

Plasma, Corona and UV-Ozone Treatment of Photopolymer Surfaces: Functionalisation, Ageing, Contamination and Bond Performance

A state-resolved qualification framework from delivered activation to locus-resolved bond performance

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Abstract

Plasma, corona and UV-ozone treatment can change a polymer surface within seconds, but the treatment name does not define the surface delivered to a bonding operation. Gas composition, power coupling, source-to-surface geometry, exposure, temperature and the printed part's wash and post-cure history influence oxidation, chain scission, crosslinking, contaminant removal, roughening and the formation of mobile low-molecular-weight material. The resulting state can then change through hydrophobic recovery, migration, adsorption and handling before a coating or adhesive is applied.

This review defines a qualification architecture for already polymerised photocurable surfaces. It separates treatment identity from delivered dose and surface state; treats wettability, chemistry, morphology and bond performance as non-equivalent evidence layers; requires the activation-to-bond delay and storage environment to be controlled; and pairs mechanical response with failure locus and conditioning. The evidence is drawn from atmospheric-plasma, UVC, UV-ozone and UV-digital-printing studies on polymers, with thermoplastic and extrusion-printing evidence used only as adjacent mechanistic support. It does not establish a universal process, dose, contact-angle target, activation lifetime, bond-strength threshold or service-life claim.

Keywords: plasma activation; corona treatment; UV-ozone; photopolymer surface; hydrophobic recovery; contamination; weak boundary layer; bond performance

1. Significance and scope

An activated photopolymer surface is a transient material state, not a permanent attribute conferred by a named process. The same nominal treatment can remove organic contamination, insert polar groups, change roughness, produce chain fragments, heat the surface or damage a thin cured skin. The balance depends on the resin network, conversion, residual species, pigments or fillers, treatment atmosphere and delivered energy. Once treatment stops, polar groups may reorient, mobile species may migrate, and airborne contamination may cover the activated surface.

ER-225 addresses qualification of plasma, corona and UV-ozone activation applied after polymerisation to photocurable coatings, printed parts and bond surfaces. Its central decision is whether the declared resin and post-cure state, delivered treatment, resulting chemistry and morphology, elapsed-time state, bonded material and locus-resolved mechanical response form a traceable chain for the intended use.

1.1 Corpus boundary

ER-053 retains generic substrate and build-platform wetting and adhesion. ER-208 retains general surface-chemistry metrology and interpretation. ER-222 retains adhesion qualification for thermoplastics and thermosets as substrate families. ER-224 retains primer chemistry, film state and recoat windows. ER-225 is restricted to the transient state created on an already polymerised photopolymer surface by plasma, corona or UV-ozone treatment, including ageing, contamination, over-treatment and subsequent bond performance. Generic adhesion, instrument theory, bulk-polymer bonding and primer formulation are outside its ownership.

2. Define the incoming photopolymer state

Activation cannot be qualified without the surface that entered the treatment. Record resin identity or controlled formulation family, print or coating route, exposed face, layer orientation where relevant, wash chemistry and duration, drying, thermal or light post-cure, storage, handling and elapsed time. Conversion, residual monomer or oligomer, additive bloom and oxygen-inhibited material can all change the treatment response.

Evidence from polyethylene, polyamide, polycarbonate, polystyrene and PEEK demonstrates material-dependent responses to plasma or ultraviolet oxidation [2–4,6]. These materials are not substitutes for cured photoreins. They show why a treatment result must be reverified on the declared network and post-cure state. A process validated on a thermoplastic sheet cannot be imported as a dose or lifetime for a filled, crosslinked or incompletely washed printed resin.

3. Specify treatment by delivered conditions, not by method name

“Plasma”, “corona” and “UV-ozone” describe families of processes. A useful treatment record identifies equipment and source type, working gas or ambient atmosphere, pressure where applicable, power or other validated output descriptor, source-to-surface distance, scan or exposure history, treated area, fixture geometry and surface temperature. For moving or three-dimensional parts, local dwell and shadowing require attention.

Trimini and co-workers paired atmospheric-plasma conditions with surface energy, morphology, chemical composition and interlayer adhesion in extrusion-printed high-performance polymers [1]. Fleischer and co-workers varied large-area plasma conditions before UV digital printing and examined surface and adhesion responses [7]. Sager and co-workers coupled in-process atmospheric-plasma activation to first-layer deposition in PEEK-on-glass printing [8]. These studies support treatment-to-deposition traceability, but their equipment settings, substrates and measured strengths are not transferable to cured photopolymers.

4. Separate wettability, chemistry, morphology and mechanics

No single surface measurement identifies all consequences of activation. Contact angle responds to the outermost surface, roughness, heterogeneity, liquid choice and measurement time. Spectroscopy can identify chemical changes within its sampling depth but does not establish load transfer. Microscopy or topography can reveal etching and damage but not the accessibility of reactive groups. A bond test integrates interface chemistry, network properties, specimen geometry and loading.

Accordingly, qualification should use at least one surface-state measure tied to the proposed mechanism and a functional mechanical test on the intended material pair. Trimini and co-workers combined energetic, morphological, chemical and adhesion observations [1]. Fleischer and co-workers used XPS, AFM or SEM and UV-ink adhesion methods [7]. Kaizu and co-workers reported dose-dependent oxidation and nanoscale change while showing that wettability alone did not predict a functional adhesion endpoint [5]. Their biological endpoint is not structural bonding, but the non-equivalence of evidence layers is directly relevant.

5. Treat contact angle as a descriptor, not a bond specification

A lower water contact angle can indicate increased apparent hydrophilicity, yet it cannot identify whether polar groups are covalently retained, whether mobile oxidised fragments remain, or whether the bonded liquid wets under its own time scale and chemistry. Roughness and surface reconstruction can produce similar contact angles through different mechanisms. A value measured immediately after treatment may also be irrelevant to a later bonding step.

Che and co-workers followed hydrophilicity and complementary chemical or morphological evidence during ageing of microplasma-modified polymers [2]. Hartung and Heim compared UVC conditions, storage and peel response for a polycarbonate-silicone overmoulding system [3]. Doi and co-workers paired plasma treatment with XPS, contact angle and a biological response on polystyrene [6]. Together, these sources support time-stamped, multi-measurement interpretation. They do not support a universal contact-angle target or conversion of contact angle into bond strength.

6. Distinguish cleaning, functionalisation and damage

Activation may remove weak contamination and expose the underlying network. It may also introduce oxygen-containing groups, break chains, crosslink the near-surface region, etch topography or create oxidised low-molecular-weight material. These effects can occur together. Apparent improvement at a moderate treatment and deterioration at a stronger treatment cannot be assigned to one mechanism without chemical, morphological and mechanical evidence.

Kaizu and co-workers linked UV-ozone dose to oxidation and nanoscale surface change [5]. Hartung and Heim distinguished UVC irradiation conditions with and without ozone generation and tested the treated polymer in a defined bonded pair [3]. Takita and co-workers combined UV-ozone treatment of PEEK with surface chemistry, roughness, wettability, primer interaction, thermal cycling and failure observations [4]. These adjacent systems support an over-treatment gate: high apparent surface energy does not waive inspection for scission products, embrittlement or a weak oxidised layer.

7. Control activation-to-bond delay

The interval between treatment and coating or bonding is part of the process. During that interval, polar groups can reorient away from the surface, mobile material can migrate, contaminants can adsorb and moisture can alter the interfacial state. The rate and extent depend on polymer mobility, treatment severity, storage temperature, humidity, atmosphere and packaging.

Che and co-workers demonstrated polymer-dependent ageing of microplasma-modified surfaces [2]. Hartung and Heim incorporated ageing or storage controls into UVC-treated polycarbonate adhesion work [3]. Fleischer and co-workers compared immediate and delayed surface or adhesion response after plasma treatment [7]. These studies support a measured process window for each declared material and storage condition. They do not establish a universal activation lifetime.

8. Treat contamination and handling as state variables

An activated high-energy surface can adsorb airborne organics and handling residues rapidly. Packaging, transport between tools, fixture contact and cleaning after activation can therefore become controlling steps. Recleaning may remove contamination but may also erase or modify the activated state. A protected surface is not necessarily unchanged if physical ageing continues beneath the packaging atmosphere.

Qualification should define permitted handling, tools, gloves, contact materials, storage container, atmosphere and maximum delay. Surface analysis after the actual delay and handling sequence is more probative than analysis performed only at the treatment tool. A contamination challenge may be useful when the production environment makes incidental exposure plausible, but its acceptance criterion must be application-specific.

9. Preserve pair-specific chemistry and cure

Activation prepares one side of an interface. Performance also depends on the applied coating, adhesive, ink or second material, its wetting kinetics, reactive chemistry, cure and shrinkage. The same activated surface may respond differently to an acrylate, epoxy, silicone or primer-assisted system. A treatment that improves one material pair may inhibit or weaken another.

Hartung and Heim evaluated UVC-treated polycarbonate against liquid silicone rubber [3]. Takita and co-workers studied UV-ozone-treated PEEK with primer and resin-cement variables [4]. Fleischer and co-workers examined plasma-treated polymer substrates with a UV-digital-printing system [7]. These results justify pair-specific verification. Their commercial materials and process conditions cannot be converted into a general recipe for printed photoresins.

For a photocurable overlayer, report source spectrum, irradiance, exposure, atmosphere, thickness, temperature and post-cure. Where treatment products or absorbed species could inhibit cure, measure a near-interface network endpoint or use a validated proxy. A good initial wetting response does not prove that the overlayer cured adequately at the activated surface.

10. Measure mechanics with failure locus

Lap shear, peel, pull-off, cross-cut and interlayer tests load different volumes and failure processes. Results require specimen geometry, bonded area, adherend compliance, rate, environment, replicates and uncertainty. Post-test inspection should distinguish separation at the treated surface, cohesive failure in a modified skin, failure within the adhesive or coating, separation at the opposing material and fixture-related failure.

Trimini and co-workers linked plasma-modified surface evidence to interlayer adhesion [1]. Hartung and Heim used peel response in a defined overmoulded pair [3]. Takita and co-workers included failure-locus assessment before and after conditioning [4]. Fleischer and co-workers used peel or cross-cut methods for UV-printed layers [7]. These methods are not interchangeable, but they support pairing every mechanical value with the material pair, treatment state and observed locus.

11. Condition the activated interface after bonding

Activation may improve initial bond formation while leaving a hydrolytically unstable or mobile interphase. Qualification should therefore repeat the relevant mechanical method after conditioning representative of moisture, temperature, cleaning fluids, light or cyclic stress. The treatment-to-bond delay and post-bond conditioning history are distinct and should not be collapsed into one ageing label.

Takita and co-workers combined UV-ozone treatment with thermal cycling in a PEEK bonding system [4]. This supports conditioning of the completed interface, not transfer of a dental cycling protocol. Where environmental exposure changes failure locus without a large change in peak load, that change remains material evidence of interphase drift.

12. Build a non-compensatory qualification matrix

Gate	Required evidence	Unsupported shortcut prevented
Incoming state	Resin, exposed face, wash, dry, post-cure, storage and handling	Treating all cured photoresins as one surface
Delivered treatment	Source, atmosphere, geometry, exposure history and temperature	Accepting “plasma” or “UV-ozone” as a complete process
Surface response	Time-stamped chemistry, wettability and morphology appropriate to mechanism	Inferring bond performance from contact angle alone
Delay and contamination	Activation-to-bond time, storage atmosphere, packaging and handling	Declaring a universal activation lifetime
Functional interface	Bonded material, cure, mechanics, conditioning and failure locus	Converting surface activation into durable adhesion without a bond test

The gates are independent. A large wettability change cannot compensate for an uncharacterised weak layer. Strong immediate adhesion cannot waive delay, contamination or conditioned-locus controls.

13. Minimum reporting set

Report resin or controlled formulation family; print or coating method; exposed face and orientation; wash, drying and post-cure; storage and initial surface age; treatment equipment, atmosphere, pressure where applicable, output descriptor, distance, scan or exposure history, fixture and temperature; treated area and three-dimensional accessibility; delay, packaging, atmosphere and handling before bonding; surface chemistry, wettability and morphology methods with measurement times; bonded material or coating identity; primer if used; liquid-contact interval; cure spectrum, irradiance, exposure, atmosphere, thickness and post-cure; mechanical method, specimen geometry, rate, replicates and uncertainty; conditioning; and failure locus.

Every numerical result must retain the resin and post-cure state, delivered treatment, delay and storage, bonded pair, cure, geometry, environment and locus. No dose, contact angle, lifetime or bond value is transferable when those qualifiers change.

14. Knowledge boundary

The evidence establishes that a treatment must be defined by delivered conditions and measured surface response rather than by method name [1,7,8]; that wettability, chemistry, morphology and functional performance are distinct evidence layers [1,5–7]; that activated polymer surfaces age at material- and storage-dependent rates [2,3,7]; that stronger oxidation can coexist with damage or an unsuitable interphase [3–5]; and that the bonded material, primer, cure and failure locus remain pair-specific [3,4,7]. Thermoplastic and extrusion-printing studies provide adjacent mechanistic evidence only [1–4,6,8]. These propositions are bounded against generic adhesion, surface-metrology theory, substrate-family bonding and primer architecture owned by ER-053, ER-208, ER-222 and ER-224.

15. Limitations

The eight primary sources span extrusion-printed polymers, polyethylene and polyamides, polycarbonate–silicone overmoulding, dental PEEK bonding, biological adhesion on UV-ozone-treated polymers, plasma-treated polystyrene, UV digital printing and PEEK-on-glass fused-filament deposition. All eight were inspected at full-text or repository-full depth, but most are mechanistically adjacent rather than experiments on cured vat-photopolymer surfaces. The corpus contains no dedicated corona-treatment experiment; corona is therefore included only within the shared qualification architecture and requires its own direct validation. No common round-robin resin, treatment source, dose metric, storage condition, bonded material or mechanical geometry is established. The corpus does not establish a commercial process, universal dose, contact angle, activation lifetime, bond threshold, acceleration factor or service life.

16. Conclusions

Plasma, corona and UV-ozone treatment of an already polymerised photopolymer must be qualified as a transient surface-state process. The incoming resin, wash and post-cure state must be declared. Treatment identity must be replaced by delivered conditions and time-stamped chemical, wetting and morphological evidence. Contact angle is not a bond specification, and severe treatment may create a weak or damaged boundary despite high apparent surface energy. Delay, storage, contamination and handling belong to the process window. Final qualification requires the intended bonded pair, cure, conditioning, mechanical method and failure locus. The resulting conclusion is specific to that complete chain and provides no universal treatment recipe or lifetime.

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