

Polyurethane, Polyurea and Urethane-Acrylate Photopolymers for Vat Photopolymerisation: Chemical Identity, Segment Architecture, Hydrogen Bonding, Hydrolysis and Qualification

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ER-103 · Engineering Review · Version 0.4 · 31 August 20

Statement of Significance

Polyurethane, polyurea and urethane-acrylate are frequently treated as interchangeable labels in photocurable materials, although they describe different structural facts. A urethane-acrylate oligomer is commonly converted into a network through acrylate polymerisation; the presence of urethane groups alone does not establish a conventional segmented polyurethane network. Urea groups can create stronger hydrogen-bonded associations, but neither bond density nor mechanical durability follows from the name. This review establishes a chemical-identity gate, links segment architecture and association to vat-photopolymerisation state, and defines the hydrolysis, thermal, liquid-exposure and retained-property evidence needed before a printable material is qualified by class or function.

Keywords: vat photopolymerisation; polyurethane; polyurea; urethane acrylate; polyurethane acrylate; non-isocyanate polyurethane; segment architecture; hydrogen bonding; hydrolysis; environmental ageing; qualification.

Abstract

Urethane- and urea-containing photopolymers occupy a large design space between low-viscosity printing resins, soft elastomers and highly crosslinked thermosets. Primary studies demonstrate flexible urethane-acrylate elastomers, multiple-hydrogen-bond poly(urethane-urea) networks, non-isocyanate acrylic polyhydroxy urethanes, dual-curable polyurethane acrylates and urea-containing photocurable monomers. These examples show that segment selection, reactive functionality, association, chain extension and post-cure can alter modulus, extension, toughness, swelling and print resolution. They do not establish a universal polyurethane property envelope. Chemical naming must identify the load-bearing network and the reaction that creates it: an acrylate-cured urethane oligomer, a step-growth polyurethane, a polyurea-containing network and a non-isocyanate polyhydroxy urethane are not equivalent structures. Hydrogen bonding can raise cohesion and dissipate energy, yet association is sensitive to temperature, water, competing solvents, conversion and morphology. Ester-bearing soft segments or pendant groups can introduce hydrolysis-sensitive sites, whereas ether-rich architectures create a different ageing balance; exact retention remains formulation- and state-specific. A defensible qualification programme therefore combines identity, conversion and extraction evidence with tensile and dynamic-mechanical response, water uptake, liquid exposure, thermal analysis, accelerated ageing and component-representative retained properties. This paper supplies that architecture without disclosing a proprietary formulation, ranking commercial materials or granting intended-use approval.

1. Scope and boundaries

ER-103 owns the identity and qualification of urethane- and urea-containing photocurable networks used in vat photopolymerisation. It covers polyurethane, polyurea, poly(urethane-urea), urethane-acrylate and polyurethane-acrylate terminology; hard- and soft-segment architecture; hydrogen bonding and phase organisation; VPP formulation state; hydrolytic and environmental ageing; and the evidence needed to connect chemistry to retained function.

The scope is separated from adjacent Engineering Reviews. ER-101 owns generic elastomer mechanics, including tear, creep, compression set and cyclic durability. ER-102 owns true silicone chemistry and the boundary between polysiloxanes and silicone-free silicone-like materials. ER-41 owns general chemical resistance and solvent uptake; ER-59 owns sequential dual cure; ER-63 owns covalent adaptable networks; ER-72 owns the general environmental-ageing framework; ER-73 owns interlayer cohesion and anisotropy; and ER-92 owns residual-reactant and manufacturing-conversion hazards [C1–C8]. ER-103 uses those domains only where urethane or urea chemistry changes the interpretation.

The paper does not supply a formulation recipe, assume that every commercial urethane resin is a polyurethane, infer hydrolysis resistance from one monomer name, or convert short-term thermal decomposition data into a service-life claim. Bio-based feedstock accounting belongs to ER-11, and recyclability through dynamic chemistry remains controlled by ER-63 [C4,C9].

2. Chemical-identity gate

A material name should state what is known about the load-bearing network, not merely what functional group appears somewhere in the formulation. Conventional polyurethane chemistry forms urethane linkages through reactions such as isocyanate with hydroxyl groups. Polyurea contains urea linkages, commonly formed from isocyanate and amine chemistry. Poly(urethane–urea) contains both. By contrast, a urethane acrylate is typically an oligomer or prepolymer carrying polymerisable acrylate functionality; irradiation builds the final network mainly through carbon–carbon propagation of those end or pendant groups. The cured network may contain many urethane groups while differing topologically from a classical segmented step-growth polyurethane.

Non-isocyanate routes require equally careful language. Buchheit et al. prepared acrylic polyhydroxy urethanes by reacting cyclic-carbonate methacrylates with diamines and then photopolymerising the resulting multifunctional urethane methacrylates [2]. The route avoids isocyanates in synthesis, but the exact network still depends on precursor structure, functionality, conversion and side reactions. The label non-isocyanate does not by itself establish reduced hazard, biodegradability, low extractables or environmental superiority.

Declared class	Minimum structural evidence	Claim that remains unproven
Polyurethane	Urethane linkages participate in the identified load-bearing polymer/network architecture	Segmented morphology, elastomeric response, hydrolysis resistance or service life
Polyurea / poly(urethane–urea)	Urea content and its network or chain role are established	A particular hydrogen-bond density, toughness or thermal limit
Urethane acrylate / PUA	Urethane-containing precursor and polymerisable acrylate functionality are identified	That the final network is a conventional polyurethane rather than an acrylate-cured network
Polyhydroxy urethane	Hydroxyurethane structure and synthetic route are supported	Non-toxicity, low emissions or recyclability
Urethane-modified photopolymer	An identified urethane-bearing constituent is present	Continuity, dominance or transfer of polyurethane-class properties

Table 1. Chemical-identity gate. Class names do not replace topology, composition and state evidence.

3. Segment architecture, association and phase organisation

Segmented polyurethane concepts divide the material into comparatively mobile soft segments and more cohesive hard segments containing urethane or urea groups. Soft-segment chemistry, length and glass transition influence low-temperature mobility, extensibility, water uptake and liquid affinity. Hard-segment fraction, sequence and association influence modulus, yield, dissipation and temperature dependence. These are design variables rather than guaranteed two-phase morphology. Evidence of microphase separation may require thermal, scattering, spectroscopic, microscopic or mechanical observations; a structural formula alone is insufficient.

Hydrogen bonds between urethane or urea groups can act as reversible physical associations. They may raise cohesion, create sacrificial interactions and contribute to rate-dependent energy dissipation. Patel et al. used an epoxy aliphatic acrylate/aliphatic urethane diacrylate system and reported formulation-specific elongation up to 1100% with Young's modulus from 0.58 to 4.21 MPa, interpreting the performance partly through hydrogen bonding [1]. This numerical result does not transfer outside its tested composition and state.

Association is conditional. Temperature changes bond lifetime and segment mobility; absorbed water or polar liquids can compete for hydrogen-bonding sites; post-cure changes conversion and network constraint; and ageing can alter morphology. Stronger association may improve room-temperature strength while raising viscosity, delaying relaxation or reducing low-temperature compliance. A mechanistic claim should therefore distinguish the existence of a functional group, evidence of association and proof that the association controls the measured response.

4. VPP formulation and process state

Vat photopolymerisation requires the uncured formulation to flow or recoat, absorb light within a controlled depth and develop sufficient green strength. Increasing oligomer molar mass or association can improve final cohesion while increasing resin viscosity. Reactive diluents reduce viscosity but may alter shrinkage, network heterogeneity, glass transition and extractable fraction. Functionality accelerates gelation and raises effective crosslink density, yet too much can reduce extension and increase cure stress. Photoinitiator identity, spectrum, absorber, inhibitor, oxygen, layer thickness and temperature jointly determine the conversion field.

Kuang et al. studied urethane-acrylate photo-inks for DLP and found that a continuous five-minute post-cure produced surface cracking in their system, whereas five one-minute exposures separated by two-minute pauses avoided those cracks without changing the reported double-bond conversion [3]. This is a useful process lesson, not a universal cure schedule: thermal gradients, oxygen, geometry, irradiance and resin absorption differ among setups. The observation shows why nominal total exposure cannot fully specify post-cure state.

Pien et al. varied PEG- and PPG-based urethane polymers and acrylate functionality, reporting a 0.4–5.3 MPa stiffness range in their study; higher acrylate content increased modulus and cure rate while reducing swelling [5]. Rudenko et al. compared ten urethane-acrylate oligomers and found that lower acrylate functionality reduced polymerisation rate and prolonged induction, while aliphatic substituents at matched functionality reduced viscosity and increased reactivity; a butyl-containing system showed approximately twice the impact toughness in that study [8]. These results support variable-by-variable screening, not class-wide rankings.

State variable	Why it matters in urethane/urea systems	Minimum report
Precursor identity and functionality	Determines network-forming route, strand length and gelation	Structure or controlled identifier; functionality distribution; lot
Reactive diluent and concentration	Controls viscosity, conversion, shrinkage, Tg and liquid affinity	Identity, fraction and whether reactive/non-reactive
Association and resin temperature	Hydrogen bonding can create temperature- and history-dependent viscosity	Temperature, dwell, mixing and viscosity method
Optical state	Initiator, absorber and colour control cure depth and conversion gradient	Spectrum, dose, layer, absorber and working-curve state
Wash, dry and post-cure	Residuals and secondary conversion alter modulus, swelling and ageing	Solvent, time, temperature, atmosphere and delay
Specimen age and conditioning	Dark cure, relaxation and moisture uptake can continue after printing	Time, humidity, temperature and storage history

Table 2. Minimum material–process–workflow state for transferable evidence.

5. Evidence routes and what they establish

The literature spans chemically and mechanically different systems. Buchheit et al. reported photocurable polyhydroxy-urethane thermosets whose functionalisation lowered viscosity to 26–156 Pa·s and, in their rigid systems, increased Young’s modulus from 2900 to 3700 MPa and glass transition from 135 to 204 °C [2]. Those results demonstrate a non-isocyanate molecular toolbox; they are not an elastomer benchmark and the reported viscosities remain setup-dependent.

Zhao et al. developed a dual-curable polyurethane-acrylate elastomer using a DCA chain extender and reported 15.8 MPa tensile strength, 499.1% elongation and 50 µm resolution for the tested formulation, with ionic zinc interactions and subsequent amide formation contributing to the final state [6]. The second reaction changes the material after the photoprinted geometry is fixed, so secondary-cure time and temperature are part of the identity of the tested object. ER-59 retains ownership of the general dual-cure framework [C3].

Liu et al. fragmented commodity thermoset polyurethane foam into a soluble mixture and formulated photo-printable resins with network-reforming additives [4]. This demonstrates a chemically enabled upcycling route, not closed-loop equivalence, universal feedstock tolerance or automatically favourable life-cycle impact. Huang et al. reported a PUA-based printed dielectric elastomer actuator delivering 270 mN blocked force and retaining 45% actuation at 100 Hz in the tested device [7]. Device output combines material, electrode, geometry and drive conditions and must not be restated as an intrinsic PUA property.

Evidence route	Supported conclusion	Transfer limit
Flexible urethane-acrylate blend [1]	Hydrogen-bonded urethane-containing acrylate formulations can combine low modulus and high extension	One formulation family; not all PUA or polyurethane
Acrylic polyhydroxy urethane [2]	Non-isocyanate synthesis can produce photocurable multifunctional urethane methacrylates	Rigid thermoset example; no generic elastomer or hazard conclusion
Post-cure scheduling [3]	Equivalent nominal exposure can yield different surface outcomes	Printer-, geometry- and thermal-state specific
PU-foam chemical upcycling [4]	Recovered PU-derived fragments can enter new photo-printable networks	Does not prove closed-loop recovery or feedstock independence
Segment/functionality series [5,8]	Backbone and acrylate functionality affect cure, swelling, viscosity and mechanics	Trends require matched formulation and process state
Dual-cure or device demonstrations [6,7]	Secondary chemistry and architecture can extend function	Final properties include cure history and device design

Table 3. Evidence routing. Demonstration values remain tied to the exact formulation and test state.

6. Hydrolysis, water and liquid exposure

Hydrolysis risk must be assigned to actual susceptible bonds and exposure state. Polyester soft segments and ester-bearing diluents or crosslinks introduce ester sites that can cleave in water, particularly when temperature, pH or catalytically active residues accelerate reaction. Polyether-rich soft segments remove that ester pathway from the segment itself, but they do not make the entire network hydrolysis-proof: urethane, urea, acrylate-derived junctions, additives, interfaces and residual species still determine behaviour. A material may also fail functionally through plasticisation or swelling before measurable backbone cleavage dominates.

Water interacts with urethane and urea groups and can compete with polymer–polymer hydrogen bonds. Early exposure may change modulus, glass transition, damping or dimensions reversibly; longer or harsher exposure can produce irreversible chemistry, leaching, cracking or interfacial damage. Mass uptake alone cannot distinguish bound water, free water, extractable loss and chemical degradation. ISO 62:2008 provides a water-absorption anchor and ISO 175:2010 provides a framework for liquid exposure, but the relevant output is retained function after controlled exposure and, where relevant, after drying [S5,S6].

A minimum study should record initial dry mass and dimensions, exposure medium composition, pH, temperature, oxygen state, specimen geometry, duration and agitation; then report wet-state and reconditioned mass, dimensions, tensile or dynamic-mechanical response, visual damage and chemical evidence appropriate to the suspected mechanism. Accelerated temperature must not silently introduce a different failure mechanism. Arrhenius extrapolation requires a stable mechanism and adequate multi-temperature data; it is not justified by one hot-immersion point.

7. Thermal and environmental ageing

Thermal qualification needs at least three distinct questions. Differential scanning calorimetry locates transitions and residual thermal events; dynamic mechanical analysis maps modulus and loss over temperature or frequency; thermogravimetry measures mass-loss behaviour under a specified atmosphere and programme. None directly supplies a long-term service temperature. ISO 11357-2:2020, ISO 6721-1:2019, ISO 6721-11:2019 and ISO 11358-1:2022 provide method anchors for those distinct measurements [S3,S4,S7,S8].

Urethane and urea associations may soften or reorganise before gross decomposition. Additional post-cure can temporarily increase conversion while oxidation, chain scission, hydrolysis or phase evolution later reduce retained properties. UV and weathering add spectral, humidity, oxygen and temperature coupling. ISO 4892-1:2024 defines general guidance and ISO 4892-3:2024 addresses fluorescent-UV exposure; neither converts exposure hours directly into outdoor life without a validated correlation [S9,S10].

The engineering endpoint should match the component: retained modulus, elongation, force, seal compression, dimensional tolerance, dielectric response or crack-free cycling. Report both during-exposure and post-recovery states when reversible plasticisation is plausible. A colour change can be useful diagnostic evidence but cannot substitute for mechanical or functional retention.

8. Qualification architecture

Identity is the first gate. Spectroscopy may support urethane, urea, acrylate conversion or degradation assignments, but overlapping bands and hydrogen-bond shifts require controlled interpretation. Precursor documentation, reaction stoichiometry, gel fraction, extractables, conversion and complementary thermal or chromatographic evidence may be needed to determine what became part of the network. Residual monomer or initiator must not be treated solely as a mechanical issue when exposure or hazard is consequential; ER-92 owns that assessment [C8].

Mechanical testing should use matched conditioning and complete curves. ISO 527-1:2019 supplies general principles and ISO 527-2:2025 specifies conditions for moulding and extrusion plastics; their application or declared adaptation to printed thermosets must include specimen geometry, orientation, rate and strain measurement [S1,S2]. Elastomeric systems may also require the rubber-oriented methods discussed in ER-101. Method choice follows material response and claim, not the convenience of a familiar coupon.

Qualification block	Minimum evidence	Release question
Chemical identity	Precursor route, functional groups, network-forming reaction, conversion, gel/extractable evidence	Is the class name structurally defensible?
Print and post-cure state	Viscosity/temperature, optical settings, orientation, wash, dry, dose and specimen age	Is the tested object reproducible?
Mechanical state	Tensile curve, DMA/DSC, relevant tear/set/cyclic evidence and anisotropy	Does the property exist over the required timescale and temperature?
Water and liquids	Uptake, dimensions, wet-state and dried-state property retention, chemistry where needed	Is change reversible, extractive or degradative?
Thermal and light ageing	Controlled atmosphere/exposure plus retained functional properties	Does the proposed duty remain within the evidenced window?
Component validation	Representative geometry, interfaces, duty cycle and failure criterion	Does coupon evidence survive application geometry?

Table 4. Qualification stack for urethane- and urea-containing VPP materials.

9. Failure-mode interpretation

- A post-cure strength increase accompanied by reduced extension can indicate higher conversion or crosslink density; verify conversion, T_g, full tensile response and shrinkage before attributing it to better polyurethane formation.
- A wet-state modulus decrease with recovery after drying suggests plasticisation or reversible association changes; incomplete recovery, mass loss or chemical change requires extraction and degradation analysis.
- Cracking after one continuous post-cure but not interrupted exposure can reflect thermal or shrinkage stress; record temperature and dose history rather than treating total time as the only state variable.
- High unnotched extension with early edge failure can reflect surface damage, conversion gradients or weak interlayer cohesion; inspect crack origin and orientation and route generic mechanics to ER-101 and ER-73.
- A second DMA transition or broad tan-delta feature may be consistent with heterogeneous segments or phase organisation but does not prove a named morphology without complementary evidence.
- A high TGA onset with early mechanical drift means decomposition is not the controlling service limit; qualify the relevant retained-property endpoint.
- Good initial performance followed by continued stiffening can arise from dark cure, residual reactivity or physical ageing; freeze specimen age and conversion state.
- Apparent recyclability after reprocessing must distinguish retained chemistry and properties from mere reshaping; dynamic-network and lifecycle claims require separate mass and property accounting.

10. Minimum workflow

- Define the permitted chemical name and identify which reaction creates the load-bearing network.
- Record soft segment, hard segment, urethane/urea content, polymerisable functionality and reactive diluent at the level allowed by confidentiality.
- Freeze resin temperature, viscosity method, optical formulation, printer settings, orientation, wash, drying, post-cure and specimen age.
- Confirm conversion, gel state and extractable fraction using methods capable of answering the actual identity and exposure questions.
- Measure tensile response and thermal/mechanical transitions under matched conditioning; add tear, set, cyclic or fracture tests when the duty requires them.
- Measure water uptake and exact-liquid response in both wet and reconditioned states, retaining mass, dimensions and relevant mechanical function.
- Separate DSC, DMA and TGA interpretations; none alone defines long-term service temperature.
- Age specimens under controlled heat, humidity, oxygen and light states and report retained function rather than exposure survival alone.
- Validate representative printed geometry and interfaces after coupon screening, including orientation and conversion-gradient risk.
- State the qualified window and exclusions. Do not transfer formulation-specific maxima to a chemical class or product family.

11. Research and standardisation priorities

- A reporting convention that distinguishes step-growth polyurethane, polyurea, urethane-acrylate precursor and acrylate-cured final network.
- Round-robin identity, conversion, extraction and mechanical testing of urethane-containing VPP systems under a shared process-state description.
- Matched polyester- and polyether-segment ageing studies that separate water plasticisation, extraction and bond cleavage.
- Direct measurements connecting hydrogen-bond population and lifetime to rate-, temperature- and humidity-dependent mechanics.
- Post-cure studies reporting irradiance, spectrum, specimen temperature, pauses, atmosphere, conversion gradients and residual stress.
- Multi-temperature retained-property datasets sufficient to test whether accelerated ageing preserves the same mechanism.
- Lifecycle accounting for recovered-polyurethane photoreins, including feedstock variability, reagent burden, recovery yield and retained performance.
- Component-level qualification linking coupon chemistry to interfaces, thin sections, trapped wash solvent and long-term duty.

12. Conclusions

Polyurethane, polyurea and urethane-acrylate photopolymers are not one material class with a common VPP property envelope. The defensible starting point is the load-bearing network and the reaction that forms it. Urethane or urea groups can organise segments and create hydrogen-bonded associations, while acrylate functionality often controls photogelation and permanent network formation. Their relative roles must be demonstrated rather than inferred from a product label.

Primary literature confirms several productive routes: flexible urethane-acrylate elastomers, non-isocyanate polyhydroxy-urethane thermosets, post-cure scheduling, dual-curable PUA, chemically upcycled polyurethane feedstocks and urea-containing physical associations. Each demonstration remains bounded by exact composition, printer state, cure history, specimen and method. The reported maxima are examples, not selection limits.

Qualification must then follow the likely failure mechanism. Water may plasticise, compete with association, extract residuals or drive hydrolysis; temperature may alter phase organisation and modulus well below mass-loss onset; light and oxygen add coupled ageing. Identity, conversion, extraction, tensile and dynamic-mechanical response, liquid exposure, ageing and component retention form one evidence chain. ER-103 closes with that chain and does not authorise a formulation, product equivalence or intended-use claim.

Limitations

This paper is a qualitative engineering review, not a systematic meta-analysis. The cited studies use different urethane and urea chemistries, diluents, printers, cure schedules, specimens and test conditions, so numerical values are not pooled or ranked. Several mechanistic interpretations require complementary analysis beyond the data typically reported. No proprietary composition, independent commercial-product assay, universal hydrolysis ranking, service-life model, intended-use qualification or regulatory conclusion is provided.

Author contributions

Juan Seguro: conceptualisation, evidence synthesis, boundary definition, engineering interpretation, manuscript preparation and final author verification.

Competing interests

The author is founder and CEO of 3Dresyns by Resyner Technologies S.L. No comparative product recommendation is made.

Data availability

No new experimental dataset was generated for this review. Scientific statements derive from the cited primary literature and standards. The review package includes a QA report and source-ledger summary for independent full-manuscript review.

Company information

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Related Engineering Review boundaries

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Version note

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