

Printed Photopolymers in Harsh Chemical-Process Environments: Mixed Chemicals, Temperature, Stress and Barrier Failure

Qualifying chemical service by coupled sorption, reaction and stress instead of extrapolating from room-temperature immersion tables

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Abstract

Chemical compatibility tables are useful screens, but harsh process service combines composition, concentration, temperature, exposure time, stress and replenishment of the fluid. A photopolymer may show little mass change in an unstressed immersion specimen yet crack under tensile stress because sorption lowers local cohesive strength, or a barrier layer may fail first and expose a more vulnerable substrate. Mixed solvents and reactive chemicals can also change swelling kinetics and extract residual network species. ER-389 therefore separates unconstrained immersion from environmental stress cracking, permeation and barrier integrity. The qualified envelope is defined by actual fluid composition, temperature, stress state and exposure history, with acceptance based on retained function and fracture resistance rather than appearance alone. [1-4]

Keywords: chemical resistance; photopolymer; environmental stress cracking; immersion; mixed chemicals; barrier failure

1. Immersion screening and stressed service answer different questions

ISO 175 deliberately addresses unconstrained immersion and excludes environmental stress cracking, which is treated in ISO 22088. [1-3] That separation is central for printed photopolymers because a fluid can cause modest swelling in an unstressed coupon yet sharply reduce crack resistance under tensile stress.

2. Define the process fluid as a composition, not a trade name

Chemical compatibility must be tested under stress because environmental stress cracking can occur at concentrations that cause little mass uptake or visible swelling in an unloaded coupon. In polycarbonate, constant-strain experiments with isopropanol, methanol and glycol ether showed strongly different critical strains and rapid failure in the most aggressive combination. The exact values are material-specific, but the study demonstrates that chemical identity and applied strain form one coupled state variable. [1-5]

Interfaces can dominate real components. A 2026 PMMA automotive study reproduced field environmental-stress cracking and found bonded interfaces much more susceptible to crack initiation than single-material regions under its test conditions. Printed assemblies therefore need separate challenges at bonds, inserts, coatings and local notches rather than relying on bulk immersion coupons. [6]

Qualification records constituents, concentration ranges, water content, pH where relevant, contaminants and temperature. Mixed chemicals can change solubility and reaction pathways relative to pure-fluid data. Batch composition limits become part of the qualified envelope.

Table 1. Chemical-process exposure modes.

Exposure mode	What it reveals	Typical failure signature
unstressed immersion	sorption, extraction, swelling or chemical attack	mass/dimension change, softening, discoloration
constant load in fluid	environmental stress cracking susceptibility	crazing, delayed fracture or life reduction
pressure gradient/permeation	barrier transport under chemical exposure	breakthrough or flux increase
cyclic wet/dry or chemistry change	reversibility and interface durability	cracking, delamination, retained swelling

3. Temperature moves both transport and reaction rates

Mixtures cannot be screened safely by testing each component independently. Competitive sorption, plasticisation and reaction can be non-additive, while temperature changes both solubility and polymer relaxation. A qualification matrix should prioritize credible service mixtures and excursions rather than attempting an impractical exhaustive chemical list. The mixture composition, concentration tolerance, temperature and exposure renewal schedule must be controlled. [1-6]

Mechanical preload should represent the component state. Constant strain, constant load and residual moulding/printing stress can produce different crack kinetics. For seals and pressure boundaries, chemical exposure should be combined with representative compression or tensile stress and followed by leak or fracture testing. [1-6]

Elevated temperature can accelerate diffusion and chemical reaction while simultaneously changing viscoelastic stress relaxation. An accelerated test therefore records which response is being accelerated. Arrhenius extrapolation is not assumed when swelling, phase change or a different degradation reaction appears.

4. Environmental stress cracking needs fracture evidence

The combined effect of solvent and tensile stress can exceed the sum of their isolated effects. The ISO 22088 methods provide ranking approaches under controlled tensile loading or deformation. Both cited 2006 editions remain current at the time of this review but are

flagged by ISO as under revision, so edition status must be rechecked when the qualification plan is frozen. [2,3] ER-389 supplements them with microscopy or fracture inspection so that bulk softening is not confused with craze- or crack-controlled failure.

5. Barrier layers and coatings fail at defects and edges

Mass and dimensions are necessary but not sufficient diagnostics. Solvent-induced crazing can reduce fracture resistance before large weight change occurs, and extraction of unreacted species can cause mass loss while the network initially stiffens. The measurement set should include uptake/extraction, hardness or DMA, tensile or flexural response, fracture or crack-growth inspection and surface chemistry where reaction is suspected. [1-6]

Barrier coatings should be tested for defects and edge attack. A coating that slows bulk uptake can still fail at scratches, corners or interfaces, creating under-film transport. Cross-sections after exposure are needed to establish whether protection is uniform and whether swelling mismatch is generating delamination. [1-5]

A chemically resistant coating can protect a less resistant printed substrate only while continuity and adhesion are retained. Qualification includes edges, holes, threads and representative surface roughness because a flat coated coupon can miss the first barrier-failure location.

Table 2. Acceptance logic for harsh chemical service.

Evidence block	Accept when	Re-test after
immersion response	mass, dimensions and critical properties stabilise within limits	fluid composition or temperature changes
stressed exposure	no unacceptable ESC or fracture-life loss	stress state or geometry changes
barrier integrity	no defect-driven breakthrough or delamination	surface prep, coating or print texture changes
recovery	post-rinse/dry state remains functional where recovery is claimed	cleaning or regeneration process changes

6. Qualification outcome

Qualification should also consider concentration gradients inside thick parts. Surface layers may swell or react first, creating residual stresses against a drier core. Section thickness can therefore change cracking susceptibility even when equilibrium compatibility is similar. Thickness series or diffusion modelling can determine whether a coupon represents the intended wall. [1-6]

Cyclic chemical exposure can be more damaging than continuous immersion because swelling and deswelling repeatedly load the network. Where cleaning, batch processing or intermittent spills are credible, repeated wet-dry or concentration cycles should be included instead of assuming that equal cumulative exposure time is equivalent. [1-6]

Mechanical joints deserve separate chemical testing. Adhesives, primers, sealants and metal/polymer interfaces can absorb process fluids differently from the bulk printed resin. Loss of adhesion or under-film transport can become the first failure mode even when neat-resin coupons appear stable. [1-6]

Analytical chemistry can strengthen diagnosis. FTIR, Raman, chromatography of extracts or surface spectroscopy can distinguish reversible sorption from hydrolysis, oxidation or extraction of residual constituents. The method should be selected according to the suspected mechanism rather than added as an untargeted characterisation step. [1-6]

A practical screening hierarchy starts with unstressed immersion, then stressed coupons, then representative interfaces and finally a subcomponent under service temperature and chemical sequence. Advancing only the combinations that survive each stage reduces test burden while preserving mechanism coverage. [1-6]

The final engineering decision should specify both allowed and excluded conditions. If evidence covers one solvent blend at 25 degrees C and moderate strain, the qualification should not silently extend to concentrated cleaning fluid, elevated temperature or higher residual stress. Explicit exclusions are part of a scientifically useful compatibility statement. [1-6]

ER-389 produces a fluid-composition, temperature, stress and time envelope. Room-temperature soak data alone are screening evidence and cannot be promoted to a harsh-process qualification. Scope boundary: ER-389 owns chemically aggressive process environments defined by composition, concentration, temperature, stress and time. High-pressure permeation and decompression belong to ER-385, while seawater conditioning, biofouling and marine fatigue belong to ER-386. Chemical-compatibility evidence therefore does not substitute for pressure-service or subsea qualification.

7. Kinetics, saturation and reversibility

Kinetic analysis should separate uptake, reaction and mechanical damage. Early mass gain can be dominated by sorption, later mass loss by extraction or dissolution, and crack growth can accelerate transport further. Sampling several intermediate times is therefore more informative than comparing only pristine and final states. [1-6]

Reversibility should be tested by controlled desorption and remeasurement. Recovery of mass does not prove recovery of fracture resistance or dimensions, while persistent mass change can reflect extracted species rather than network scission. [1-6]

Temperature ramps should avoid crossing transitions unintentionally. Near T_g, stress relaxation and diffusion can accelerate sharply, changing the failure regime. If service crosses such a transition, separate low- and high-temperature mechanisms should be characterised rather than collapsed into one compatibility rating. [1-6]

Chemical attack at interfaces should be examined with cross-sections. Wicking along bondlines or layer boundaries can penetrate much faster than bulk diffusion and may be invisible from the external surface until debonding occurs. [1-6]

Residual stress from printing and post-cure should be treated as part of the applied stress state. Annealing or additional cure can change environmental stress-cracking susceptibility even when nominal chemistry is unchanged. Bridging studies are needed after such process changes. [1-6]

For process plants, excursions can dominate lifetime. Short exposure to a high concentration during cleaning or upset conditions can initiate cracks that later propagate during normal service. Qualification should therefore include credible transient maxima rather than only nominal steady composition. [1-6]

The final compatibility statement should identify the tested mixture, temperature, stress, time and specimen state. A broad label such as 'chemical resistant' discards the variables that control failure and should not be used as a substitute for the qualified envelope. [1-6]

Sorption-driven mass change may approach equilibrium slowly, while chemical reaction or extraction can continue after apparent mass saturation. Time-series measurements are therefore used to distinguish diffusion-limited uptake from ongoing degradation. After exposure, a controlled rinse/dry step can reveal which changes are reversible and which reflect permanent network or interface damage.

For mixed chemicals, the process composition is refreshed or monitored when preferential evaporation, reaction or absorption could shift concentration during a long test. Otherwise, the specimen may experience a different fluid from the one specified.

8. Minimum harsh-chemical reporting set

Chemical-service qualification should include start-up, steady operation, shutdown and cleaning fluids when they differ. A component may tolerate the process fluid but crack during cleaning because temperature, concentration or imposed stress changes. The service history is therefore a sequence of chemical states rather than one immersion condition. [1-6]

Extraction and swelling can be reversible while stress cracking is not. Measuring mass only after drying can erase evidence of transient plasticisation that occurred under load. Wet-state dimensions and mechanical testing, or at least a defined transfer time from bath to test, are needed when the service component is loaded while saturated. [1-6]

Crack initiation sites should be mapped against print orientation and local geometry. Layer interfaces, support-contact surfaces and sharp internal corners may interact with chemical plasticisation to reduce the effective critical strain. Smooth bulk coupons should therefore be supplemented with representative notched or joined specimens. [1-6]

For mixed chemicals, analytical verification of bath composition can matter during long tests because preferential evaporation, uptake or reaction changes concentration. Closed versus open exposure cells and solution renewal schedules should be declared. [1-6]

Barrier qualification should include cyclic damage. A coating may remain intact during static immersion but crack under strain or thermal cycling, exposing the substrate abruptly. Coated specimens should therefore be flexed or thermally cycled within the intended service envelope before and after chemical exposure. [1-6]

The central evidence gap is a mechanistic database for crosslinked VPP networks that links solvent parameters, network conversion and applied stress to crack initiation. Until such data exist, qualification should rely on direct service-mixture testing under representative stress rather than compatibility tables based solely on unstressed immersion. [1-6]

Service-life acceleration is valid only while the same failure mechanism persists. Raising temperature may move the polymer through T_g or change sorption regime; increasing chemical concentration can change from slow plasticisation to dissolution or reaction. Arrhenius or time-temperature models should therefore be bounded by spectroscopic, mechanical and morphological evidence of mechanism continuity. [1-6]

The qualification envelope should be written as chemical composition x concentration x temperature x stress x time, with explicit acceptance metrics. Any formulation or post-cure change that alters crosslink density, residual monomer or polarity should trigger bridging because those variables directly affect sorption and stress-cracking susceptibility. [1-6]

Table 3. ER-389 reporting set.

Block	Required information
chemical environment	constituents, concentration range, impurities, pH if relevant and renewal/monitoring method
thermal/mechanical state	temperature, load or strain, pressure if applicable and exposure duration
material state	print/cure history, thickness, surface finish and barrier/coating details
response	mass/dimensions, critical property retention, crack/fracture evidence and barrier breakthrough
recovery	post-exposure conditioning and whether function is reversible or permanently changed

A compatibility claim that reports only appearance or mass change remains a screening result. Harsh-process qualification requires the stressed functional response that controls actual service failure.

References

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L.; ER-389 contains no comparative recommendation between commercial products.

Data availability

ER-389 is a literature-based engineering review; no new experimental dataset was generated.