

Adhesion of Photopolymer Coatings and Printed Features to Metals: Oxide State, Surface Preparation, Cure Stress and Durability

A metal-specific qualification architecture from adherend identity to aged failure locus

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Abstract

Adhesion of a photocurable coating or printed feature to a metal is not a property of the resin alone. It is the response of a declared alloy, its near-surface oxide, hydroxide and contamination state, the applied liquid, the evolving cured network, the specimen geometry and the conditioning history. A contact angle, cross-hatch class or pull-off strength can be useful, but none identifies the controlling interface or establishes durability by itself.

This review defines a metal-specific qualification architecture. It begins with alloy and surface-state identity, verifies what cleaning, abrasion, activation, conversion or priming changed, and separates wetting, interfacial chemistry, cure conversion, residual stress and mechanical failure. It then requires locus-resolved adhesion testing before and after controlled humidity, immersion, thermal, corrosion or deformation histories. The evidence supports paired chemical and mechanical measurements and shows why aluminium, copper, steel and zinc-coated substrates cannot be placed on a universal adhesion scale. It does not establish a commercial preparation recipe, universal roughness or surface-energy target, transferable cure-stress limit, adhesion threshold, ageing acceleration factor or service-life claim.

Keywords: photopolymer adhesion; metal oxide; surface preparation; cure stress; failure locus; durability; corrosion; photocurable coating

1. Significance and scope

The term “metal substrate” hides the variables most likely to govern adhesion. Alloying, temper, fabrication history, oxide growth, hydroxylation, adsorbed water, organic contamination, corrosion products and previous treatments can all alter the surface presented to a photocurable liquid. Cure then changes the other side of the interface through conversion, vitrification, shrinkage, modulus development and thermal contraction. The measured response is therefore a coupled system rather than an intrinsic coating constant.

ER-221 addresses the evidence needed to qualify adhesion of photocurable coatings and printed features to metals. It does not prescribe a production process. Its central question is whether the declared substrate state, interphase, cure history, stress state, mechanical test and ageing history form a traceable chain that supports the intended use.

1.1 Corpus boundary

ER-053 retains general substrate and build-platform adhesion, wetting and detachment in vat photopolymerisation. ER-195 retains generic cure-shrinkage stress models and substrate-modulus or thermal-mismatch analysis. ER-165 and ER-186 retain structural joining and general light-curable-adhesive or bondline formulation. ER-168 retains coatings and encapsulation on reactive printed photopolymer substrates. ER-079 retains metallisation and electroforming on photopolymer parts. ER-072 and ER-170 retain general environmental ageing and accelerated-life claims. ER-166 retains inserts, threads, press fits and load introduction. ER-172 retains incoming raw-material acceptance, and ER-205 retains broader spatial cure-state mapping and propagation questions. ER-221 is restricted to metal-specific substrate state, interphase evidence, adhesion measurement, failure locus and durability.

2. Define the adherend as a measured material state

The adherend specification should identify the metal or alloy, grade and temper where relevant, forming or machining history, exposed face, coating or plating, storage history and time since final preparation. A surface that is nominally aluminium may present aluminium oxide, hydroxylated regions, machining residues, adsorbed organics or a conversion layer. A steel substrate may be bare, galvanized, phosphated, passivated or covered by corrosion products. Those states are not interchangeable.

At minimum, record the preparation sequence, elapsed time to coating, storage atmosphere and handling. Surface chemistry should be measured when a mechanistic claim is made. X-ray photoelectron spectroscopy, infrared methods, Raman spectroscopy, Auger analysis or another justified technique may identify elemental and functional states; topography and roughness require a separate method. Moritz and co-workers combined several surface-sensitive methods on native copper and aluminium oxides and resolved hydrogen-bonding and ionic-carboxylate evidence for an adjacent cyanoacrylate system [1]. That result demonstrates why the oxide and the interface must be measured. It does not establish the mechanism of a radiation-cured acrylate coating.

3. Verify what surface preparation changed

Cleaning, abrasion, plasma treatment, conversion coating and priming are process names, not material states. Two nominally identical treatments can leave different contamination, oxide chemistry, roughness, wettability or weak boundary layers. Qualification should compare the initial and final surface using measurements aligned with the proposed mechanism.

A preparation record should include bath or tool identity, controlled variables, rinse and drying history, handling, delay before coating and the surface measurements that verify the change. Contact angle can indicate a change in wetting response but cannot prove oxide removal, chemical coupling or absence of contamination. Roughness can increase apparent area or provide mechanical interlocking while also trapping contamination or generating stress concentrators. Neither quantity is a universal target.

Aslamazova and co-workers related XPS-resolved near-surface chemistry of several metal substrates to acrylic-polymer response [2]. Their correlations support direct chemical characterization but do not produce a transferable oxide ranking. A process is qualified only for the declared alloy, surface state, formulation and timing.

4. Separate wetting from durable adhesion

A liquid must reach the surface, but favourable wetting is not equivalent to a durable interface. A contact angle is affected by liquid composition, surface heterogeneity, roughness, absorption, evaporation and time. It does not measure interfacial fracture resistance or identify whether failure will occur at the coating–oxide boundary, inside a conversion layer, within the oxide, in the coating or in the metal.

Wetting evidence should therefore be paired with conversion and mechanical tests. The liquid state at application, coating thickness, levelling time, atmosphere and temperature must be declared. If a primer or conversion layer is present, its continuity and adhesion to the metal require independent verification. The final joint or coating test cannot assign which interface was strengthened.

Onen and co-workers evaluated photocurable coatings on a declared aluminium-alloy surface through formulation, cure, wetting and coating-property measurements [3]. Yan and co-workers combined cure-time variation with adhesion, morphology and corrosion-related observations for an aluminium-containing UV-curable coating system [4]. These studies illustrate multi-response evaluation; their numerical optima and test classes remain specific to their formulations and procedures.

5. Treat interfacial chemistry as evidence, not assumption

Proposed hydrogen bonding, acid–base interaction, coordination, covalent coupling or ionic bonding should be linked to an analytical observation and an appropriate control. Functional groups present in the bulk formulation may be depleted, shielded or reoriented at the interface. Conversely, a spectroscopic change can arise from cure, hydrolysis or oxidation rather than bonding to the metal.

Useful controls include the uncoated prepared metal, the coating cured away from the metal, a surface-state comparator and a formulation lacking the proposed coupling group. The information depth and sampling geometry must be compatible with the interphase. Moritz and co-workers showed how film thickness and complementary XPS, MIES, UPS and IRRAS measurements change the confidence of an interfacial assignment [1]. The lesson transferred here is methodological: mechanism claims require interface-sensitive evidence and cannot be inferred from final strength alone.

6. Measure cure state at the interface and in the coating

Metal reflectivity, absorption, heat flow and oxygen access can make the interfacial cure history differ from that of a free film. A top-surface conversion measurement does not necessarily represent the coating–metal region. Report spectrum, irradiance, exposure, geometry, atmosphere, temperature, coating thickness and post-exposure history. Where a conversion gradient is plausible, measure it at sufficient spatial resolution or state that it remains unresolved.

The cure endpoint should be separated from adhesion. Choi and co-workers found coupled effects of reactive-diluent architecture and cure atmosphere on mechanical, adhesive and forming response of UV-cured polyurethane-acrylate coatings on pre-coated metal [5]. Their observations show that flexibility, hardness, adhesion and formability may move in different directions. They do not support a universal atmosphere, diluent or conversion target.

7. Quantify shrinkage and restraint without inferring stress from strength

Polymerisation shrinkage becomes interfacial stress only through restraint, modulus development, geometry and time. Thermal contraction and post-cure can add or relax stress. A simple conceptual balance is

$$\varepsilon_{misfit}(t) = \varepsilon_{cure}(t) + \Delta\alpha \Delta T(t) - \varepsilon_{relax}(t)$$

where the cure strain, thermal-expansion mismatch and relaxation terms must be defined for the actual coating and substrate. Stress then depends on the evolving constitutive response and boundary conditions; it cannot be assigned from shrinkage alone.

Lin and co-workers used digital image correlation to characterize time-resolved shrinkage behaviour in photocurable resins [6]. That work supports independent measurement of deformation during cure. It is adjacent to, not proof of, stress at a specific metal interface. The dynamic-thiourethane coating study linked network relaxation and pull-off response in a particular UV-curable metal-coating system [8]. Neither numerical result can be transferred as a general stress limit.

8. Preserve coating thickness, modulus and geometry

Thickness affects light absorption, oxygen inhibition, defect population, stress distribution and the energy available for delamination. Modulus and toughness affect whether deformation is accommodated or transferred to the interface. Edge shape, substrate thickness and fixture compliance can change a pull-off or bend result. These variables must travel with every numerical adhesion value.

Radiation-cured coil-coating studies have treated adhesion and flexibility as coupled but distinct outcomes [5,7]. A coating that survives a cross-hatch test can still crack during forming; a compliant coating can preserve attachment while failing a hardness or wear requirement. Qualification therefore uses a response set chosen for the intended loading rather than a single ranked score.

9. Choose a mechanical test that answers the decision question

Cross-hatch, pull-off, peel, lap shear, bend, impact and fracture-based tests load different geometries and report different measurands. Cross-hatch classifications are ordinal and method-dependent. Pull-off strength combines fixture, adhesive, coating and substrate responses. Peel includes bending and large-deformation work. Lap shear is sensitive to adherend and bondline geometry. None is a universal adhesion property.

The report should state specimen dimensions, coating thickness, cure and conditioning, fixture and loading rate, environment, replicate count, uncertainty and failure locus. A test result without a locus is incomplete. If the fixture adhesive or substrate fails first, the measured value is a lower bound on the target interface, not its strength.

10. Resolve the failure locus

Failure should be classified using post-test inspection capable of distinguishing:

- 1 coating–metal or coating–conversion-layer separation;
- 2 failure within a primer or conversion layer;
- 3 oxide rupture or corrosion-product separation;
- 4 cohesive failure in the photocured material;
- 5 substrate yielding or fracture; and
- 6 fixture-adhesive or mixed failure.

Optical inspection alone may be insufficient for thin residue. Surface spectroscopy, microscopy or elemental mapping can determine which material remains on each face. Mixed failure should be quantified or bounded rather than forced into a binary label. Strength changes cannot be interpreted mechanistically if the locus changes between specimens or after ageing.

11. Age the complete interfacial system

Initial adhesion does not establish durability. Water can plasticize the network, hydrolyse susceptible groups, alter oxide hydroxylation or reach defects. Thermal cycling changes misfit strain. Corrosion can create a weak boundary layer or underfilm pressure. Mechanical deformation can open transport paths. The conditioning protocol must specify environment, temperature, duration, cycling, specimen geometry and whether stress was applied during exposure.

Post-conditioning evaluation should repeat the relevant chemical, visual and mechanical measurements and record the new failure locus. Yan and co-workers paired coating properties with corrosion-related assessment in a defined aluminium system [4]; Onen and co-workers included water resistance among the coating responses on a declared alloy [3]. These studies support remeasurement after exposure, not a general acceleration factor or service-life conversion.

12. Build a qualification matrix

The minimum architecture contains independent gates:

Gate	Required evidence	Unsupported shortcut prevented
Adherend identity	Alloy/grade, surface history, oxide or conversion state	Treating all metals as equivalent
Preparation effect	Measured chemical/topographic/wetting change	Accepting a process name as proof
Cure and stress state	Optical/thermal history, conversion, thickness and deformation or justified model	Inferring stress from final strength
Mechanical response	Declared test geometry, rate, uncertainty and failure locus	Calling one test a universal adhesion value
Durability	Declared conditioning plus repeated state and locus measurements	Equating initial adhesion with service life

Passing one gate cannot waive another. The acceptance criteria are application-specific and must distinguish measurement capability from product requirement.

13. Minimum reporting set

Report alloy, grade, temper, plating or conversion layer; initial storage and handling; exact preparation and delay to coating; chemical-state, contamination, topography and wettability methods; formulation identity and relevant composition; applied amount and coating thickness; source spectrum, irradiance, exposure, atmosphere, temperature and post-cure; conversion method; shrinkage, deformation or stress method when used; mechanical-test standard and deviations; geometry, rate, replicates and uncertainty; failure-locus method; conditioning environment and duration; pre- and post-conditioning results; and formulation-specific acceptance criteria.

Every numerical source comparison must retain metal identity, surface state, preparation, coating chemistry, thickness, cure, test geometry and failure locus. Values from aluminium, copper, bare steel and zinc-coated steel must not be pooled without a justified common basis.

14. Knowledge boundary

The primary evidence establishes that interface-sensitive spectroscopy can resolve interactions between polymers and oxidized metals [1,2]; that photocurable coatings on declared metal substrates can be evaluated through coupled wetting, cure, mechanical and durability responses [3–5]; that shrinkage should be measured independently of final adhesion [6]; and that flexibility or network relaxation can alter metal-coating response without defining a universal optimum [7,8]. It does not establish equivalence among metal oxides, a universal preparation process, a single controlling adhesion mechanism, a transferable coating thickness, cure time, stress limit, adhesion threshold, acceleration factor or service life.

ER-221 provides a qualification architecture for metal-specific photocurable interfaces. General build-platform adhesion remains with ER-053, generic cure-stress theory with ER-195, structural joint design with ER-165 and ER-186, and general ageing or life prediction with ER-072 and ER-170.

15. Limitations

The evidence spans cyanoacrylate model interfaces, acrylic polymers, bio-based photocurable coatings, aluminium-filled coatings, polyurethane-acrylate coil coatings and dynamic networks. Metal identities, preparation, coating chemistry and tests are heterogeneous. Four sources were inspected at full-text depth and four through publisher abstract or bibliographic depth. The abstract-depth sources support only the propositions visible at that depth. Several studies report conventional coating tests rather than interfacial fracture energy. No common round-robin method, reference surface or transferable durability model is established by this corpus.

16. Conclusions

Photopolymer adhesion to metal is qualified only when the metal and its near-surface state are declared and measured. Surface preparation must be verified by its effect, not accepted by name. Wetting, interfacial chemistry, cure state, shrinkage, residual stress and mechanical adhesion are non-equivalent quantities. Every mechanical result requires geometry, rate and failure locus, and durability requires remeasurement after a declared conditioning history. The evidence supports metal-specific qualification matrices and rejects universal rankings, recipes and thresholds.

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