

Surface Functionalisation of Nano- and Microparticles for Photocurable Composites

Wetting, dispersion, interface formation and cure coupling

Juan Seguro

3Dresyns by Resyner Technologies S.L.

© 2026 Juan Seguro. All Rights Reserved.

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

ER-217 · Engineering Review · Version 0.2 · 17 September 2026

Abstract

Surface functionalisation can alter how a nano- or microparticle is wetted by a photocurable resin, how it aggregates, how the formulation flows, how light and reactive species reach the interface, and how the cured network transfers stress across that interface. These outcomes are related but not interchangeable. A supplier treatment label, an infrared band or a stable suspension does not by itself prove covalent grafting, complete surface coverage, network coupling or retained composite performance.

This review defines a qualification architecture that follows the particle from incoming surface state through treatment verification, wetting and dispersion, photopolymerisation, cured morphology and interface-sensitive properties. Primary studies on modified silica, alumina, zirconia, hydroxyapatite and glass fillers show the value of complementary chemical, thermal, colloidal, rheological, kinetic, microscopic and mechanical measurements. They also show that different endpoints can reach different extrema within the same formulation series. The evidence therefore supports matched untreated and treated controls, state-resolved measurements and formulation-specific acceptance boundaries. It does not support a universal coupling agent, treatment concentration, hydrolysis condition, mixing history, filler loading or process recipe.

Keywords: particle functionalisation; silanisation; surface coverage; wetting; dispersion; agglomeration; interphase; photocurable composite; cure kinetics; interface qualification

1. Significance and scope

Nano- and microparticles present large interfacial areas relative to their volume. Their surface chemistry can dominate resin wetting, particle–particle attraction, dispersion stability and the mobility of reactive species near the interface. When the modifier bears a polymerisable group, the same surface may also participate in network formation. These possible functions make surface treatment attractive, but they also create a chain of assumptions that must be tested separately.

This review addresses the qualification of particle-surface chemistry for photocurable matrices. It connects verified surface state with pre-cure wetting and dispersion, cure response, cured morphology and interface-sensitive properties. It does not prescribe a commercial silanisation or grafting recipe, a universal treatment concentration, a filler loading, a sonication condition or a mixing sequence.

1.1 Corpus boundary

ER-217 owns verification of functionality on particle surfaces, wetting, agglomeration, dispersion stability, treatment-species state, cure coupling and interphase formation. ER-036 retains bulk rheology, recoating and dispersion control of highly filled VPP suspensions. ER-044 retains photoabsorbing-filler optical response and cure-depth control. ER-076 retains absorption, scattering, refractive-index contrast and feature broadening in particle-filled VPP. ER-087 retains magnetic-particle dispersion, magnetic state and field-programmed response. ER-099 retains general dispersant chemistry and selection. ER-156 retains nano/micron raw-material form, loading and direct or indirect manufacturing routes. ER-157 retains electrical and thermal filler function, percolation and anisotropy. ER-172 retains incoming raw-material identity and lot-equivalence acceptance. WP-024 retains commercial reactive reinforced-composite positioning.

2. Define the particle and surface states

The starting record must identify the particle composition, nominal size and size distribution, specific surface area when available, morphology, porosity, surface hydroxylation or other reactive sites, adsorbed water, prior coating and storage history. A surface treatment cannot be interpreted without this baseline because equal mass additions expose different interfacial areas and reactive-site populations.

At least four states should be distinguished where they exist: untreated particle, particle immediately after treatment, particle after washing or extraction, and particle dispersed in the actual resin. The last state matters because a treatment stable in a dry powder can rearrange, desorb, hydrolyse or promote bridging after contact with monomers and additives.

3. Verify chemical identity and coverage

Nominal treatment is not evidence of the chemical state obtained. Spectroscopy can identify functional groups or elemental changes, thermal analysis can estimate an organic fraction, and extraction or washing can challenge weakly bound species. Microscopy and particle-size methods can reveal treatment-induced agglomeration. Strong claims of grafting or surface coverage should rely on complementary methods that probe different failure modes.

An apparent surface excess may be reported as

$$\Gamma_{app} = \frac{m_{org}}{A_p}$$

where Γ_{app} is the method-dependent apparent organic mass per accessible particle area, m_{org} is the treatment-associated mass assigned by a declared analytical model, and A_p is the particle area represented by the specimen. The quantity is not automatically a grafting density: retained solvent, condensed oligomer, physisorbed modifier and uncertainty in accessible area can all contribute.

Parmornsupornvichit and co-workers combined FTIR, XPS, electron microscopy, dynamic light scattering and zeta potential to distinguish post-silanisation states of zirconia nanoparticles [4]. Their evidence illustrates why detection of a silane-related signal and attribution of a particular bonding state are different claims.

4. Wetting is a particle–resin relation

Wetting depends on both the particle surface and the liquid formulation. Contact-angle or surface-energy measurements made with a probe liquid can support comparison, but the actual resin contains monomers, oligomers, photoinitiators and additives that may adsorb selectively. Powder compaction, surface roughness and porosity can further affect apparent angles.

For a declared test geometry, the work-of-adhesion descriptor may be written as

$$W_A = \gamma_L (1 + \cos \theta)$$

where W_A is the apparent work of adhesion, γ_L is the liquid surface tension and θ is the measured contact angle. This relation does not prove chemical bonding or predict cured interfacial strength. It is useful only when specimen preparation, liquid composition, time and temperature are controlled.

5. Dispersion state and stability require time-resolved evidence

Dispersion is not a single number. Particle-size distributions, microscopy, sedimentation or backscattering profiles, zeta potential and rheology sample different aspects of the population. Dynamic light scattering can be dominated by larger clusters, while microscopy samples limited fields. A visually clear formulation can still contain aggregates, and a temporarily stable suspension can still form a weak cured interface.

Sadej, Gojzewski and Andrzejewska linked dispersion stability, cure kinetics, morphology and properties in two methacryloxy-modified silica systems [1]. Their correlated transition belonged to defined silica grades, a PEGDMA matrix and the tested processing history. It is evidence for a multi-measurand workflow, not for transferring the reported loading to another particle/resin pair.

The dispersion record should include material age, mixing energy and sequence, temperature, time since agitation, sampling height and observation interval. General bulk-slurry optimisation remains outside this review; ER-217 requires only enough dispersion evidence to interpret the particle-surface state and the later interphase.

6. Adsorbed, grafted and condensed species are distinct

A coupling-agent treatment can leave covalently attached species, physically adsorbed molecules, self-condensed oligomers and unreacted residues. These fractions may have different effects on wetting, viscosity, cure and storage. Washing or extraction can remove weakly bound material, but a reduction in organic content does not by itself identify what remained.

The zirconia study by Parmornsupornvichit and co-workers showed that post-treatment processing changed both spectroscopic evidence and colloidal behaviour [4]. Ryu and co-workers found that modifier addition, adsorbed amount, dispersion stability, photocure response and printing result did not vary as one monotonic endpoint in their alumina–acrylate system [3]. Together these studies support a state-resolved interpretation rather than a simple treated/untreated label.

7. Surface chemistry can couple to cure kinetics

Functional groups on a particle may participate in polymerisation, alter local mobility, adsorb initiator or inhibitor species, change heat transfer, or modify optical attenuation. Cure kinetics must therefore be measured in the complete formulation using a method that declares atmosphere, temperature, irradiation spectrum and sampling geometry.

Let $\alpha(t)$ be functional-group conversion from a declared analytical band. An apparent maximum rate may be defined as

$$R_{\max} = \max \left(\frac{d\alpha}{dt} \right)$$

but equal $R_{\max}$ values do not prove equal final conversion, gel state, interphase structure or printed integrity. Song and co-workers compared different organofunctional silanes through coating morphology, dispersion, rheology and printed mechanical response [2]. Ryu and co-workers observed different formulation outcomes at different treatment levels [3]. Neither study establishes a universal coupling-agent ranking.

8. Interphase formation must be measured after cure

The interphase is the region in which network structure or mobility differs because of the particle surface. Its existence and mechanical function cannot be inferred from pre-cure stability alone. Evidence may include cured-state microscopy, spectroscopy, thermal transitions, nanoscale modulus mapping, fracture morphology, bulk mechanical testing or another interface-sensitive method.

Sadej and co-workers measured pre-cure dispersion, photopolymerisation and cured morphology and properties in the same model systems [1]. The related dataset by Gojzewski and co-workers documented viscosity, dispersion and bulk response for hydrophobised silica in two acrylate matrices [6]. Palhares and co-workers compared hydroxyapatite states in a methacrylated polycaprolactone resin using chemical verification, cured morphology, surface response, mechanics and VAT printability [5]. These studies demonstrate the required connection

across states, while remaining specific to their materials.

9. Optical and processing effects are confounders

Changing a particle treatment can change refractive-index matching, aggregate size and scattering, which can alter the local exposure field. It can also change viscosity and therefore mixing, recoating or sedimentation. A measured cure or printability change cannot be attributed solely to chemical coupling unless optical and processing changes are controlled or independently measured.

ER-044 and ER-076 govern the detailed optical consequences. ER-036 governs highly filled slurry rheology and recoating. Within ER-217, the necessary control is narrower: record whether surface treatment changed attenuation, dispersion or viscosity enough to confound the proposed interfacial mechanism.

10. Matched controls establish attribution

A defensible experiment holds particle identity, particle loading, resin composition, photoinitiator package, absorber, mixing history, irradiation and specimen geometry constant while changing the surface state. Useful controls include untreated particle, treated but unwashed particle, washed treated particle, modifier added freely to the resin, and resin without particle where feasible.

Zanchi and co-workers varied silane concentration on glass microparticles and measured conversion-related and mechanical or sorption responses in a defined dental composite [7]. The result supports treating modifier amount as an experimental variable. Its concentrations, application and acceptance endpoints cannot be transferred to a VPP nanocomposite.

11. Qualification workflow

The qualification sequence is: identify the starting particle; verify the treatment and removable fraction; measure wetting and dispersion in the actual resin; measure cure response under controlled irradiation; examine cured morphology and interphase-sensitive properties; and repeat after a declared storage or conditioning interval when stability is part of the decision.

An acceptance decision should be vectorial:

$$\mathbf{Q} = \left(S_{chem}, S_{disp}, S_{cure}, S_{morph}, S_{prop} \right)$$

where *Schem* is verified surface state, *Sdisp* is dispersion state, *Scure* is cure response, *Smorph* is cured morphology and *Sprop* is the relevant property result. Passing one component cannot substitute for a failure or missing measurement in another.

12. Interpretation matrix

Observation	Supported interpretation	Not established
Modifier-related signal appears	Treatment-associated chemistry is detectable	Complete coverage or covalent grafting
Washing changes the organic signal	A removable fraction was present	Identity or uniformity of the retained layer
Apparent contact angle decreases	Wetting changed in that test state	Cured interfacial strength
Sedimentation slows	Dispersion stability improved over that interval	Network coupling or retained properties
Cure rate changes after treatment	Surface state affected the measured cure response	A universal beneficial mechanism
Cured morphology and properties improve	That treated system performed better under the protocol	Transferable treatment identity or concentration

13. Minimum reporting set

Report particle composition, morphology, size distribution, specific surface area, initial surface state, moisture and storage history; modifier identity and concentration basis; solvent, hydrolysis, treatment, washing and drying conditions when experimentally relevant; chemical and thermal verification methods; resin composition, particle loading and mixing history; dispersion method, time and sampling position; viscosity and optical changes needed to interpret cure; source spectrum, irradiance, exposure, atmosphere and temperature; conversion method and calibration; cured morphology and interface-sensitive property method; controls, replicates, uncertainty and conditioning history.

Every numerical result must retain particle identity and size, surface chemistry, resin composition, modifier basis, treatment and washing state, mixing history, irradiation and measurement method. A study-specific optimum must be labelled as such.

14. Knowledge boundary

Primary evidence establishes that surface modification can change chemical state, dispersion, rheology, cure kinetics, morphology, printability and properties, and that these responses may reach different extrema within one formulation series [1–7]. It does not establish a universal silane, coupling agent, concentration, hydrolysis condition, treatment time, drying protocol, filler loading, sonication history or mixing sequence. Nominal treatment does not prove grafting or coverage, and improved dispersion does not prove stronger load transfer.

15. Limitations

The evidence spans silica, alumina, zirconia, hydroxyapatite and glass fillers; nano- and microparticle scales; dental, biomedical and ceramic-printing formulations; and different analytical access depths. Some studies directly verify surface chemistry, while others use treatment labels supported by a narrower method set. Numerical comparison across particle/resin pairs is not justified. Long-term ageing, biological acceptance, electrical or thermal percolation and commercial processing recipes are outside this review.

16. Conclusions

Surface functionalisation should be qualified as a chain of states rather than a treatment label. Chemical verification, wetting, dispersion, cure response, cured morphology and interface-sensitive properties are separate measurands. Matched untreated and treated controls are required to attribute change, and optical or rheological confounders must be bounded. The evidence supports formulation-specific qualification and rejects universal recipes or treatment rankings.

References

- 1 Sadej M, Gojzewski H, Andrzejewska E. Photocurable polymethacrylate-silica nanocomposites: correlation between dispersion stability, curing kinetics, morphology and properties. *Journal of Polymer Research*. 2016;23:116. <https://doi.org/10.1007/s10965-016-1011-8>
- 2 Song SY, Park MS, Lee JW, Yun JS. A study on the rheological and mechanical properties of photo-curable ceramic/polymer composites with different silane coupling agents for SLA 3D printing technology. *Nanomaterials*. 2018;8:93. <https://doi.org/10.3390/nano8020093>
- 3 Ryu KH, Kim US, Kim JH, Choi JH, Han KS. Impact of optimal silane concentration on the rheological properties and 3D printing performance of Al₂O₃-acrylate composite slurries. *Materials*. 2024;17:5541. <https://doi.org/10.3390/ma17225541>
- 4 Parmornsupornvichit T, Katheng A, Tonprasong W, Kongkon P. Interfacial chemical selection via post-silanization processing governs dispersion stability of 3Y-TZP nanoparticles: a qualitative assessment of interfacial characteristics. *Polymers*. 2026;18:1089. <https://doi.org/10.3390/polym18091089>
- 5 Palhares TN, Lovo JFP, Rodrigues GC, et al. Assessment of methacrylated poly(ϵ -caprolactone)/silanized hydroxyapatite composite resin for high-resolution scaffolds via vat photopolymerization 3D printing. *Polymers for Advanced Technologies*. 2026;37:e70523. <https://doi.org/10.1002/pat.70523>
- 6 Gojzewski H, Sadej M, Andrzejewska E, Kokowska M. Dataset for acrylate/silica nanoparticles formulations and photocured composites: viscosity, filler dispersion and bulk Poisson's ratio. *Data in Brief*. 2017;12:528–534. <https://doi.org/10.1016/j.dib.2017.04.040>
- 7 Zanchi CH, Ogliari FA, Silva RM, et al. Effect of the silane concentration on the selected properties of an experimental microfilled composite resin. *Applied Adhesion Science*. 2015;3:27. <https://doi.org/10.1186/s40563-015-0054-0>

Copyright

© 2026 Juan Segurola. All Rights Reserved.