

Pigment–Dye–Photoinitiator Competition in Coloured Photopolymers

Spectral overlap, inner filtering, surface cure and colour stability

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Abstract

Coloured photopolymers contain several wavelength-dependent competitors for the incident light field. Dissolved dyes absorb, pigments absorb and scatter, photoinitiators consume photons, and photoinitiators or colourants may bleach or generate coloured products. The resulting optical state changes with depth, conversion and irradiation history. A bulk spectrum, top-surface conversion or nominal cure depth therefore cannot by itself establish through-cure, surface response, colour retention or dimensional fidelity.

This review defines a measurement architecture for separating absorption, scattering, inner filtering, photoinitiator response, depth-dependent conversion, surface cure and colour-state evolution. Primary evidence includes depth-resolved acrylate cure, photoabsorbing fillers in VAT photopolymerisation, independent surface and deep conversion in a black ink, pigmented-system kinetic studies, pigmented thiol–ene chemistry, clear-versus-pigmented photoinitiator comparisons and photoinitiator-dependent colour stability in printed resin. The studies use different colourants, chemistries, geometries, sources and analytical methods, so their numerical results cannot be transferred as a universal exposure multiplier, spectral window or formulation recipe. Qualification requires matched optical, chemical and geometric evidence under declared processing and conditioning.

Keywords: coloured photopolymer; pigment; dye; photoinitiator; spectral overlap; scattering; inner filter; surface cure; depth conversion; colour stability

1. Significance and scope

Colourants are often treated as passive appearance additives, but in a photocurable formulation they can redirect the initiation field. A dye can compete by molecular absorption, while pigment particles introduce both absorption and scattering. Photoinitiator depletion, photobleaching and coloured photoproducts can change the competition during exposure and post-cure.

This review addresses formulation-level competition among pigments, dyes and photoinitiators and connects it to surface conversion, depth-dependent cure and colour-state stability. It does not prescribe a commercial recipe, dispersion method, universal colourant concentration, exposure multiplier, layer thickness, spectral window or post-cure compensation.

1.1 Corpus boundary

ER-216 owns spectral-overlap and attenuation maps for pigment/dye/photoinitiator combinations; separation of absorption, scattering, inner filtering and photobleaching or photoproduct colour; formulation-level links to cure depth, through-cure and surface conversion; and qualification matrices that preserve colour, conversion and geometry as distinct outputs. ER-078 retains CIELAB, CIEDE2000, metamerism, gloss, texture and appearance-metrology ownership. ER-196 retains oxygen inhibition and photon competition in thin pigmented graphic films where surface cure governs performance. ER-159 retains functional optical, photonic, luminescent and high-refractive-index materials. ER-202 retains action-spectrum and quantum-yield metrology. ER-203 retains radiometric traceability. WP-022 retains the commercial colours portfolio. WP-025 retains general colour stability and light-fastness guidance. WP-040 retains dental-family positioning. ER-216 is not an ink-only review, a pigment-dispersion recipe or a general colour-measurement standard.

2. Define the colourant state before measuring competition

The formulation record must distinguish dissolved dyes from particulate pigments and identify mixtures. For a pigment, report chemical identity, surface treatment, primary-particle or aggregate information available, dispersion state, concentration basis and settling history. For a dye, report identity, ionic or neutral form, solvent environment and evidence of complete dissolution. Photoinitiator, coinitiator, absorber, stabiliser and monomer or oligomer identities complete the optical inventory.

Geometry belongs to the state definition. Film thickness, layer height, vat depth, substrate reflectance, build orientation and measurement path can change the observed field. A spectrum in a dilute cuvette is not automatically representative of a filled resin layer.

3. Build a spectral competition map

At each wavelength, the map should include source spectral irradiance, formulation transmission or diffuse optical response, photoinitiator absorption and colourant contribution. For a non-scattering solution, an absorbance model can be useful within a validated concentration and path range. A particulate formulation requires an independent scattering treatment.

An operational attenuation coefficient may be expressed as

$$\mu_{\text{eff}}(\lambda) = \mu_{\text{abs}}(\lambda) + \mu_{\text{sca}}(\lambda)$$

where μ_{eff} is measured effective attenuation in the declared geometry, μ_{abs} is the absorption contribution and μ_{sca} is the scattering contribution under the chosen model. The decomposition is not obtained from transmission alone unless the method resolves the two terms. Wieckowski and Erb demonstrated why particle, resin and light-package variables must be treated factorially in photoabsorbing VAT systems [2].

4. Inner filtering is spatial, not merely spectral

Inner filtering occurs when upstream components reduce or reshape the light available downstream. It depends on wavelength, path length, concentration, conversion and optical redistribution. A component can have acceptable spectral overlap with the source and still receive insufficient local excitation at depth.

For measured spectral transmittance $T(\lambda, z)$ to depth z , an optical-depth descriptor is

$$\tau(\lambda, z) = -\ln T(\lambda, z)$$

where τ remains an empirical descriptor of that specimen and collection geometry. In a scattering resin it must not be interpreted automatically as a molecular Beer–Lambert absorbance. Scherzer's depth profiling work showed that photoinitiator screening, photobleaching, absorber filtering and white pigmentation can produce different conversion-depth behaviour [1].

5. Photobleaching and photoproduct colour change the field

Photoinitiator or sensitiser absorption can decrease during irradiation, increasing penetration, while coloured photoproducts can introduce or shift absorption. Dyes and pigments can also bleach, react or change aggregation state. Consequently, the pre-exposure spectrum may not describe the later exposure field.

Time-resolved or dose-resolved spectra should be paired with conversion measurements. A decrease in absorbance is not proof of productive radical generation, and improved depth cure is not proof that colour stability improved. Clear-resin optimisation cannot be transferred automatically to a pigmented formulation, as direct clear-versus-pigmented photoinitiator comparisons have shown [7].

6. Measure conversion as a function of depth and side

Let $\alpha(z, t)$ denote conversion at depth z and time t for a declared reactive band. The depth gradient is

$$g_{\alpha}(z, t) = \frac{\partial \alpha(z, t)}{\partial z}$$

where g_{α} is a spatial conversion-gradient descriptor, not a material constant. Sampling volume, depth resolution, specimen orientation and surface designation must be reported.

Scherzer used real-time FTIR-ATR depth profiling to examine cure through acrylate systems [1]. Simon and Langenscheidt distinguished surface and deep conversion in a black UV-curable ink [3]. These studies support depth- and side-specific measurement; their films, bands and optical paths do not define a universal coloured-VAT profile.

7. Surface cure and through-cure answer different questions

Top-surface conversion is sensitive to oxygen, irradiance, colourant distribution and method sampling depth. Bottom or deep conversion is governed additionally by attenuation, scattering, substrate effects and prior layers. A cured depth or surviving thickness is a dimensional endpoint and cannot substitute for chemical conversion at either surface.

A minimum comparison should distinguish the irradiated surface, the opposite surface or interior, and the dimensional survival criterion. Simon and Langenscheidt demonstrated the value of separating surface and deep performance in a defined black formulation [3]. ER-196 retains the dedicated thin-film graphic-ink boundary where migration and surface performance impose additional requirements.

8. Pigment and dye competition are not interchangeable

A dissolved dye can often be treated initially through molecular absorption and concentration, subject to aggregation and reaction. A pigment introduces interfaces, particle-size distribution, agglomeration, multiple scattering and possible surface chemistry with the resin or initiator. Equal apparent colour or equal bulk absorbance does not imply equal cure behaviour.

Pigment dispersion can also be non-uniform with depth because of settling, flotation or recoating history. The qualification specimen must therefore represent the material age, mixing state and time between agitation and exposure. ER-216 does not prescribe dispersion processing, but it requires the dispersion state to be measured or bounded.

9. Chemistry changes the optical competition outcome

The same pigment can interact differently with radical acrylate, thiol–ene or hybrid formulations because oxygen response, propagation, gelation and photobleaching differ. Roper and co-workers studied pigmented thiol–ene systems using kinetic, optical, colour and morphology measurements [5]. Kardar and co-workers showed that a pigmented UV-curable system's observed response depended on irradiance and temperature [4].

These results do not create a universal chemistry ranking. They show that an exposure correction derived in a clear or chemically different resin is not automatically valid after pigmentation.

10. Colour state must be separated from cure state

Colour can change during initial exposure, washing, post-cure, water or solvent conditioning, thermal ageing and light ageing. The measurement condition must state illuminant, observer, background, geometry and specimen state according to the appearance method governed by ER-078. ER-216 uses the resulting colour-state evidence but does not redefine the colour metric.

An engineering response vector can be written as

$$\mathbf{r} = \left(\alpha_{surf}, \alpha_{deep}, h_c, \Delta C, \Delta d \right)$$

where α_{surf} and α_{deep} are surface and deep conversion under declared sampling methods, h_c is a declared cure-depth or dimensional endpoint, ΔC is change in the chosen colour metric, and Δd is dimensional change. All symbols refer to separately measured outputs. None is a proxy for the others.

11. Photoinitiator selection is a multi-output decision

Photoinitiator identity affects spectral competition, radical production, photobleaching, residual colour and post-cure evolution. Segurolo and co-workers directly compared commercial near-UV photoinitiator activity in clear and pigmented systems [7]. Kim and co-workers evaluated colour stability alongside conversion, dimensional accuracy and other properties in a defined printed dental resin [6].

Those studies support keeping conversion and colour in the same qualification matrix. They do not establish that one initiator is universally colour-stable or transferable between dental, coating, ink and filled-VAT formulations. Application-specific biological or migration conclusions remain outside ER-216.

12. Interpretation matrix

Observation	Supported interpretation	Not established
Colourant and initiator spectra overlap	Direct optical competition is possible	Local absorbed-photon share or conversion outcome
Bulk transmission decreases after adding pigment	The measured specimen attenuates more light	Absorption/scattering split or depth conversion
Top-surface conversion passes	The sampled surface met that conversion criterion	Through-cure, bottom conversion or dimensional accuracy
Cure depth increases with exposure	A dimensional endpoint changed in that system	Uniform conversion or preserved colour
One initiator gives lower colour change	Better colour retention under that protocol	Universal initiator superiority or equal cure state
Pigmented and clear systems respond differently	Colourant state altered the tested response	A universal exposure multiplier

13. Minimum reporting set

Report colourant identity, dye or pigment classification, surface treatment, concentration basis, dispersion state and material age; monomers, oligomers, photoinitiator and coinitiators; source spectrum, wavelength, irradiance and exposure sequence; formulation spectrum and collection geometry; specimen thickness, layer height, substrate and build orientation; atmosphere and temperature; mixing and settling interval; conversion band, calibration, sampling side and depth; cure-depth or dimensional criterion; post-cure and washing; colour metric and measurement geometry; conditioning and ageing; replicates, dispersion, spatial sampling and uncertainty.

Every numerical comparison must retain colourant state, chemistry, optical path or geometry, irradiation spectrum, atmosphere, conversion method and colour-test condition. Where absorption and scattering are separated by a model, report its assumptions and validation.

14. Knowledge boundary

Primary evidence establishes that coloured or strongly absorbing photopolymers can show depth-dependent conversion, distinct surface and deep response, chemistry-dependent pigment effects and photoinitiator-dependent colour evolution [1–7]. It does not establish a universal pigment, dye or photoinitiator ranking, spectral window, concentration, exposure multiplier, cure threshold or post-cure schedule. The evidence requires colour, conversion and geometry to remain distinct outputs.

15. Limitations

The sources span acrylates, epoxy-acrylates, thiol–ene systems, black ink, dental resin, clear and pigmented coatings, and particle-filled VAT formulations. Their colourants, sources, paths and analytical methods differ. Direct numerical comparison is not justified. This review does not define appearance acceptance, commercial colours, ink migration limits, pigment-dispersion recipes or application-specific dental thresholds.

16. Conclusions

Pigment, dye and photoinitiator competition is a spatially and temporally evolving formulation problem. Molecular absorption, particulate scattering, inner filtering, photobleaching and coloured photoproducts must be separated where the decision requires it. Surface conversion, deep conversion, cure depth, colour change and dimensional response are different measurands. A reliable qualification uses matched optical and chemical measurements in the actual formulation geometry and refuses universal exposure or colour corrections unsupported by that system.

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