

Transcarbamoylation and Urethane-Exchange Networks in Photocurable Materials: Catalysis, Creep, Repair and Reprocessing

Dynamic urethane and urea exchange, activation windows and qualification of reprocessable photocurable networks

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Abstract

Urethane and carbamate exchange reactions can convert permanently crosslinked polyurethane-like photopolymers into networks that relax, repair or reprocess at elevated temperature. The relevant chemistry includes catalyst-promoted urethane-urethane exchange, hydroxyl-mediated transcarbamoylation, hindered-urea pathways that generate or exchange urethane bonds, and related covalent adaptable network architectures. This review distinguishes the photochemical step that fixes printed geometry from the thermal or chemical exchange processes that subsequently change network topology. The central engineering problem is separation of timescales: the printed part must remain dimensionally and mechanically stable during service, yet exchange must become sufficiently fast under a controlled repair or reprocessing treatment. Published polyurethane-vitrimer and photo-printable dynamic-network studies show that catalysts, free hydroxyl content, steric environment, temperature and network architecture strongly affect stress relaxation and recyclability. However, fast relaxation can also increase creep, catalyst residues can alter ageing, and post-print exchange may change shape as well as properties. A qualification framework is proposed around exchange-mechanism identification, relaxation and creep, thermal history, catalyst retention, recovery efficiency, dimensional fidelity and repeated reprocessing cycles. Keywords: transcarbamoylation; urethane exchange; polyurethane vitrimer; photocurable network; DLP; stress relaxation; creep; reprocessing; hindered urea

1. Significance and scope

Polyurethane and poly(urea-urethane) networks are attractive for photocurable materials because urethane chemistry can provide a broad range of stiffness, toughness and segmental architecture. Conventional thermoset networks, however, are difficult to reshape or recycle once crosslinked. Dynamic urethane and urea chemistries introduce exchange pathways that can preserve network connectivity while allowing topology change. This review owns transcarbamoylation and urethane-exchange networks in photocurable materials: catalysis, creep, repair and reprocessing. It does not replace ER-311 on transesterification vitrimers or ER-312 on disulfide exchange. Hindered urea is considered only where it couples directly to urethane formation, exchange or the qualification of polyurethane-like printed networks.

1.1 Corpus boundary

ER-13 retains the umbrella scope for self-healing and interlayer repair across photopolymer additive manufacturing. ER-113 retains acid-triggered de-crosslinking, reprocessing and polymer recovery. ER-311 retains transesterification vitrimers, and ER-312 retains non-cyclic disulfide-exchange networks. ER-316 is limited to transcarbamoylation, urethane exchange and dynamic urea/urethane network architectures in photocurable materials, including the distinction between associative exchange, dissociative urethane reversion and hindered-urea dissociation.

2. Exchange mechanisms and terminology

Transcarbamoylation is an exchange of carbamate functionality, commonly involving a urethane group and an alcohol. Depending on formulation, the process may be catalyst-promoted or may exploit built-in neighbouring hydroxyl groups. Urethane-urethane exchange can also occur under appropriate catalytic conditions. Depending on urethane structure and conditions, exchange may be associative or may involve dissociative urethane reversion; associative pathways can enable stress relaxation without a large loss of crosslink density. The term polyurethane vitrimer should therefore be reserved for networks in which topology rearrangement is experimentally demonstrated and linked to an exchange mechanism. A decrease in modulus after heating is not proof of exchange, because thermal softening, phase transitions, residual monomer or partial degradation can produce similar macroscopic effects. [1,5,6]

3. Catalysis, free hydroxyl groups and activation window

Polyurethane-vitrimer literature shows that catalysts can accelerate urethane exchange but introduce additional variables: catalyst concentration, mobility, deactivation, extraction and toxicity. Catalyst-free approaches based on poly(hydroxy urethane) architectures instead use pendant hydroxyl groups to promote transcarbamoylation, typically at elevated temperature. Catalyst identity matters because organometallic, base and Lewis-acid catalysts can differ in selectivity and thermal stability. A catalyst that accelerates exchange during an accelerated test may also catalyse side reactions during ageing. Where catalyst migration or extraction is possible, its concentration after washing and after repeated reprocessing should be treated as a state variable. For photocurable materials, the activation window must be compatible with the photopolymer network. A printed object can contain acrylate, methacrylate, thiol-ene or other covalent structures in addition to urethane segments. Exchange

treatment should not be assumed to leave these structures unchanged. Post-treatment can simultaneously drive residual conversion, physical ageing, phase rearrangement and urethane exchange. [1]

4. Photo-printable dynamic polyurethane networks

Photo-printable dynamic networks containing hindered urea bonds and pendant hydroxyl groups demonstrate how two exchange modes can be programmed into one printed network. Homolytic hindered-urea exchange can support geometric reconfiguration, while conversion of hindered urea to urethane through reaction with hydroxyl groups can alter mechanical properties. This is a useful example of orthogonal post-print programming, but it also illustrates why the mechanism must be tied to the exact thermal protocol. Recent DLP-compatible polyurethane and poly(urea-urethane) systems extend the concept to reprocessable thermosets. The literature supports feasibility of photocurable resins that can later be hot-pressed, remoulded or recycled, but the temperatures and pressures required vary widely. Reprocessability should therefore be reported as a process window rather than as a binary material attribute. The photopolymerisation route should also be separated from the dynamic-bond route. Acrylate or methacrylate conversion can determine green strength and feature fidelity, while urethane or urea exchange becomes relevant later. Calling the whole system a dynamic photopolymer can obscure which bonds actually carry the printing process and which bonds govern rework. Where hindered urea is used, steric substitution changes bond dissociation and exchange behaviour. Hindered-urea chemistry should not be generalised to ordinary urea or urethane linkages, whose kinetic barriers and hydrogen-bonding environments differ. [2-5]

5. Stress relaxation versus creep

Stress relaxation is commonly used to demonstrate vitrimer behaviour because exchange allows the network to dissipate imposed stress. The same molecular mobility can cause service creep when a constant load is applied. These tests answer different questions and should be paired. A robust comparison reports temperature, specimen dimensions, strain level, atmosphere, conditioning and the fitted relaxation model. Arrhenius analysis is useful only over a regime in which the same mechanism dominates. Near phase transitions or when exchange competes with degradation, a single activation energy can be misleading. [1-4]

6. Repair, reprocessing and recycling

Repair may involve crack closure, interfacial welding or recovery of mechanical performance without gross shape change. Reprocessing requires larger-scale topology rearrangement, usually under heat and pressure. Recycling may mean remoulding the same network, chemically recovering constituents, or blending reprocessed material into another polymer stream. These routes should not be conflated. For urethane-exchange systems, repeated processing can alter catalyst distribution, microphase separation, residual hydroxyl content and the balance between hard and soft segments. Mechanical retention after one cycle is therefore not a sufficient durability claim. Multiple-cycle testing with thermal and chemical characterisation is needed. [2-6]

7. Minimum qualification matrix

A qualification programme should identify the exchange route, establish the activation window and then test whether service stability and post-service rework can coexist. The most important comparison is between the timescale of exchange under intended service and the timescale under deliberate repair or reprocessing.

Table 1. Minimum qualification matrix for transcarbamylation and urethane-exchange photocurable networks.

Domain	Minimum measurement	Primary failure interpretation
Mechanism	Spectroscopic or chemical evidence consistent with urethane/urea exchange under the stated treatment	Thermal softening or post-cure can be misidentified as dynamic exchange
Dynamics	Stress relaxation at multiple temperatures with model residuals and regime definition	A single relaxation time is insufficient to establish a stable exchange law
Service stability	Creep, dimensional retention and ageing below the rework window	Fast exchange can become unacceptable load-dependent deformation
Catalyst / hydroxyl state	Catalyst retention or leaching where used; hydroxyl availability before and after cycling	Exchange capacity and ageing may drift with composition
Repair / reprocess	Defined weld, damage or hot-press protocol with matched controls	Recovery must be separated from simple annealing
Repeated cycles	Mechanical, dimensional and thermal metrics after multiple cycles	Accumulated degradation or phase change can masquerade as reversible processing

8. Interpretation and design boundary

The engineering target is not the fastest possible transcarbamylation. A network that relaxes rapidly near service temperature may be unsuitable despite excellent reprocessability. Conversely, a network that requires extreme temperature or pressure to exchange may be impractical to repair even if the chemistry is formally dynamic. The preferred design window therefore separates three states: processing, service and rework. Photocuring must generate sufficient green strength and dimensional fidelity; service must suppress unwanted topology change; and rework must accelerate exchange without causing unacceptable degradation or loss of geometry. These states should be demonstrated experimentally rather than inferred from chemical structure alone.

Table 2. Interpretation matrix for urethane-exchange network observations.

Observation	Plausible interpretation	Discriminating control
Modulus falls during heating	Thermal softening, phase change or exchange may contribute	Isothermal recovery, spectroscopy and matched non-dynamic control
Stress relaxes rapidly near service temperature	Exchange window may overlap service and create creep risk	Long-duration creep and dimensional testing under representative load
Hot-pressed material regains tensile strength	Network reconnection is possible, but annealing may also contribute	Unreprocessed annealed control and fracture-location analysis
Relaxation slows after cycling	Catalyst loss, hydroxyl consumption or morphology change may limit exchange	Catalyst/functional-group tracking plus thermal analysis
Reprocessed part is stronger but less ductile	Phase segregation, residual conversion or network densification may dominate	DMA/DSC, conversion measurement and swelling/crosslink comparison

9. Limitations and evidence gaps

Photocurable urethane-exchange systems are still represented by a limited set of chemistries and processing windows. Data from bulk polyurethane vitrimers can establish mechanisms but cannot by itself prove DLP or SLA printability, optical stability or dimensional fidelity. Relaxation data are often collected at temperatures well above intended service. Extrapolation to lower temperature is uncertain when phase morphology, catalyst state or residual conversion changes across the range. Repeated reprocessing studies also vary in material yield, pressure and addition of virgin polymer. Circularity claims should therefore be interpreted with a complete mass balance and process history rather than mechanical retention alone. [1-6]

10. Conclusions

Transcarbamoylation and urethane-exchange chemistries can add repair, reprocessing and recycling functions to photocurable polyurethane-like networks. Published work supports both catalyst-assisted and catalyst-free pathways, and recent 3D-printing studies demonstrate dynamic urea/urethane architectures with programmable post-print response. Qualification must nevertheless distinguish exchange from thermal softening, post-cure and degradation. Stress relaxation should be paired with creep; reprocessing should include dimensional and mechanical retention; catalysts and hydroxyl groups should be tracked across ageing and cycling. The decisive variable is the separation of timescales between stable service and deliberate network rearrangement. [1-6]

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Competing interests

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

Data availability

No new experimental dataset was generated for this review. The analysis is based on the cited literature and the stated engineering scope.