

Adhesion of Photopolymer Materials to Thermoplastics and Thermosets: Solubility Parameters, Interdiffusion, Primers and Ageing

A substrate-state framework for compatibility, activation, interphase formation and durability

Juan Segurola

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

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Abstract

Adhesion of a photocurable material to a thermoplastic or thermoset depends on the state of both polymeric materials and the interphase produced between them. Surface energy and solubility parameters can screen candidate pairs, but they do not measure swelling, dissolution, interdiffusion, primer anchoring, cure arrest, environmental stress cracking or durable joint performance. A treatment that initially improves wetting can recover, contaminate or damage the substrate before bonding.

This review defines a polymer-substrate qualification architecture. It requires polymer identity, grade, additives, crystallinity or cure state and prior ageing; separates thermodynamic screening from direct interdiffusion and mechanical evidence; records activation-to-bonding delay and hydrophobic recovery; verifies primer anchoring independently from adhesive-facing function; and resolves failure locus before and after environmental conditioning. The evidence supports substrate-family decision maps and shows why contact angle, surface energy, nanoscale adhesive work, peel and lap shear are non-equivalent. It does not establish a commercial treatment or primer recipe, universal Hansen or Hildebrand distance, surface-energy target, activation window, diffusion coefficient, adhesion threshold or ageing factor.

Keywords: polymer adhesion; thermoplastic; thermoset; solubility parameter; interdiffusion; plasma activation; primer; hydrophobic recovery; ageing

1. Significance and scope

Polymeric adherends are not inert generic solids. Their surface composition can differ from the bulk because of additives, mould release, oxidation, crystallinity, migration, orientation and ageing. A liquid photopolymer can wet without interdiffusing, swell without producing a strong interface, or attack the substrate and create crazing or a weak boundary layer. Cure can immobilize a favourable interphase or arrest it before it forms.

ER-222 addresses the evidence needed to qualify adhesion of photocurable materials to thermoplastics and thermosets. It does not prescribe a surface-treatment or bonding process. Its central decision is whether the declared substrate state, compatibility or activation evidence, primer state, cure history, mechanical response and ageing history support the intended interface.

1.1 Corpus boundary

ER-053 retains general substrate and build-platform wetting and adhesion. ER-165 and ER-186 retain structural joint design and general adhesive or bondline cure. ER-168 retains coatings on reactive printed photopolymer substrates where barrier or migration is central. ER-043 and ER-073 retain multimaterial vat-photopolymerisation interfaces and printed interlayer cohesion. ER-039, ER-068, ER-069 and ER-070 retain bulk time dependence, toughening, fatigue-crack growth and fracture toughness. ER-072 and ER-170 retain general ageing protocols and life-claim validity. ER-190 and ER-195 retain permanently undercured pressure-sensitive layers and generic cure-shrinkage stress. ER-222 is restricted to the state of conventional thermoplastic or thermoset adherends, compatibility, activation, primer anchoring, interphase formation, locus-resolved adhesion and aged response.

2. Specify the polymeric substrate

A polymer family name is insufficient. Record resin grade, molecular-weight range where relevant, additives, fillers, reinforcement, pigments, plasticizers, stabilizers, flame retardants, mould release, processing route, orientation, crystallinity, cure state and prior environmental history. A plasma-treated polypropylene grade cannot be treated as equivalent to another PP containing a migratory slip additive. A cured epoxy surface depends on stoichiometry, conversion, post-cure and contamination.

The relevant surface state also includes cleaning, machining or moulding history, time since manufacture and storage. Surface chemistry, topography and wettability should be measured when invoked. Mechanical properties and thickness are needed where substrate deformation affects the adhesion test.

3. Use solubility parameters as screens, not adhesion measurements

Hildebrand and Hansen parameters can organize cohesive-energy similarities, but any distance depends on the parameter set, temperature and composition. A crosslinked network has a distribution of local environments and cannot equilibrate like a low-molecular-weight liquid. Additives and copolymer composition may dominate the near surface. A small parameter distance therefore does not prove wetting, diffusion or strength, and a larger distance does not rule out adhesion through a primer or specific interaction.

Nikulova and Chalykh measured phase equilibrium and bidirectional interdiffusion in polystyrene–polyacrylate systems [1]. The study demonstrates that direct phase and diffusion measurements carry information absent from a single compatibility number. Its elevated-temperature polymer–polymer results are adjacent evidence and cannot be used as ambient photopolymer-bondline coefficients.

4. Distinguish wetting, swelling, dissolution and interdiffusion

Four events should remain separate:

- 1 wetting, the ability of the liquid to contact the surface;
- 2 swelling, uptake that changes substrate volume or mobility;
- 3 dissolution or extraction, loss of substrate or additive into the liquid; and
- 4 interdiffusion, mutual molecular transport across the original boundary.

Each depends on time, temperature, molecular size and conversion. A favourable contact angle can coexist with negligible interdiffusion. Swelling may increase chain mobility but can also generate residual stress, dimensional error or environmental stress cracking. Cure can freeze a gradient whose thickness depends on the pre-cure dwell and reaction rate.

Where interdiffusion is claimed, use direct spatial or compositional evidence with a stated resolution, or a validated mass-uptake or diffusion experiment under the relevant temperature and time. Mechanical strength alone cannot distinguish interdiffusion from surface reaction or mechanical interlocking.

5. Account for crystallinity, cure state and mobility

Amorphous and crystalline regions differ in free volume and molecular mobility. Processing and orientation can change both the bulk and near-surface state of a thermoplastic. For thermosets, cure conversion and post-cure determine residual functionality, glass transition and swelling response. These variables should be included in the substrate specification and conditioning record.

Compatibility data obtained above a glass transition or melting-related transition must not be transferred to ambient service without direct validation. The relevant interphase time may be short because photopolymerisation rapidly increases viscosity and network connectivity. Accordingly, screening should be followed by a test that reproduces liquid contact time, temperature and cure history.

6. Measure activation and its decay

Plasma, corona, flame and UV-based treatments can introduce polar groups, remove contamination, roughen the surface, cleave chains or create low-molecular-weight oxidized material. The resulting state changes with treatment severity, atmosphere, time and storage. Hydrophobic recovery may involve reorientation, diffusion of functional groups or migration from the bulk. The activation-to-bonding delay is therefore part of the specimen state.

Gacs and co-workers compared epoxy adhesion on several plasma-treated thermoplastics and reported that surface-energy change did not map uniquely onto adhesion [4]. Hartung and Heim followed UVC-induced polycarbonate activation, ageing and peel or failure response in an overmoulding system [5]. Caykara and co-workers coupled plasma-state measurement, UV polymerisation and ageing or washing observations on PET for an adjacent anti-adhesive application [3]. Together, these studies support time-resolved state measurement. Their treatment conditions and numerical windows are not transferable to a photocurable bondline.

7. Separate improved wettability from substrate damage

Oxidation may improve wetting while chain scission weakens the near-surface layer. Solvents may remove contamination while also extracting additives, crazing a stressed part or changing crystallinity. A maximum surface-energy response is not necessarily a maximum durable adhesion response.

Controls should include untreated substrate, treatment-only substrate, treated substrate after the intended storage delay, and the final bonded or coated specimen. Surface chemistry, mass or dimensional change, microscopy and a substrate-sensitive mechanical test may be needed. Environmental stress cracking should be evaluated where the liquid formulation or wash chemistry can attack the polymer under strain.

8. Verify primer anchoring and adhesive-facing function separately

A primer must attach to the substrate and present functionality compatible with the adhesive or coating. Final joint strength cannot demonstrate both steps. Morgese, Siegmann and Winkler designed a polyolefin primer with surface-anchoring and adhesive-facing functions and assessed chemical retention, surface state, lap shear, failure behaviour and storage durability [2]. Their work illustrates the value of independent evidence for each side of the primer.

The particular PFPA-based chemistry is study-specific and is not reproduced here as a formulation instruction. For any primer, qualification should measure coverage, retention after a justified challenge, remaining reactive or interactive groups, thickness and continuity, cure compatibility, storage time and final failure locus. A primer that remains attached but inhibits photopolymer cure has not passed the interface gate.

9. Couple interphase formation to photopolymer cure

The liquid contact interval before and during exposure controls how long wetting, swelling and diffusion can proceed. As conversion rises, diffusivity and interfacial relaxation may decrease. Light absorption or reflection by the substrate, oxygen at the interface and heat transfer can also change the local cure state.

Report spectrum, irradiance, exposure, specimen temperature, coating or bondline thickness, atmosphere, pre-exposure dwell and post-exposure history. Measure conversion or a validated network endpoint near the interface when feasible. Ge and co-workers evaluated a UV/moisture-curable polyurethane-acrylate adhesive on untreated PET [6], while Gilberts and co-workers studied UV-curable hybrid coatings on polycarbonate [7]. These direct substrate examples support coupled formulation–substrate–cure evaluation but do not establish a universal untreated-substrate solution.

10. Preserve the meaning of the adhesion test

Nanoscale pull-off work, probe tack, peel, lap shear, pull-off and fracture tests load different volumes and failure processes. Haartsen and co-workers mapped nanoscale adhesive work and additive-related surface/bulk differences in UV-cured films on PET [8]. That measurement is informative about local surface response but is not equivalent to peel, lap shear or long-term joint durability.

Every reported value requires substrate grade and state, treatment and delay, primer, formulation, bondline or film thickness, cure, specimen geometry, loading mode and rate, environment, replicates, uncertainty and failure locus. Substrate yielding, bending or crazing can dominate the apparent response. Cross-study numerical rankings are invalid when those conditions differ.

11. Resolve failure locus and weak boundary layers

Post-test inspection should distinguish:

- 1 separation at the polymer–primer boundary;
- 2 separation at the primer–photopolymer boundary;
- 3 cohesive failure inside the substrate surface or an oxidized weak layer;
- 4 cohesive failure in the primer or photocured material;
- 5 substrate yielding, crazing or fracture; and
- 6 mixed or fixture-related failure.

Microscopy, spectroscopy or elemental mapping may be needed to identify thin residue. A strength increase accompanied by a locus shift is a different result from an increase at an unchanged interface. If the substrate fails first, the result is a lower bound on interfacial capacity rather than a direct interface strength.

12. Requalify after ageing

Humidity, water, solvent, heat, ultraviolet exposure, oxidation and mechanical cycling can change the substrate, primer, interphase or photocured network. The conditioning record must identify which materials were exposed, whether specimens were stressed, and the time and temperature. The activation-to-bonding delay and bond-to-test delay are separate quantities.

After conditioning, repeat relevant surface or interphase measurements and the same mechanical method, recording the failure locus. Morgese and co-workers examined storage durability of primed polyolefin substrates [2]; Hartung and Heim tracked activation ageing before overmoulding [5]; Caykara and co-workers assessed recovery and durability-related surface response on treated PET [3]. These studies demonstrate state change over time, not a universal primer shelf life, activation window or service-life factor.

12.1 Qualification matrix

Gate	Required evidence	Unsupported shortcut prevented
Substrate identity	Grade, additives, crystallinity or cure state, processing and ageing	Pooling polymer families
Compatibility	Wetting plus direct swelling, extraction or interdiffusion evidence where claimed	Treating a solubility parameter as adhesion
Activation or primer state	Chemistry, coverage, damage and activation-to-bonding delay	Treating process name or contact angle as proof
Cure and mechanics	Interfacial cure history, thickness, test geometry, rate and locus	Comparing non-equivalent adhesion methods
Ageing	Declared conditioning and repeated state/mechanical measurements	Converting initial strength into durability

The gates are independent. A strong initial lap-shear result cannot waive substrate-damage or ageing controls. Acceptance limits belong to the declared application and measurement capability.

13. Minimum reporting set

Report polymer family, exact grade, additives, fillers, reinforcement, mould release, processing route, orientation, crystallinity or thermoset cure state; prior storage and ageing; cleaning and preparation; solubility-parameter source and temperature if used; direct swelling, extraction or interdiffusion method; activation equipment, atmosphere, dose or treatment history; activation-to-bonding delay; surface chemistry, topography and contact-angle method; primer identity, anchoring, thickness and adhesive-facing functionality; photopolymer formulation identity; liquid-contact interval; source spectrum, irradiance, exposure, atmosphere, temperature and post-cure; film or bondline thickness; mechanical-test geometry, rate, replicates and uncertainty; failure locus; conditioning history; and formulation-specific acceptance criteria.

Every numerical comparison must preserve polymer grade and state, treatment, delay, primer, formulation, thickness, cure, test method and failure locus. PE, PP, PET, PC, PA, PBT, PPS and cured thermosets must not be pooled as a single “plastic” class.

14. Knowledge boundary

The evidence establishes that phase behaviour and interdiffusion require direct measurement beyond a compatibility number [1]; that primer anchoring and adhesive-facing function can be verified separately [2]; that activation state can recover or damage the polymer and that surface energy does not map uniquely to adhesion [3–5]; that direct UV-curable adhesive or coating systems on PET and PC are formulation-specific [6,7]; and that nanoscale adhesive work is not equivalent to macroscopic joint performance [8]. It does not establish a universal solubility distance, surface energy, contact angle, diffusion coefficient, treatment dose, activation delay, primer lifetime, peel or shear threshold, acceleration factor or service life.

15. Limitations

The sources span polymer blends at elevated temperature, polyolefin primers, plasma and UVC treatment, epoxy overmoulding, UV/moisture-curable PET adhesive, sol–gel hybrid coatings and AFM measurements. Six sources were inspected at full-text depth and two through publisher abstract or bibliographic depth. The abstract-depth sources support only the propositions exposed by those records. Several systems are adjacent rather than identical to photocurable bondlines. No common interlaboratory reference surface or universal compatibility equation is established.

16. Conclusions

Adhesion to thermoplastics and thermosets must be qualified as a substrate-state and interphase problem. Solubility parameters and contact angle are screening tools, not adhesion measurements. Wetting, swelling, dissolution and interdiffusion are distinct. Activation can recover or damage the surface, so treatment-to-bonding delay must be recorded. Primer anchoring and adhesive-facing function require separate verification. Mechanical methods are non-equivalent and every result requires a failure locus. Durability is established only by remeasurement after a declared ageing history. The resulting decision framework is specific to the polymer grade, formulation and process and does not provide a universal recipe or threshold.

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