

Surface-Chemistry Mapping of Printed Photopolymers

XPS, ToF-SIMS, ATR-FTIR, contact angle and contamination attribution

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Abstract

The outer surface of a printed photopolymer is not necessarily a representative slice of its bulk network. Oxygen inhibition, contact with a vat film or build platform, washing, secondary exposure, abrasion, migration and storage can produce a chemically and physically distinct interphase. Surface analysis is therefore useful for diagnosing adhesion failures, wetting drift, residues and unexpected functional response, but no single technique can identify all of these causes.

This review defines a bounded measurement architecture for mapping the surface chemistry of vat-photopolymerised and related printed photopolymers. X-ray photoelectron spectroscopy provides elemental and chemical-state information from the near surface; time-of-flight secondary-ion mass spectrometry provides fragment-sensitive spectra and chemical images; attenuated-total-reflectance Fourier-transform infrared spectroscopy probes vibrational groups over a larger interaction volume; and contact-angle measurements report a coupled wetting response rather than composition alone. The review connects sampling, controls, mapping, ageing and contamination attribution. Its central conclusion is that contamination is an inference supported by converging evidence, not a label generated by one peak or one water droplet. A defensible study preserves specimen history, uses clean and deliberately contaminated controls, separates topography from chemistry, and states the depth and spatial scale represented by every result.

Keywords: surface chemistry; photopolymer; XPS; ToF-SIMS; ATR-FTIR; contact angle; contamination; wetting; mapping; attribution

1. Significance and scope

The surface controls adhesion, coating, fluid transport, optical scattering, biological contact and the first stages of environmental attack. In vat photopolymerisation, that surface can be created against air, a transparent window, a support interface or uncured resin. Subsequent cleaning and post-curing may remove, redistribute or react residual species. Consequently, two specimens made from one resin lot can present different surfaces even when their bulk conversion and mechanical properties are similar.

The measurement problem is not simply to detect carbon, oxygen or a familiar infrared band. It is to decide whether a difference is real, where it occurs, whether it is chemical or topographical, and whether the proposed source is uniquely supported.

1.1 Corpus boundary

ER-208 owns analytical mapping and attribution of printed-photopolymer surface chemistry. ER-088 owns surface topography, finishing and roughness metrology. ER-168 owns coating and encapsulation performance on reactive photopolymer substrates. ER-175 owns printer changeover, cleaning validation and cross-contamination control. ER-180 owns reconstruction of cure state, exposure history and contamination from a returned failed component. ER-225 owns plasma, corona and UV-ozone treatment as surface-engineering processes. ER-208 may measure surfaces created by those operations, but it does not prescribe the operations or replace their qualification.

2. Define the surface state before analysis

A surface result is conditional on specimen history. At minimum, record resin and lot; printer and build location; surface orientation; contact with air, window, platform or supports; wash solvent, time and agitation; drying; post-cure spectrum, radiant exposure and temperature; elapsed time; packaging; handling; abrasion; and environmental exposure.

Sampling should distinguish the as-printed surface from a machined or fractured interior. Gloves, wipes, labels, storage films and mounting media are possible contamination sources. A chain-of-custody blank should travel with the specimens whenever contamination attribution is an objective.

3. Complementary information depths and fields of view

The four method families interrogate different physical quantities and different material volumes. XPS is surface sensitive and spatially averaged over the selected analysis area. ToF-SIMS can generate spectra, lateral maps and depth profiles, but ion yield is matrix dependent and sputtering can alter soft matter. ATR-FTIR samples a larger evanescent-field volume and its effective depth depends on wavelength, crystal, angle and refractive indices. Contact angle integrates interfacial forces, roughness, heterogeneity, droplet history and the test liquid.

Agreement between methods is therefore not numerical identity. It is consistency between observations made at declared scales. A contaminant confined to a very thin patch may be visible in ToF-SIMS yet diluted in ATR-FTIR. A large wetting change may occur without a resolvable new XPS element when molecular orientation or topography changes.

4. X-ray photoelectron spectroscopy

XPS measures the kinetic energies of emitted photoelectrons and reports elemental composition and chemically shifted components after calibration and interpretation. ISO 15472 provides an official framework for calibrating XPS energy scales [1]. The energy scale, charge compensation, reference convention, source, pass energy, take-off geometry, analysed area and fitting constraints belong to the reported method.

For a set of corrected peak areas A_i and sensitivity factors S_i , an apparent atomic fraction is commonly expressed as:

$$\chi_i = \frac{A_i/S_i}{\sum_j A_j/S_j}$$

This value is model dependent. It is not a bulk formulation assay, and peak fitting does not create unique chemical identity. Insulating photopolymers can charge non-uniformly. Adventitious carbon, wash residues and migrated additives can overlap with the polymer envelope. Sputter cleaning can remove the evidence of interest or chemically damage an organic network. Best-practice literature identifies charging, referencing, spectral overlap and sputter damage as central interpretation risks [2], while NIST SESSA provides reference data and simulation support for quantitative electron-spectroscopy interpretation [3].

5. Time-of-flight secondary-ion mass spectrometry

ToF-SIMS detects secondary ions generated by a pulsed primary-ion beam. It can distinguish polymer fragments with similar elemental composition, map lateral heterogeneity and, with a separate sputter cycle, obtain depth-resolved information. The complete mass spectrum at each image pixel is valuable for locating release agents, silicone-like residues, surfactants, photoinitiator fragments or cleaning-derived species.

Signal intensity is not concentration without a suitable calibration because ion yield depends on matrix, polarity, primary ion, dose and local chemistry. Fragment assignment should use exact mass, isotope pattern and reference specimens rather than one nominal m/z . Multivariate clustering may reveal domains, but the analyst must report preprocessing, normalisation and the loadings that drive separation. Polymer ToF-SIMS guidance emphasises spectral analysis, imaging and depth profiling as distinct modes with different compromises [4].

6. ATR-FTIR and conversion-sensitive bands

ATR-FTIR measures vibrational absorption in the region coupled to the internal-reflection element. It can compare uncured resin, washed part, post-cured surface and deliberately treated controls. ASTM E1252 describes general techniques for obtaining infrared spectra for qualitative analysis [5]. Contact pressure, crystal material, background, resolution, number of scans and normalisation method affect comparison.

For a reactive band R and an internal reference band Q , a relative conversion estimate may be written as:

$$DC = 1 - \frac{(AR/AQ)_{\text{cured}}}{(AR/AQ)_{\text{uncured}}}$$

The result is valid only if the reference remains invariant and the spectral model is justified. Surface ATR measurements on stereolithographic materials have been used to follow functional groups and subsequent surface reaction [6,7]. These examples establish feasibility, not universal band assignments across proprietary resins.

7. Contact angle and wetting response

For an ideal smooth, chemically homogeneous and equilibrium surface, Young's relation is:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

Real printed surfaces violate several of these assumptions. Report test liquid, temperature, droplet volume, deposition rate, dwell time, image-fitting method, advancing and receding angles where feasible, and the surface direction. ISO 19403-2 provides an official contact-angle route for estimating solid surface free energy in its stated domain [8].

Static water angle alone cannot distinguish chemical change from roughness, trapped air, swelling, dissolution or contact-line pinning. Full-text evidence for DLP prints shows that layer direction and thickness can change roughness, angle and hysteresis together [9]. Contact angle is therefore a functional response to be interpreted with topography and chemistry, not a direct chemical assay.

8. Separate topography from chemistry

Each analysed location should have a topography record at a relevant scale. Profilometry or optical microscopy can identify layer steps, polishing tracks, pores and local slope. The chemical specimen and topography specimen should be identical or demonstrably equivalent.

A practical design includes a smooth moulded or cast control of the same formulation, multiple print orientations, and a polishing control. If wetting changes after polishing while XPS and ATR-FTIR remain stable, geometry is a plausible driver. If chemical spectra change on a topographically matched pair, chemical attribution is strengthened. Neither comparison alone proves causality.

9. Contamination attribution as a hypothesis test

Attribution should begin with candidate sources: base resin, build-window transfer, platform coating, wash solvent, detergent, lubricant, glove, wipe, release film, airborne deposit, packaging or a later process. Each candidate needs a reference spectrum or controlled exposure.

Evidence is strongest when:

- 1 a diagnostic signal is absent from a clean negative control;
- 2 the signal is present in the suspected source and affected specimen;
- 3 its spatial distribution matches the contact or process history;
- 4 an orthogonal method detects a compatible change;
- 5 blanks remain clean; and
- 6 removal or controlled addition changes the signal predictably.

A ubiquitous hydrocarbon envelope or a single silicon-containing fragment is insufficient by itself. Shared components, laboratory background and matrix-dependent fragmentation must be considered.

10. Ageing, migration and measurement time

Low-molar-mass species can bloom, evaporate, react or diffuse after printing. Hydrophobic recovery can follow an oxidising treatment. A cleaned surface may recontaminate during storage. Measurement time is therefore a controlled variable.

Use a time-zero definition and predeclared intervals. Store controls in the same container and atmosphere as test specimens. Where vacuum methods are used, distinguish changes caused by pre-analysis vacuum residence from changes that occurred in service. Repeat spectra at the same position only when beam damage has been evaluated.

11. Mapping and statistics

A single survey spectrum cannot represent a heterogeneous build. Sampling should cover declared locations such as centre, edge, up-facing, down-facing, support-contact and channel interior. Replication must distinguish multiple locations on one part from independent parts and builds.

For a mapped quantity y , a hierarchical description is appropriate:

$$y_{\{bpl\}} = \mu + B_{\{b\}} + P_{\{p(b)\}} + L_{\{l(bp)\}} + \epsilon_{\{bpl\}}$$

where B , P and L represent build, part and location contributions. The design need not fit this exact model, but it should preserve the hierarchy so that many pixels are not mistaken for many independent specimens.

11.1 Validation and controls

Minimum controls include an untreated clean specimen, handling blank, substrate or mounting blank, method reference, repeat analysis and at least one deliberately exposed positive control when attribution is claimed. Instrument performance should be checked with method-appropriate references. Analysis order should be randomised or blocked, and the operator should not infer treatment solely from specimen labels.

Destructive sequence matters. Contact angle can leave liquid residues; ATR contact can deform a soft surface; XPS and ToF-SIMS require vacuum; sputter profiling is destructive. Allocate separate matched specimens or define an order that cannot contaminate earlier measurements.

12. Interpretation matrix

Observation	Supported interpretation	Unsupported leap
XPS composition differs from a clean control	Near-surface elemental or chemical-state response differs under the stated model	The contaminant source is uniquely identified
ToF-SIMS fragment map follows a contact region	A chemically distinct ion pattern is spatially associated with that region	Signal intensity is a concentration map
ATR-FTIR reactive-band ratio changes	The sampled vibrational response differs from the reference	The outermost surface has a uniform conversion value
Contact-angle hysteresis rises	Wetting heterogeneity or pinning increased	Surface chemistry alone caused the change
Two orthogonal methods track a deliberate exposure	The exposure is a credible contributor	No other source contributed in the production specimen

13. Minimum reporting set

Report formulation class and lot; printer, orientation and build location; complete wash, drying and post-cure history; storage and handling; sampled face and coordinate; topography; instrument and calibration; analysis area and depth model; acquisition and processing settings; reference spectra; blanks and controls; replicate hierarchy; map-registration method; raw and processed data retention; uncertainty or sensitivity; and the exact reasoning used to assign or reject a contamination source.

14. Knowledge boundary

Published evidence establishes that complementary surface methods can distinguish chemical, spatial and wetting responses in selected polymers and printed photopolymers. It does not establish a universal spectral library for proprietary vat formulations, a unique mapping from one signal to one contaminant source, or reference materials that reproduce the coupled migration, reaction and ageing of every printed network. Quantitative attribution therefore remains conditional on formulation-specific controls, declared information depth and converging measurements.

15. Limitations

This review does not prescribe cleaning validation, surface activation, coating, biological evaluation or universal acceptance limits. XPS and ToF-SIMS can alter organic surfaces, and neither provides an automatic molecular formulation. ATR-FTIR averages over a larger volume than the outermost interface. Contact angle is not composition. Proprietary formulations can make spectral attribution non-unique, and reference materials may not reproduce migration or reaction in a printed network.

16. Conclusions

Printed-photopolymer surfaces are process histories expressed as interphases. XPS, ToF-SIMS, ATR-FTIR and contact angle become powerful when their different depths, fields of view and response functions are used deliberately. The defensible unit of evidence is a controlled, spatially registered and time-resolved comparison. Contamination attribution requires a candidate source, reference evidence, clean blanks and convergence across methods. One peak, one image or one droplet is evidence of a response, not proof of origin.

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