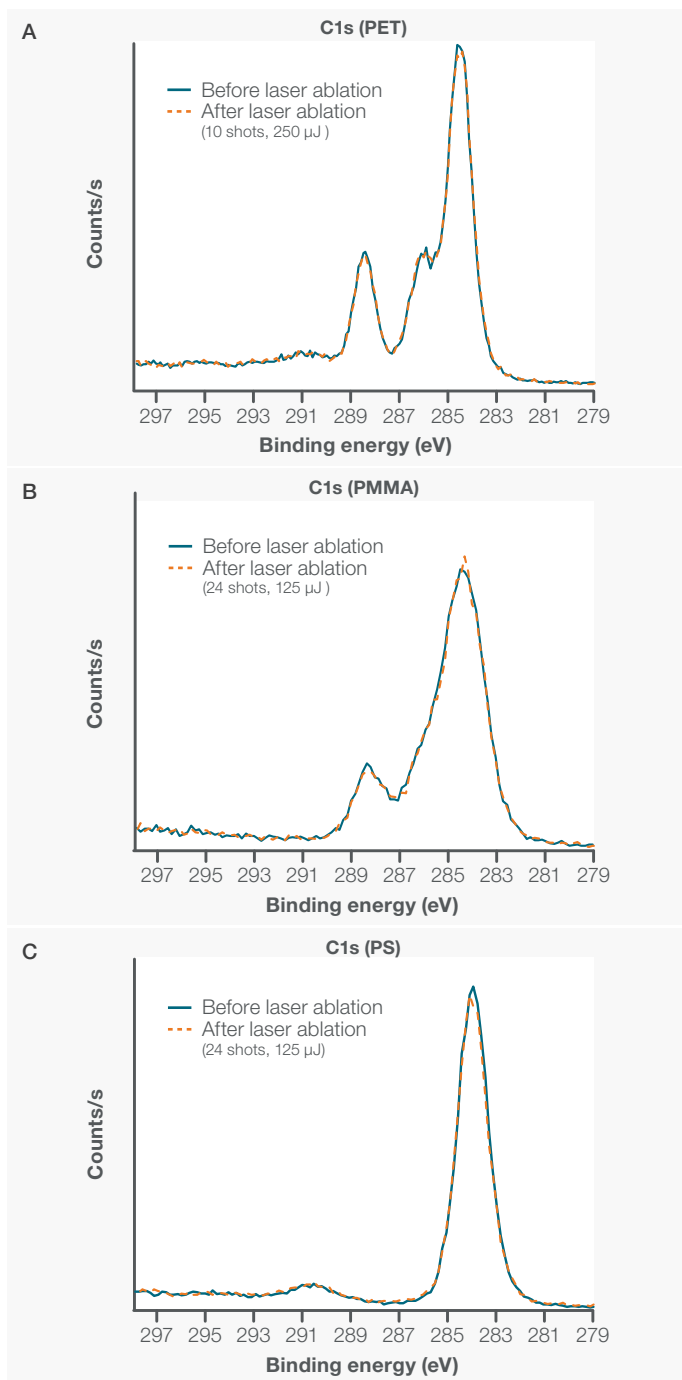


Figure 1. XPS spectra of the C1s region for three test polymers (PET, PMMA, and PS), taken before and after femtosecond laser ablation.

Paint layer analysis

In traditional ion-beam depth profiling, analytical depths are generally limited to several hundred nanometers, up to a micrometer. This means that it is extremely difficult to analyze the interfaces between multiple micrometer-thick layers in a sample without the use of additional techniques such as ultra-low-angle microtome (ULAM) sectioning.¹ The introduction of fs-LA technology, however, allows micrometers of material to be removed rapidly, enabling the characterization of layered samples.

As an example, a multi-layer paint specimen (provided by the University of Surrey, UK) was depth profiled using the Thermo Scientific™ Hypulse™ Surface Analysis System. The sample consists of an aluminum substrate coated with a 5 μm layer of polyurethane primer followed by a 25 μm PMMA/PVdF topcoat.

The depth profile was generated using a 1,030 nm laser with an energy of 250 μJ for ablation, along with a 30 μm X-ray spot size for data collection. XPS spectra were collected after each ablation cycle to obtain an atomic concentration plot through both paint layers into the substrate material (Figure 2).

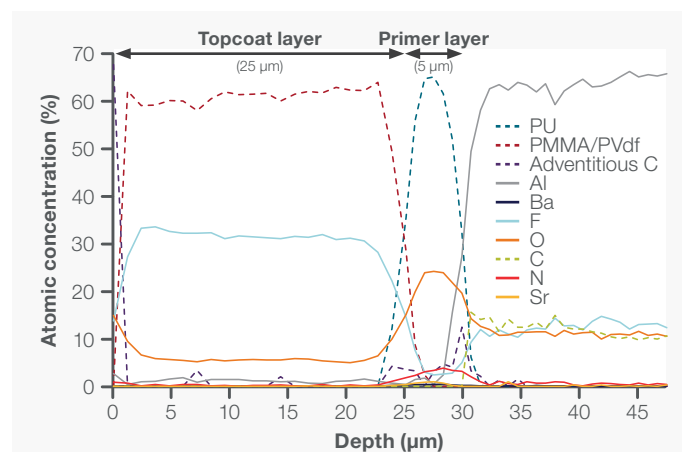


Figure 2. XPS and fs-LA depth profile of a paint sample, which consists of an aluminum substrate coated with a 5 μm PU primer layer and a 25 μm PVdF/PMMA topcoat.

5 distinct regions throughout the analyzed depth can be seen. The top surface of the sample consists of an adventitious layer of carbon contamination, which is commonly found on samples exposed to air. The second layer is the 25 μm PVdF/PMMA topcoat, and the third layer is the PU primer. Between the primer and the final aluminum substrate layer, a clear increase in adventitious carbon is observed, similar to the signal seen at the top sample surface. This suggests residual carbon contamination was present on the substrate before the paint layers were applied.

It would take hours to produce the XPS depth profile shown in Figure 2 using traditional ion beam approaches. Even with the use of a monatomic beam with a high energy per atom, the length of the analysis could still be just as long, depending on the sample material, and would sacrifice the chemistry of any organic/polymeric materials. The combination of fs-LA depth profiling and snapshot XPS acquisition, meanwhile, can reduce the experimental time to less than 20 minutes without inducing any chemical damage to the sample surface.

Summary

One of the most critical aspects of successful polymer XPS depth profiling is the preservation of the sample chemistry during material removal. Additionally, experiment time can be a significant limiting factor, and thicker samples could lead to reduced time for repeat experiments. The femtosecond laser ablation capabilities of the Hypulse Surface Analysis System provide fast, efficient, and chemical-damage-free material removal from a sample surface, enabling analysis multiple micrometers into a sample. This means that hidden sample interfaces, that were largely inaccessible before, can now be analyzed easily and efficiently.

References

1. Hinder SJ, et al. **Surface and interface analysis of complex polymeric paint formulations.** *Surf Interface Anal* 38:4 (2006). doi: [10.1002/sia.2325](https://doi.org/10.1002/sia.2325)
2. Baker MA, et al. **Femtosecond laser ablation (fs-LA) XPS – A novel XPS depth profiling technique for thin films, coatings and multi-layered structures.** *Appl Surf Sci* 654 (2024). doi: [10.1016/j.apsusc.2024.159405](https://doi.org/10.1016/j.apsusc.2024.159405)

 Learn more at thermofisher.com/hypulse

thermo scientific