

Spatial Cure-State Mapping by Raman and Infrared Spectroscopy

Sampling volume, conversion gradients and calibration boundaries

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Abstract

Raman and infrared spectroscopy can map the consumption of reactive groups in photopolymers, but a spectral map is not automatically a map of network state. Each pixel or depth point represents a finite sampling volume shaped by optics, refractive index, absorption, scattering, confocal response, surface contact and data reduction. Reactive-band loss may correlate with conversion while remaining sensitive to band overlap, orientation, baseline, photobleaching and the stability of the chosen internal reference. ATR-FTIR, transmission FTIR and confocal Raman therefore observe different volumes and cannot be merged without a transfer model.

This review establishes a measurement framework for spatial cure-state mapping. It defines band-ratio conversion, calibration against independent chemistry, point-spread and depth-response characterisation, uncertainty propagation and rules for interpreting gradients. Confocal Raman is treated as a three-dimensional optical measurement whose apparent depth can be distorted by refractive-index mismatch; infrared methods are separated by transmission, reflection and evanescent-wave sampling. The review proposes an acquisition and validation sequence for surfaces, sections, layers and volumes, together with minimum reporting requirements. Conversion is kept distinct from gel fraction, crosslink density, modulus and residual extractables. The result is a method-specific chemical map with declared spatial resolution and calibration boundaries, not a universal cure-state image.

Keywords: Raman spectroscopy; FTIR; ATR; confocal microscopy; degree of conversion; depth profiling; photopolymer; spatial resolution; calibration; chemical imaging

1. Significance and scope

Photopolymer parts can contain through-thickness and lateral gradients caused by attenuation, oxygen, multiple exposures, interfaces, pigment, filler or thermal history. Bulk spectroscopy hides such gradients. Spatial Raman and infrared measurements can reveal them, but only when the sampling function and chemical calibration are understood.

The measured spectrum is a convolution of local composition and instrument response. A sharp chemical boundary may appear broad; a uniform material may appear graded if focus, path length or reference-band response changes with depth.

1.1 Corpus boundary

ER-205 owns method-specific spatial mapping by Raman and infrared spectroscopy. ER-027 retains the general conversion-metrology and spatial-heterogeneity umbrella. ER-035 retains working-curve interpretation. ER-182 retains the non-equivalence of conversion, gel fraction, crosslink density and modulus. ER-180 retains returned-part analysis, while ER-208 will own broader surface-chemistry mapping using XPS, ToF-SIMS, ATR-FTIR and contact angle.

2. Define the spectral measurand

For an acrylate, a conversion estimator often uses a reactive C=C band relative to an internal reference:

$$\lceil X=1-\frac{(Ar/A\{ref\})_t}{(Ar/A\{ref\})_0} \rceil$$

where Ar and $Aref$ are peak areas or heights under a fixed processing rule. These compact prose names correspond to the subscripted symbols in the equation. The equation estimates loss of the selected spectral population. It is valid only if the reference response is stable, bands are assigned correctly and the sampling volumes before and after cure are comparable.

Other chemistries require other observables: epoxy ring opening, thiol loss, ene consumption, acid- or base-sensitive markers, or product-band formation. A universal “degree of cure” axis should not combine these without a validated common state variable.

3. Raman contrast and perturbation

Raman spectroscopy provides molecular-vibration contrast with visible or near-infrared excitation and can be confocal. Fluorescence, local heating, photochemistry and orientation can alter spectra. The excitation wavelength, power at sample, dwell time and cumulative exposure should therefore be tested for measurement-induced change.

Lange and co-workers used Raman spectroscopy to quantify dual-colour photopolymerisation in xolography, demonstrating that chemically distinct reactions can be followed through selected spectral features [1]. The method's usefulness depends on chemistry-specific band assignment and calibration; it does not make Raman intensity a universal conversion scale.

Polarisation can change relative band intensity in oriented or stressed materials. When orientation is possible, polarisation geometry should be fixed or varied deliberately.

4. Confocal sampling volume

A confocal Raman point is a three-dimensional response, not an infinitesimal voxel. Lateral and axial resolution depend on wavelength, numerical aperture, pinhole or aperture, refractive index and aberration. The effective signal is:

$$S(x,y,z) = \iiint C(x',y',z')P(x-x',y-y',z-z')dV$$

where C is the local spectroscopic quantity and P is the instrument's three-dimensional point-spread or sampling function. Deconvolution requires a validated P and can amplify noise.

Boldrini and co-workers showed that objective aperture and magnification influence confocal depth experiments and that nominal geometrical depth is not automatically the sampled depth [3]. Resolution should therefore be measured with an appropriate interface or standard under optics resembling the specimen measurement.

5. Refractive-index mismatch and apparent depth

Focusing from air or immersion medium into a polymer with a different refractive index shifts and broadens the axial response. Apparent stage displacement is not equal to physical depth. Spherical aberration grows with depth and can create an artificial decline or broadening in a concentration profile.

Courtecuisse and co-workers specifically investigated depth characterisation of photopolymerised films using a confocal Raman immersion objective [2]. At the access depth available here, that work supports the need for immersion-aware correction but not a universal correction factor. Each optical configuration and material requires validation.

Cross-sections can reduce depth distortion but introduce cutting, polishing, smearing, contamination and stress. Surface and section measurements should be treated as different preparation states.

6. Infrared sampling modes

Transmission FTIR integrates through the optical path and can map thin sections when absorption remains within the detector's useful range. Reflection modes mix surface and subsurface response depending on optics. ATR-FTIR samples an evanescent field whose effective penetration depends on wavelength, incidence angle and refractive indices:

$$dp = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2\theta - (n_2/n_1)^2}}$$

for an ideal interface. Contact pressure, roughness and gaps change the effective response. ATR is therefore surface-weighted, not a fixed-depth slice. Scherzer's real-time ATR work supports the use of infrared response for cure-depth profiling under a defined geometry [5], but transfer to another crystal, angle or material requires recalibration.

7. Baseline, bands and internal references

Baseline choice, smoothing, cosmic-ray removal, fluorescence subtraction and peak integration can dominate small conversion differences. Processing rules should be frozen before comparing groups. Raw spectra must be retained.

An internal reference band should be chemically invariant, resolved and affected similarly by focus and sampling. Carbonyl bands are convenient in many acrylates but can change shape or environment during cure. A reference stable in a simple resin may not remain stable in a hybrid, phase-separating or hydrogen-bonding system.

Multivariate models can exploit more of the spectrum but need representative calibration, independent validation and protection against batch or instrument confounding. A visually smooth prediction map is not evidence of chemical accuracy.

8. Calibration to chemical conversion

Calibration can use mixtures of known reactive-group fraction, time-resolved spectra under a mass-balance model, or an orthogonal assay. Each route has limitations. Prepared mixtures may not reproduce optical or conformational changes during polymerisation. Time-resolved calibration assumes no interfering band evolution. Orthogonal chromatography or NMR may sample a different volume.

Lempel and co-workers combined micro-Raman conversion measurements with HPLC monomer elution, illustrating the value of orthogonal observables [4]. Elution and spectral conversion are not expected to be identical; their relationship depends on network and extraction conditions.

Calibration should report range, residuals, independent-validation performance and whether it predicts absolute conversion or only relative change.

9. Gradient acquisition design

Map spacing should follow the effective sampling volume and the smallest gradient relevant to the engineering question. Oversampling can improve visual continuity but does not create new spatial resolution. Acquisition order should minimise drift and exposure-induced cure; randomised or interleaved controls can reveal time effects.

For depth profiles, record the interface location, stage coordinate, optical correction, signal-to-noise and rejection criteria. For lateral maps, fiducials and coordinate registration are needed to compare spectroscopy with geometry or process pixels. Repeated maps should distinguish positioning repeatability from spectral repeatability.

10. From band conversion to cure state

Reactive-group conversion is one coordinate of cure state. Gelation, crosslink density, vitrification, phase separation, residual monomer and modulus can differ at equal conversion. A spatial conversion map should therefore not be labelled a modulus or network-density map without independent calibration.

The distinction is especially important in dual-cure and hybrid systems. One band may report acrylate conversion while an epoxy or thiol reaction continues. Dark cure can change the state after the optical exposure. Time between processing, sectioning and measurement is part of the specimen definition.

11. Uncertainty and detection of gradients

Uncertainty includes spectral noise, baseline, band fitting, reference stability, calibration model, focus, depth correction, specimen preparation, positioning and spatial heterogeneity below the sampling volume. Adjacent pixels are not independent when point-spread functions overlap.

A gradient claim should exceed both measurement uncertainty and the spatial-resolution limit. Report confidence or uncertainty maps alongside conversion maps. A colour scale should not imply more significant digits than the calibration supports.

12. Interpretation matrix

Observation	Supported interpretation	Unsupported leap
Reactive/reference ratio decreases	Selected reactive spectral population decreased under the model	Crosslink density increased proportionally
Raman profile broadens with depth	Chemistry and/or axial response varies	Chemical gradient is exact without optical correction
ATR and confocal Raman disagree	Sampling volumes, band models or specimen state differ	One method is necessarily wrong
Map correlates with exposure pixels	Process pattern and spectral response are associated	Local absorbed dose is known
High conversion region is spatially uniform	Chosen spectral conversion is uniform at resolved scale	Network, residuals and properties are uniform

13. Minimum reporting set

Report chemistry and specimen history; measurement time after cure; surface or section preparation; instrument, excitation wavelength, power, objective, numerical aperture, confocal aperture and acquisition time; FTIR mode, crystal, angle and contact; spatial step and effective resolution; refractive indices and depth correction; bands, baselines and processing; calibration and validation; raw-data retention; uncertainty; and the precise state variable represented by the map.

14. Knowledge boundary

Spatial spectroscopy can resolve method-specific chemical heterogeneity, but absolute three-dimensional conversion remains challenging in optically heterogeneous materials. Refractive-index and scattering fields may evolve during cure. Reference bands and calibration models rarely transfer unchanged across resin families.

15. Limitations

This review does not cover general surface contamination, XPS or ToF-SIMS, which belong to ER-208. It does not replace gel-fraction, mechanical or extractables testing. It does not prescribe wavelength, laser power or universal band assignments for proprietary formulations.

16. Conclusions

Raman and infrared mapping can make cure gradients visible only when the sampling volume and calibration are part of the result. Confocal depth is distorted by optical mismatch; ATR is an evanescent, contact-sensitive measurement; band ratios depend on reference stability and chemistry. The defensible output is a spatial map of a named spectral state variable with measured resolution and uncertainty. Conversion, network state and performance remain related but distinct quantities.

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