

Ionising-Radiation Ageing of Printed Photopolymers: Dose, Atmosphere, Chain Scission, Crosslinking and Property Change

Interpreting radiation exposure through competing network reactions and measured functional drift rather than dose alone

Juan Segurola

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Correspondence: info@3Dresyns.com · www.3Dresyns.com

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Abstract

Ionising radiation deposits energy throughout polymer networks and can drive both chain scission and additional crosslinking. Which process dominates depends on backbone chemistry, dose, dose rate, oxygen availability, temperature, crystallinity or network heterogeneity, fillers and residual species. Printed photopolymers add spatial cure gradients and interfaces that may respond differently from homogeneous bulk specimens. Consequently, a single retained tensile-strength value after irradiation cannot identify mechanism or guarantee dimensional, dielectric or fracture performance. ER-387 requires the radiation field and atmosphere to be declared, distinguishes chemistry change from property change, and uses dose-series measurements to identify whether embrittlement, softening, swelling, mass change or interfacial degradation controls the service limit. [1-4]

Keywords: ionising radiation; photopolymer; chain scission; crosslinking; dose; dose rate; radiation ageing

1. Dose is necessary but not mechanistically sufficient

Absorbed dose measures deposited energy per unit mass, but polymers can respond through competing crosslinking and chain-scission pathways. Ashfaq and co-authors show that chemistry, oxygen, dose rate and physical state influence which pathway dominates. [1] A service claim therefore requires both the radiation field and at least one chemistry-sensitive response.

2. Atmosphere changes oxidation depth and post-irradiation evolution

Ionising radiation can drive chain scission and crosslinking concurrently, and the observed property change reflects their competition. Classical PMMA irradiation experiments showed that radiation quality can shift the balance between these mechanisms: low-LET gamma and electron irradiation favoured degradation in the tested PMMA, whereas high-LET ions promoted more crosslinking. The result should not be generalized numerically to photopolymer networks, but it establishes LET and chemistry as state variables rather than treating absorbed dose as a complete description. [1-5]

Atmosphere is equally important because oxygen converts radiation-generated radicals into oxidative pathways. Dose delivered in air, vacuum or inert gas can therefore produce different molecular-weight and surface outcomes. A qualification report should state radiation type, spectrum or energy, total dose, dose rate, temperature and atmosphere, together with starting conversion and post-cure. [1-4]

Oxygen can convert radiation-generated radicals into oxidative chemistry, while vacuum or inert environments suppress some of those reactions. Thick parts may develop an oxidised surface and a less oxidised core. Printed parts with pores or thin walls can shift that balance, so specimen thickness and atmosphere are part of the test definition.

Table 1. Radiation-ageing evidence chain.

Layer of evidence	Example measure	Question answered
field definition	radiation type, energy spectrum, dose, dose rate	what exposure was delivered?
chemistry/network response	FTIR, gel fraction, molecular-weight proxy, mass change	scission, crosslinking or oxidation?
thermal response	Tg, transition width or thermal stability	did network mobility change?
functional response	strength, elongation, fracture, dielectric or dimensional metric	does the intended function remain inside limits?

3. Property drift can be non-monotonic

A recent additive-manufacturing study gives a direct photopolymer anchor. Krizsma et al. applied Co-60 gamma post-treatment to material-jetting photopolymer parts at 0, 25, 50, 100 and 200 kGy. Tensile modulus increased from 1.92 GPa at 0 kGy to 2.76 GPa at 200 kGy, tensile strength from 38.1 MPa to 64.6 MPa, and glass-transition temperature from 46.7 °C to 59.6 °C; the study also reported little additional gain between 100 and 200 kGy for some responses, indicating saturation rather than a monotonic unlimited benefit. These results support a state model in which irradiation can increase crosslink density under the tested material-jetting and post-treatment conditions, but they do not establish the same response for other photopolymer chemistries or dose-rate regimes. [6]

Mechanical qualification should therefore track more than tensile strength. DMA, Tg, elongation, fracture response and mass or spectroscopy can reveal embrittlement or network change before strength falls. For optical or dielectric applications, transmission, colour and leakage/breakdown may be more sensitive than bulk strength. [1-6]

Additional crosslinking can initially increase stiffness while reducing ductility; later scission or oxidation can reverse the trend. A single endpoint at the highest dose can therefore hide a useful or dangerous transition. Dose-series data are preferred whenever a service limit is being set.

4. Printed state and interfaces are explicit factors

Cure conversion, layer orientation, filler content and residual species can change radical chemistry and fracture paths. Bulk resin literature is used to identify mechanisms, but transfer to a printed part requires confirming that the part-specific response follows the same trend.

5. Separate radiation ageing from sterilisation qualification

Dose-rate effects should be challenged directly when translating between gamma, electron beam and mission radiation. At the same total dose, radical recombination and oxygen diffusion can differ by orders of magnitude in time scale. Accelerated irradiation is acceptable only if the dominant chemistry and property trajectory remain equivalent within the intended decision. [1-4]

Spatial dose uniformity also matters for thick or filled printed parts. Attenuation and secondary-particle generation can create through-thickness gradients, while fillers can alter local energy deposition. Dosimetry should therefore be coupled to specimen geometry and density rather than reported only as a facility setpoint. [1-3]

ER-387 addresses radiation ageing as a materials phenomenon across service environments. ER-388 addresses requalification after a validated radiation sterilisation process. A sterilisation dose can contribute to cumulative radiation ageing, but the two decisions are not merged.

Table 2. Decisions supported by ER-387.

Decision	Evidence	Boundary
dose limit for function	dose series plus functional drift and uncertainty	valid for declared atmosphere and temperature
dominant degradation mechanism	chemistry/network data linked to property change	not inferred from colour alone
inspection interval or replacement point	measurable precursor linked to unacceptable drift	requires monotonic or otherwise modelled relation

6. Qualification statement

Radiation-induced dimensional change should be measured explicitly because network densification, volatilisation or differential cure can create shrinkage even when strength improves. For precision parts, coordinate metrology before and after exposure can be more relevant than a bulk mechanical test. [1-6]

Residual photoinitiator and unreacted groups can alter early-dose behaviour. Two specimens with the same nominal resin but different post-cure histories may show different radical yields and oxygen consumption. Starting conversion or a practical proxy such as FTIR residual double-bond signal should therefore be part of a mechanistic comparison. [1-6]

Surface and bulk radiation responses may diverge. Oxygen-rich surfaces can undergo oxidative scission while the interior crosslinks, producing a hard or embrittled skin over a differently evolving core. Microhardness, sectioned spectroscopy or depth-resolved microscopy can reveal such gradients. [1-6]

Radiation combined with mechanical preload can accelerate crack initiation because embrittlement and stress act together. Components expected to carry load during irradiation should therefore include stressed or constrained specimens rather than only freely supported coupons. [1-6]

Dose-rate equivalence should be rejected when the direction of property change differs across rates. In that case, a single total-dose lifetime model has no physical basis. Separate regimes or a chemistry-informed kinetic model are required. [1-6]

For qualification, the most conservative useful statement is often a bounded retained-property envelope over the tested dose-rate/atmosphere range. This is stronger than an unsupported radiation-hardness label and easier to update as additional exposure data accumulate. [1-6]

No universal radiation-resistant label is assigned. The output is a dose- and atmosphere-bounded response map for the printed state tested, with the mechanism and functional endpoint both recorded.

7. Dose-rate and post-irradiation effects

Dose measurement should be traceable to the specimen position. Facility nominal dose can differ from absorbed dose in the material because of geometry, shielding and composition. Dosimeters should bracket the specimen or be related through a validated dose map. [1-6]

Radiation temperature should be controlled because beam heating changes radical mobility and can alter the balance between recombination, crosslinking and scission. A temperature-matched control is therefore part of a mechanistic irradiation study. [1-6]

Oxygen diffusion can make thick parts chemically heterogeneous after irradiation in air. Surface oxidation may coexist with a less oxidised interior, so spectroscopy at only the outer surface cannot establish bulk state. Sectioned analysis or depth-sensitive methods should be used when wall thickness is relevant. [1-6]

Electrical and optical functions can drift independently of mechanical properties. For conductive or dielectric photopolymers, resistivity and breakdown should be included; for transparent materials, spectral transmission and haze should be measured. Radiation qualification is function-specific. [1-6]

Radiation-induced property improvement should be treated cautiously. An increase in Tg or modulus can accompany embrittlement, shrinkage or residual stress. The qualification endpoint should therefore require the full functional property set to remain inside limits, not reward movement in one favourable metric. [1-6]

If radiation is used intentionally as a post-treatment, process capability becomes part of quality control. Dose uniformity, batch geometry and thermal history must be controlled just as for UV post-cure, and the final state should be verified rather than inferred from exposure time. [1-6]

For ageing studies, the most useful future datasets will report chemical-state markers together with mechanical, optical and electrical properties over multiple dose-rate/atmosphere combinations. This would allow mechanism maps rather than isolated end-point comparisons. [1-6]

Equal absorbed dose delivered at different rates can change the balance between radical generation, oxygen diffusion and recombination. Where dose rate differs substantially from service, a comparison at more than one rate or a mechanistic justification is needed before extrapolation. Post-irradiation storage time is also fixed because chemistry can continue to evolve after the source is removed.

For radiation-sensitive optical or electrical functions, measurements are scheduled both promptly after exposure and after a defined conditioning interval. This separates transient radical effects from persistent network change.

8. Minimum radiation-ageing report

Radiation testing should include an unirradiated specimen that experiences the same thermal and atmospheric history as the irradiated group. Beam facilities can heat specimens or require vacuum/inert handling, and those secondary exposures can otherwise be misattributed to dose. [1-6]

Post-irradiation ageing should be sampled at defined times because trapped radicals can continue reacting after exposure. Mechanical or spectroscopic properties measured immediately, after days and after an accelerated oxidative hold can reveal whether the apparent endpoint is stable. [1-6]

Filled photopolymers require special attention because high-Z or absorbing fillers can alter local dose deposition, while conductive fillers can change charge dissipation. The same nominal facility dose may therefore create a different microscopic energy distribution than in an unfilled network. [1-6]

Radiation-induced crosslinking can improve modulus or T_g while reducing toughness or elongation. A qualification matrix should therefore include at least one stiffness/thermal metric and one failure/ductility metric so that an apparent performance improvement is not mistaken for universal durability. [1-6]

For space or nuclear service, cumulative dose should be paired with dose-rate and temperature scenarios representative of the mission. For deliberate post-treatment, process uniformity and dose mapping become manufacturing controls. These are different qualification questions even when the same radiation source is used. [1-6]

The evidence gap is systematic comparison of radical, cationic, hybrid and filled VPP networks under controlled gamma, electron and particle irradiation. Existing data demonstrate competing scission and crosslinking, but material-specific response maps are required before radiation-hardness claims can be generalized. [1-6]

A defensible lifetime model links dose and dose rate to measurable network-state variables rather than fitting property loss blindly. Gel fraction, spectroscopic markers or crosslink-density proxies can help identify whether the same mechanism persists across acceleration levels. A change in sign of modulus or T_g response is evidence that one extrapolation law no longer applies. [1-6]

The qualification envelope should include radiation type, dose, dose rate, atmosphere, temperature, shielding/geometry, initial cure and all functional metrics. Requalification is triggered by photoinitiator, pigment, filler or thickness changes that may change absorption or radical chemistry. [1-6]

Table 3. ER-387 reporting set.

Field	Required content
radiation field	type, energy where relevant, absorbed dose, dose rate and dosimetry method
environment	air/inert/vacuum, specimen temperature and packaging or shielding
material state	print/cure history, thickness, fillers/pigments and surface condition
mechanism evidence	chemistry, network or thermal response linked to the proposed degradation path
functional evidence	property used to set the dose limit and its uncertainty

This reporting set prevents a nominal dose value from being detached from the conditions that determine whether scission, crosslinking or oxidative degradation controls the response.

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L.; ER-387 contains no comparative recommendation between commercial products.

Data availability

ER-387 is a literature-based engineering review; no new experimental dataset was generated.