

Direct Ink Writing and Paste Extrusion

Silicones, Hydrogels, Highly Filled Polymers, Shape Retention, Drying/Cure and Qualification

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Statement of Significance

Direct ink writing is often described by a syringe, a nozzle diameter and an observation that a paste is shear-thinning. Those facts do not establish a manufacturable process. A released feedstock must survive storage, conditioning, loading, pressure delivery, tubing and mixer residence, converging flow, wall shear, extension at the nozzle entrance, start-stop cycles and deposition without separation, air ingestion, cure inside the delivery path or uncontrolled drift. After exit, the filament must recover an adequate material state, wet or fuse where required, resist spreading and collapse, span or remain supported, preserve interfaces, complete drying or cure without unacceptable shrinkage and deliver the specified geometry and function after support removal and conditioning. ER-144 compares unsupported and embedded routes for silicones, hydrogels and highly filled polymer pastes through that complete state chain. It distinguishes flowability from buildability, printable appearance from accepted properties and material-extrusion speed from factory throughput. The result is a qualification architecture for specialist soft, reactive and particle-filled materials whose advantages—ambient or low-temperature processing, high loading, freeform deposition and local composition control—are inseparable from pressure, residence, rheology, conversion and post-process burdens.

Keywords: *direct ink writing; paste extrusion; robocasting; yield stress; shear thinning; thixotropy; viscoelasticity; silicone; hydrogel; highly filled polymer; embedded printing; support bath; filament; cure; drying; shape fidelity; process qualification*

Abstract

Direct ink writing and paste extrusion deposit continuous or interrupted filaments from flowable, often non-molten feedstocks. Their material range can include one- and two-part silicones, moisture- or photo-reactive elastomers, hydrogels, adhesives, sealants, thermosets and particle- or fibre-filled polymer pastes. The same breadth makes generic process claims unsafe. This qualitative engineering review follows the complete route from released feedstock to accepted component. It examines material genealogy; temperature-, time- and shear-dependent rheology; yield and recovery; phase separation and air; cartridge and reservoir state; pressure, pump and mixer behaviour; nozzle geometry and residence; start-stop transients; die swell, drawdown and slip; filament placement, wetting and fusion; spanning, stacking, sag and buckling; embedded/support-bath interactions; drying, cure, cooling, shrinkage and conditioning; geometry, surface, anisotropy, function, throughput, safety and change control. Published studies demonstrate useful mechanisms but not universal windows: colloidal, epoxy, silicone, hydrogel and support-bath results remain formulation-, apparatus-, geometry- and state-specific. The review therefore rejects viscosity-only printability, nozzle-diameter resolution, cure-time transfer and as-printed visual success as release evidence. It proposes a staged qualification gate built around controlled feedstock identity, time-resolved rheology and conversion, delivery-path capability, state-labelled line/stack/feature artefacts, final-part properties, accepted-component throughput and requalification triggers. Thermoplastic FFF, inkjet, vat photopolymerisation, construction-scale extrusion and final dense ceramic or metal qualification are outside scope.

1. Purpose and scope

ER-144 applies the state-resolved selection framework of ER-139 to non-molten filament deposition. ISO/ASTM 52900:2021 supplies the additive-manufacturing process vocabulary [1]. ISO/ASTM 52920:2023 places qualification controls around the production system and site [2], and ISO/ASTM 52910:2018 structures design and manufacturability decisions [3]. ISO/ASTM 52903-1:2020 addresses feedstock materials for plastic material extrusion [4], but it does not declare one rheology window for every paste. ISO/ASTM 52924:2023 and ISO/ASTM 52927:2024 help classify part characteristics and corresponding tests [5,6]. ISO/ASTM 52902:2023 supports geometric-capability artefacts [7], while ISO 17295:2023 removes ambiguity from position, axes and orientation [8]. None of these standards qualifies a material because it exits a nozzle or preserves one printed line.

The controlling category boundary is material state and delivery mechanism. ER-140 owns thermoplastic filament and pellet extrusion, plus reactive thermoset extrusion only where a melt-capable screw or large-format extrusion head performs bulk conveying, thermal conditioning and pressure generation. ER-144 owns premixed or independently metered non-molten inks and pastes delivered from cartridges, syringes, reservoirs or pumps, including two-part static- or dynamic-mixer routes, when rheological recovery, drying, cooling, cure, physical association or another defined transition retains the deposited form. ER-143 owns discrete-droplet material jetting. ER-142 owns selective conversion in a vat. `DIW`, `paste extrusion`, `robocasting`, `microextrusion`, `syringe printing` and `embedded ink writing` can describe overlapping implementations, but no label substitutes for the material, hardware and state record.

In scope are unsupported and support-assisted deposition of silicones and other elastomers; hydrogels and soft aqueous networks; polymer adhesives, sealants, gels and putties; highly filled thermosets and functional composite pastes; and multimaterial combinations where the deposited phase remains a polymer or polymer composite at acceptance. ER-152 owns

ceramic direct ink writing and robocasting when the deposited object is a ceramic green body whose delivered qualification includes drying, debinding and sintering; ER-144 treats particle-filled material only through polymer-paste feed and deposited-state controls when the accepted state remains a polymer or polymer composite. Other bound or green routes and final dense ceramic or metal acceptance belong to ER-151–ER-155. Construction, concrete and other macroscale high-volume extrusion are excluded. Food, pharmaceutical and biological studies are used only for transferable process mechanisms; dose, sterility, cell viability, biocompatibility and clinical suitability are not inferred.

Commercial names also require boundaries. The 3Dresyns putty, gel, filler and sealant page identifies durable and sacrificial cured-paste families [27], but it does not establish that any listed material is qualified for DIW. The silicone-like resin page describes vat-photopolymer elastomers and explicitly distinguishes them from direct silicones [28]. A silicone-like photopolymer, an addition-cure silicone, a moisture-cure silicone and a silicone organogel are different material systems even when their final tactile behaviour appears similar.

2. Route families and material-state transitions

DIW routes share controlled extrusion but not a common pre-deposition state or conversion. A colloidal or particle-filled ink can behave as a yield-stress solid at rest, flow under sufficient stress and recover after deposition. A one-part moisture-cure silicone begins reacting after exposure to water and may develop a cure front controlled by diffusion. A two-part silicone requires accurate metering and mixing before a time-limited residence. A photo-reactive paste may remain weak until pinning or irradiation. A thermoset composite can depend on thermal cure, while a hydrogel can recover through reversible physical bonds and then receive a secondary covalent crosslink. A solution paste can retain apparent shape initially and later shrink as solvent leaves. These are different production chains.

Smay, Cesarano and Lewis demonstrated direct assembly from concentrated colloidal inks whose flow and post-deposition behaviour supported periodic structures [9]. Lewis subsequently described a wider DIW architecture for functional materials [10]. Those studies establish the value of a designed flow-to-solid-like transition, not a universal composition or rheology. Gratson et al. further showed that the printed scaffold can be an intermediate template converted downstream into another material architecture [11]. The accepted deliverable must therefore be named: wet print, dried scaffold, cured elastomer, retained composite, sacrificial pattern or downstream converted part.

Unsupported writing deposits onto a substrate or prior filament and relies on the ink's own recovery and the growing structure. It offers direct access, simple material accounting and potentially easier support removal, but overhangs, spans, tall thin walls and soft formulations can sag or collapse. Layerwise support can provide local scaffolding but adds material compatibility, placement and removal operations. Embedded writing deposits inside a bath or host that supplies distributed support; it can enable soft inks and non-planar paths, but bath yielding, nozzle disturbance, trapped support, interfacial contamination and release become part of the qualification boundary. Sacrificial-core or mould-assisted routes can transfer geometry indirectly, yet they add cure inhibition, access and removal risks.

Table 1. Route-specific opportunities and control burdens

Route	Conditional benefit	Dominant burden	Minimum evidence before escalation
Unsupported yield-stress paste	Direct deposition, open access, no separate bath	Sag, spreading, buckling, span failure and layer accumulation	Flow/recovery state, line/stack/span artefacts, start-stop and final cure/dry geometry
One-part reactive extrusion	Simple single-stream loading and fewer ratio errors	Skinning, moisture/oxygen dependence, storage and nozzle cure	Exposure history, depth/time conversion, purge limits and internal-property evidence
Two-part reactive extrusion	Cure can begin after controlled mixing; broad chemistry	Ratio, mixer homogeneity, residence distribution, pot life, dead zones and blocked hardware	Independent stream metering, mixed-state uniformity, residence challenge and cure mapping
Photo- or thermally triggered paste	Spatial or temporal control over pinning and final conversion	Dose/temperature gradients, shadowing, exotherm, shrinkage and property gradients	Irradiance/temperature map, conversion and dimensions through final condition
Embedded/support-bath writing	Stabilises soft materials and freeform paths	Bath yielding, path closure, drag, contamination, trapped support and removal	Ink/bath compatibility, disturbance/recovery, release/cleanliness and final geometry
Highly filled functional composite	High solids and local fibre/particle orientation; direct functional patterning	Dispersion, wear, filtration, phase separation, anisotropy and cure coupling	Full PSD/agglomerates, solids basis, flow history, orientation and final functional tests

The best route is component- and cell-specific. A bath can stabilise geometry yet make cleaning or enclosed-channel acceptance impossible. A rapid cure can increase build height yet shorten the available residence and worsen nozzle blockage. More filler can raise yield stress and function but increase pressure, wear, anisotropy and void sensitivity. A larger nozzle can reduce pressure and particle blockage while destroying a feature requirement. Route selection must compare the complete accepted-component state, not one attractive mechanism.

3. State-resolved production chain

Production begins with a released material identity. Grade, revision, lot, storage, age, temperature history, container opening, mixing and prior conditioning are checked. The feedstock is homogenised, degassed, dried, diluted, thickened, warmed, cooled or combined only under an approved procedure. For filled systems, the particle or fibre population, dispersion state and phase-separation history travel with the batch. For reactive systems, exposure to moisture, oxygen, light, catalyst, inhibitor or heat begins a measurable clock.

The material is loaded into a cartridge, syringe, reservoir or pump. Air removal, follower-piston contact, seal compatibility, wall wetting and headspace are controlled. One or more streams pass through tubing, valves, connectors and, where applicable, a static or dynamic mixer. Pressure, displacement or rotational delivery creates a flow history and residence distribution. The conditioned material enters a nozzle whose length, diameter, taper, roughness, temperature and wear state define the final delivery restriction. A priming and purge operation establishes a known outlet state before production deposition.

During building, commanded flow and path speed generate a filament. The system starts, accelerates, turns, decelerates and stops while coordinating nozzle height, layer spacing, substrate or bath response and any cure trigger. The filament swells, draws, bends, wets, fuses, stacks, spans or remains suspended. Its rheology recovers while drying, cooling or reaction changes the state. The sequence repeats while material age, pressure, nozzle temperature, mixer residence, bath condition and cure history continue to evolve. Pauses and restarts are production states, not interruptions outside the process.

After deposition, the object may remain wet, green or only partially converted. It can require a dwell, staged thermal cure, irradiation, humidity exposure, solvent evaporation, extraction, washing, support-bath release, sacrificial-core removal, drying and conditioning. Inspection must occur at the state named in the product specification. A dimension measured wet cannot silently qualify the dried part. A tensile bar cured uniformly in a mould cannot qualify a printed wall with interfaces and a different thermal history.

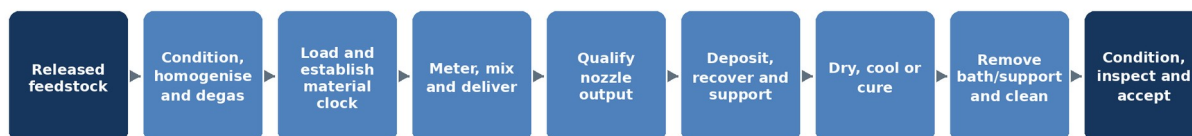


Figure 1. State-resolved DIW and paste-extrusion production chain

Each measurement must carry the state in which it was obtained. A low-shear viscosity in a cup does not describe the entrance extension or wall shear in the nozzle. A pressure trace without a measured flow does not establish delivered volume. A neat line at steady speed does not qualify a corner, restart or material switch. A stack that stands for five minutes does not establish stability through a six-hour build or a thermal cure. The process record must join material genealogy, machine state, time, geometry and final acceptance.

4. Feedstock identity and rheological state

The feedstock record must identify every function-bearing phase: polymer or prepolymer; solvent or carrier; crosslinker, catalyst, initiator or inhibitor; thickener or rheology modifier; particle, fibre, agglomerate and surface treatment; colourant, surfactant, plasticiser, humectant, defoamer and any reactive diluent. Mass and volume fractions are not interchangeable. Density, volatile content, moisture, storage modulus, loss modulus, yield measure, viscosity, recovery, cure state and particle-size distribution require stated methods and temperatures. A trade label such as `paste`, `gel` or `high solids` is not a material specification.

Many DIW feedstocks are represented conditionally by the Herschel–Bulkley relationship:

$$\tau = \tau_y + K \dot{\gamma}^n, \text{ for yielded flow}$$

where `tau` is shear stress, `tau\_y` a fitted yield term, `K` the consistency index, `gamma\_dot` shear rate and `n` the flow index. The corresponding apparent viscosity depends on shear rate:

$$\eta_{app} = \tau / \dot{\gamma}$$

These equations organise measurements; they do not prove a true material yield point or predict every nozzle flow. Wall slip, thixotropic structural breakdown, elasticity, particle migration, extensional flow, temperature change, reaction and a non-uniform stress history can make a steady shear fit inadequate. Yield stress can depend on protocol, ramp direction, preshear, rest time and selected criterion. Storage-modulus crossover is not automatically the same event as flow initiation or structural failure.

Printability requires at least three different behaviours. First, the material must enter and traverse the delivery path without excessive pressure, separation, fracture or reaction. Second, it must leave the nozzle as the intended continuous or interrupted filament without uncontrolled swell, sharkskin, pulsing, curling or air. Third, the deposited state must recover or convert fast enough to preserve geometry while allowing the required wetting, fusion and interface formation. Maximising the low-shear modulus can improve self-support yet produce poor interlayer contact. Maximising shear thinning can reduce steady pressure yet worsen rest/start hysteresis. A single ratio or printability number cannot close these competing requirements.

Time dependence is especially important. Thixotropy describes structural evolution under changing shear and rest, not merely a downward viscosity curve. A three-interval test can probe rest, high shear and recovery, but the imposed sequence must resemble loading, residence, nozzle passage and interlayer time. Oscillatory recovery can be useful while still missing irreversible damage, evaporation or cure. A material that recovers quickly in a rheometer may recover differently after a long narrow tube, a static mixer or repeated pressure cycles.

Smay et al. and Lewis show why colloidal interactions, concentration and particle organisation can enable flow followed by shape retention [9,10]. Romberg and Kotula show another coupled state: in the tested thermoset composites, temperature and reaction changed the yield and storage behaviour during post-cure [14]. Their two-step cure logic is important evidence that cure can first destabilise and later strengthen a structure, but the specific loading, temperatures and response cannot be transferred to unrelated pastes. Rheology must be measured along the actual material and conversion path.

5. Reservoir, metering, mixing and nozzle flow

Delivery hardware is part of the material system. Pneumatic pressure can be simple and compliant, but gas compressibility, cartridge deformation, seal friction and changing plunger position can delay or distort flow. A syringe or linear actuator provides commanded displacement yet can accumulate pressure elastically in tubing and fittings. A progressive-cavity pump can meter viscous material continuously, but rotor/stator condition, backflow, particle wear and cleaning matter. Augers can handle high solids while imposing mixing, heating and residence. The same paste can behave differently across these architectures.

Cartridge loading must prevent air pockets and preserve material homogeneity. Degassing before loading does not eliminate air introduced at a piston edge, connector, refill or A/B junction. Compression can dissolve gas that reappears at the nozzle. Filled systems can sediment, cream, filter or migrate during storage and extrusion; fibres can align; a liquid phase can bleed ahead of solids. A top, middle and heel sample may therefore differ even when the batch was initially homogeneous. The release and end-of-cartridge rules need evidence.

For a straight circular capillary under idealised fully developed conditions, the wall shear stress can be organised as:

$$\tau_w = \Delta P \times R / (2L)$$

where ΔP is the pressure drop, R the radius and L the length. A production nozzle rarely satisfies the complete simplification. Entrance contraction, taper, needle hub, fittings, roughness, slip, viscoelasticity, non-isothermal flow and upstream mixer can dominate. Gauge pressure includes the complete flow path, not just the tip. A setpoint therefore requires a measured outlet flow, pressure trace, material state and hardware revision.

Nozzle selection couples pressure, particles, feature size and damage. A smaller bore can increase nominal spatial control but raises restriction, wall stress, heating, residence sensitivity and blockage risk. A longer nozzle can improve directionality or access while increasing pressure and exposure duration. A conical nozzle can change entrance losses and stress duration. Friedrich, Gunther and Seppala found geometry-dependent trade-offs between stress exposure and filament shape in their simulated embedded-bioprinting system [24]. Those results cannot set a universal nozzle rule, but they show why 'larger is gentler' and 'conical is better' are incomplete claims.

Two-part systems add ratio and mixing control. Each stream needs its own identity, temperature, pressure/flow and depletion state. The mixer must achieve an accepted composition distribution over the production flow range and through starts and stops. Dead volume, residence-time distribution and recirculation or backflow can create under-mixed leading material and over-aged trailing material. Gharai et al. used a study-specific two-stream static-mixer system and documented the linked pressure and low-flow mixing problem [20]. The general conclusion is not that one mixer geometry is preferred; it is that metering, homogeneity, pressure, residence and cleanout must be qualified together.

This cartridge-, pump- and mixer-defined material clock is the two-part reactive-paste route owned by ER-144. Reactive thermoset extrusion in which a melt-capable screw or large-format extrusion head performs bulk conveying, thermal conditioning and pressure generation remains outside this boundary and is treated in ER-140.

Nozzle output qualification should include mass or volume per commanded interval, steady-state variation, delay from command to flow, decay after stop, restart response, pressure signature, filament continuity and evidence of separation or cure. The test must challenge the minimum and maximum planned flows, typical path accelerations, pauses, build duration, material age and allowable cartridge depletion. Prime and purge quantities become waste and must be included in throughput and genealogy.

6. Deposition kinematics, filament geometry and transients

In an ideal incompressible steady deposition with a circular strand and no swell, slip, drawdown or loss, continuity gives a useful first estimate:

$$D_{s,ideal} = \sqrt{4Q / (\pi \times v_{path})}$$

where $D_{s,ideal}$ is ideal strand diameter, Q volumetric flow and v_{path} path speed. This is a bookkeeping relationship, not a resolution equation. Actual diameter and cross-section depend on die swell, tensile drawdown, nozzle gap, substrate contact, gravity, wetting, recovery, fusion, bath drag, material conversion and the measurement state. The deposited section can be oval, flattened, necked, rough or hollow. A line width measured from above does not provide its height, area or void content.

The ratio between flow and path speed must remain controlled through acceleration and curvature. If motion begins before flow stabilises, the line starts thin; if flow begins too early, a blob forms. At a corner, the nozzle slows while pressure and flow may lag, producing overfill. At the end, stored elastic and pneumatic energy can continue discharge after the command stops. Retraction can pull air, separate phases or disturb the filament. A restart after a short pause can differ from one after a long dwell because pressure, structural recovery, cure and temperature have changed.

Nozzle height and layer pitch affect both confinement and fusion. Excessive gap can stretch or misplace a filament; insufficient gap can plough, overcompress, raise pressure or contaminate the tip. Some routes intentionally press a bead to create contact, while

others require a freely deposited circular filament. The intended section and overlap must be defined. `Layer height` cannot be copied from a different nozzle, material or cure state.

Wetting is conditional. Too little substrate or prior-layer affinity produces rolling, detachment and weak interfaces. Too much spreading erases gaps, reduces height and destabilises walls. Surface energy can change with cure, drying, contamination, plasma treatment, release agent or support contact. The first layer and later layers therefore need separate evidence. A filament that adheres to a clean glass coupon may not behave on a partially cured elastomer or a fibre-rich composite surface.

Start-stop, corner and intersection artefacts should be measured as deliberately as straight lines. A qualification coupon needs isolated lines, paired lines with controlled spacing, crosses, corners, circles, starts, stops and restarts. It should then progress to walls, stacks, bridges, overhangs, channels and representative interfaces. Ribeiro et al. proposed measured shape-fidelity approaches for hydrogel printing [25]; the transferable lesson is to quantify rather than visually label filaments, while keeping each metric tied to its material and apparatus.

7. Shape retention, stacking, spanning and collapse

Flow through the nozzle and stability after deposition are competing states. A deposited filament must resist gravity, capillary-driven spreading, pressure from upper layers, tool interaction, cure or drying stress and any support-bath forces. Yet adjacent filaments must form the required contact and interfaces. Complete non-flow can preserve an isolated strand while preventing fusion. Excessive fluidity can create a smooth surface while closing channels and collapsing stacks. Shape fidelity is therefore feature- and time-specific.

Yield and elastic response organise self-support but do not alone predict it. The gravitational stress grows with density and characteristic height; capillary pressure grows as curvature tightens; a tall stack accumulates load and time. A filament can retain width while creeping in height. A wall can appear stable during deposition and buckle after the nozzle moves away or the temperature rises. A span can fail by sag, necking, rotation at its supports or progressive creep. Each mode needs a geometry and observation interval relevant to production.

Smay et al. printed periodic colloidal structures by balancing flow and recovery in their investigated inks [9]. Lewis described spanning and three-dimensional writing across multiple material systems [10]. Compton and Lewis used a fibre-filled epoxy route to create lightweight cellular composites [12], while Lewicki et al. demonstrated how deposition can organise fibres and produce strongly direction-dependent properties [13]. These studies show conditional opportunities—open lattices, programmed anisotropy and high loading—not proof that another paste will bridge the same distance or deliver the same property.

Geometry can fail through material accumulation rather than one weak layer. A bottom filament experiences the longest time under load and the full downstream thermal or solvent history. Repeated nozzle passes can disturb a compliant wall. A curing lamp or heater can create a gradient across the build. Evaporation can form a skin over a wet interior. An embedded bath can yield repeatedly around dense toolpaths. Qualification must therefore include a representative build duration and feature density, not only one small demonstration object.

Orientation is a material-processing variable. Filaments place interfaces and can align fibres, particles or polymer chains. Properties measured parallel to a path can differ from transverse, through-thickness or intersection regions. Path planning can exploit this for stiffness, conductivity or shrinkage control, but CAD material assignment does not guarantee realised orientation. The measurement record must state axes using ISO 17295 [8], toolpath, specimen extraction and load direction.

Shape retention also depends on conversion timing. Early pinning or heating can arrest sag yet reduce wetting or trap voids. A long open time can improve fusion but increase collapse. Romberg and Kotula observed a study-specific loss and recovery of stabilising rheological properties during thermal cure [14]. The production window must therefore overlay deposition time, recovery, interlayer delay, cure kinetics, temperature and feature load. There is no universal `printable` state outside that sequence.

8. Drying, cooling, cure and delivered material state

The deposited filament is often an intermediate. Drying removes liquid and can create shrinkage, gradients, skinning, cracking, warpage, porosity or solute migration. Cooling establishes a physical state that may later creep or crystallise. Chemical cure changes molecular weight, modulus, shrinkage, adhesion, heat generation and extractables. Irradiation adds spatial dose and attenuation. A secondary thermal step can complete conversion while simultaneously weakening an uncured support state. The release specification must state which transitions are required and which final condition is accepted.

Solvent loss depends on exposed area, path spacing, layer sequence, temperature, humidity, airflow and solvent activity. An isolated line does not dry like a dense wall or an enclosed region. A surface can appear dry while retaining solvent internally. Subsequent layers can seal or redissolve a prior surface. Mass change, dimensional change and relevant chemical or physical endpoints need time-resolved evidence. `Dry to touch` is not an industrial conversion criterion.

One-part moisture-cure systems add diffusion and ambient dependence. Thick sections and enclosed cavities can retain under-cured material after a surface skin forms. Plott and Shih investigated moisture-cured silicone extrusion and void control in their apparatus [21]. Their evidence supports the need to control material delivery, ambient exposure and internal state; it does not establish a general cure depth, nozzle or actuator performance for other silicones.

Two-part systems shift the boundary to metering, mixing and residence. The mixed material begins an age distribution rather than one exact pot-life clock. Material at the wall, in a mixer dead zone, at the nozzle and in the deposited component can occupy different conversion states. Gharaie et al. compared a specific two-part silicone route with moulded specimens [20]. Such

comparison is useful only when mix ratio, cure, geometry and test state remain explicit. A moulded coupon cannot be assumed to reproduce printed interfaces, voids or path orientation.

Photo- and thermally cured pastes need mapped energy delivery. Optical attenuation, pigment or filler scattering, shadowed interfaces and surface oxygen can generate conversion gradients. Thermal cure depends on heater geometry, contact, convection, part thickness, exotherm and tool/bath thermal mass. Romberg and Kotula's rheo-Raman study demonstrates why rheology and reaction should be measured together for a tested thermoset composite [14]. A cure schedule is qualified for a defined build and loading range, not merely for a resin name.

Sacrificial scaffolds and indirect conversion create additional acceptance states. Gratson et al. used direct-written polymer scaffolds as precursors to converted silicon structures [11]. In other routes the printed paste may be a pattern, mould, support or green body. Shrinkage, infiltration, burnout, debinding or sintering can dominate the final geometry. ER-144 can identify that hand-off but does not qualify final dense ceramics or metals. The genealogy must connect the printed intermediate to the later process record without assigning final-material properties prematurely.

9. Embedded writing, support baths and removal

Embedded writing replaces unsupported free-surface stability with a coupled ink–bath–tool system. The bath should yield locally as the nozzle moves, support deposited material after passage and recover without dragging, displacing or merging features. The ink should remain distinct enough to preserve composition and geometry, while the interface permits the intended adhesion or release. Density mismatch, interfacial tension, osmotic exchange, solvent transfer, cure inhibition, particle migration and temperature can all alter the result.

Muth et al. embedded conductive ink inside highly stretchable elastomer matrices, demonstrating a route to integrated strain sensors [16]. Highley, Rodell and Burdick printed shear-thinning hydrogels into self-healing hydrogel supports and used secondary crosslinking [17]. Hinton et al. demonstrated FRESH printing of soft hydrogel structures in a reversible support medium [18]. Hinton and colleagues later printed PDMS in a hydrophilic bath and released the part after cure [19]. Each study proves a particular compatible system and workflow; none proves that arbitrary ink and bath pairs are interchangeable.

The moving nozzle imposes a stress field in the bath. Path spacing and sequence can make later passes disturb earlier filaments. A bath can heal macroscopically while retaining local channels, composition gradients or entrained fragments. Friedrich et al. modelled trade-offs among nozzle geometry, stress exposure and filament defects in an embedded-bioprinting context [24]. For industrial transfer, the bath must be qualified by yield/recovery method, temperature, age, reuse, contamination and path-density challenge, not by a generic `self-healing` label.

Support removal is a manufacturing operation. Heating can soften or distort the part; dilution can swell a hydrogel; washing can extract components; solvent can attack a silicone or polymer; mechanical removal can tear soft features. Enclosed channels can retain bath that is visually hidden. A release protocol needs access paths, time, temperature, agitation, fluid identity, bath loading, rinse, drying, residue test and dimensional recheck. Cleanliness criteria depend on the application and cannot be inferred from optical appearance.

Embedded printing can reduce the rheological burden on the ink, but it does not remove qualification. It exchanges unsupported sag and collapse for bath compatibility, path disturbance, release and residue risks. Unsupported writing can be preferable for accessible, sufficiently stable shapes; a bath can be preferable for soft or freeform geometries; a sacrificial core can be preferable when a defined removal route exists. The decision begins with the delivered component, especially internal access and cleanliness, rather than with the visual complexity of a demonstration.

10. Silicones and elastomeric direct writing

`Silicone` does not identify one DIW mechanism. Systems may cure through addition, condensation, moisture, heat, light or other chemistry; contain one or two metered parts; use volatile or non-volatile diluents; depend on reinforcing silica or another rheology modifier; or form organogels. Catalyst sensitivity, inhibitor compatibility, stoichiometry, mixing, degassing, adhesion, cure depth, extractables and post-cure differ. A supplier cure time belongs to a specified specimen, temperature and condition and does not qualify a printed wall or enclosed channel.

Silicone DIW offers conditional benefits: low-temperature deposition, elastomeric final states, soft interfaces, sealing, pneumatic or fluidic structures and integration with sensors or rigid inserts. Its constraints are equally strong. Low uncured modulus and surface wetting can cause spreading; high viscosity increases pressure; additives used for yield can change final properties; two-part cure introduces ratio and residence; one-part cure can be diffusion-limited; and platinum systems can be inhibited by incompatible sulphur-, amine-, tin- or other contaminant-bearing materials. Support, nozzle, mixer and cleaning chemistry therefore belong to the cure qualification.

Hinton et al. demonstrated PDMS printing in a compatible hydrophilic support bath [19]. Plott and Shih investigated moisture-cure extrusion [21]. Gharaie et al. developed and tested one specific two-part delivery and static-mixing route [20]. Luo et al. used carbon nanotubes both to modify PDMS ink behaviour and create electrical response [22]. Li et al. designed photo-crosslinkable silicone organogel inks in which rheology and final soft properties could be adjusted across their formulation family [23]. These are valuable but mutually non-equivalent systems. No ratio, loading, pressure, temperature, resolution or property from one should be carried into another.

The author's earlier project record for an addition-cure/platinum A+B silicone stated a 90-minute pot life at 23 °C, 24-hour cure at 23 °C and geometry down to 0.3 mm. ER-144 records that only as an example of the metadata a real project needs. It is not

independent published evidence, a universal capability or an instruction for another silicone. The same record noted that breakable support could be acceptable and dissolution preferable; route selection still requires compatibility and residue testing because some sacrificial photopolymers can inhibit platinum cure.

Final elastomer qualification must measure the printed state. Hardness is only one screen. Tensile response, tear, compression set, cyclic hysteresis, fatigue, creep, permeability, bond strength, ageing, fluid or chemical exposure, temperature, sterilisation where applicable and feature integrity may matter. Wall thickness, toolpath, voids, interfaces and cure state can dominate. The printed component must be compared with the relevant conventional alternative, which may be moulding, casting, coating, dispensing or assembly—not with an abstract ‘non-printed’ baseline.

ER-102 is the primary corpus source for the distinction between true silicones and silicone-like elastomers in vat photopolymerisation [29]. The 3Dresyns silicone-like collection is retained only as a manufacturer scope source identifying a vat-photopolymer family, not direct silicone [28]. That distinction prevents a common category error. A silicone-like resin can be selected for an elastomeric response in VPP, while a direct silicone route can retain silicone chemistry; neither is automatically superior. Selection depends on geometry, material identity, support, cure, surface, scale, throughput and final-service evidence.

11. Hydrogels and other soft aqueous networks

Hydrogels make the conflict between extrusion and retention especially visible. High water content and low final modulus can enable soft, hydrated functions while producing spreading, dehydration, osmotic change and fragile handling. Reversible physical networks may shear-thin and recover; covalent or ionic secondary crosslinks may stabilise the printed geometry. Temperature, pH, ionic strength, concentration, polymer substitution, ageing and evaporation can change both flow and final behaviour. ER-067 owns hierarchical and double-network hydrogels in vat photopolymerisation; ER-144 retains extrusion, retention and final-state qualification at this boundary.

Highley, Rodell and Burdick demonstrated an ink/support system based on reversible supramolecular interactions and secondary crosslinking [17]. Hinton et al. used a reversible support medium in FRESH printing [18]. These studies show how a bath and an ink can be co-designed. They do not establish that ‘self-healing’, ‘shear-thinning’ or ‘hydrogel’ is sufficient for production. Recovery time must be compared with nozzle-passage time, interlayer delay and build duration; crosslink must be measured through the intended section; and bath removal must preserve geometry and composition.

Water activity and evaporation create state drift even when no deliberate drying is planned. A cartridge can concentrate near an exposed outlet. A thin filament can lose water faster than a reservoir sample. A long build can create age differences between early and late regions. Swelling after release can change gaps and channel dimensions; an ionic bath can exchange species; washing can remove uncrosslinked material. Wet, equilibrated and dried dimensions are different measurands.

Bioprinting studies add a process warning without granting biological claims. Nozzle stress magnitude and duration, temperature, residence and material chemistry can affect cells, but ER-144 does not set viability thresholds. Friedrich et al. show that stress-reduction and shape-fidelity choices can conflict in a modelled embedded route [24]. Ribeiro et al. show the value of measured shape-fidelity tests [25]. Cell survival, sterility, biological function and clinical use require independent evidence and regulation beyond this paper.

Industrial hydrogel qualification begins with the delivered function. A seal, optical phantom, soft actuator, absorbent structure, microfluidic matrix or biological-adjacent component requires different swelling, modulus, permeability, extractables, ageing and cleanliness tests. A beautiful wet print is not a stable product. Packaging, storage, hydration medium, transport, temperature and time can be as important as deposition.

12. Highly filled and functional polymer pastes

Particles and fibres can create a printable yield-stress network, increase solids, reduce shrinkage, reinforce a polymer or add electrical, thermal, magnetic, optical or other function. They also introduce agglomeration, sedimentation, filtration, wall slip, nozzle wear, migration, alignment, voids, roughness, cure attenuation and anisotropy. The raw material identity, surface treatment, full particle/agglomerate distribution, shape, density and moisture must be linked to the mixed paste and final component.

Solids content needs an unambiguous basis. Weight and volume fraction lead to different interpretations, especially for high-density fillers. ‘Nanoparticle’ primary size does not reveal agglomerates or contamination. A nominal maximum size does not define the tail that encounters a nozzle. Fibre length can change through mixing and extrusion. The production record should include mixing energy/order, degassing, residence, sampling, dispersion method, sedimentation or phase separation, redispersibility and a justified nozzle-to-particle/fibre relationship. ER-099 owns dispersant chemistry for photo-curable resins, oligomers and monomers; this review retains only the DIW paste-state and nozzle-delivery consequences.

Compton and Lewis demonstrated DIW of fibre-filled epoxy cellular composites [12]. Lewicki et al. reported mesostructurally ordered carbon-fibre/polymer composites with pronounced directional behaviour [13]. Luo et al. used carbon nanotubes in PDMS to change both rheology and electrical function [22]. These results illustrate the opportunity to program local orientation and function, but also why a filler name or loading cannot predict the delivered property. Toolpath, shear history, cure, porosity, contacts and measurement direction are part of the material state.

High loading can make the paste appear dimensionally stable while limiting wetting and interlayer fusion. More rheology modifier can support a wall yet dilute or disrupt the intended function. A conductive network can cross a percolation transition but remain contact- and direction-sensitive. A thermal filler can increase local conductivity while interfaces and porosity dominate the

component. A ceramic or metal loading can support a green body while final debinding and sintering generate shrinkage or defects outside ER-144's acceptance boundary.

NIST's Romberg and Kotula study shows that filler content, temperature, cure conversion, yield stress and storage modulus can interact [14]. Allen, Levin and Maier record the continuing need for shared feedstock/end-product data and round-robin evidence for ceramic DIW industrialisation [15]. These sources support a conservative conclusion: material formulation and final qualification cannot be separated, and the evidence gap is not closed by a successful single-machine build.

The 3Dresyns putty, gel, filler and sealant page identifies durable and sacrificial material families [27]. In ER-144 it is a scope source only. A material developed for hand application, sealing, repair, moulding or light-cured filling is not automatically suited to extrusion. DIW feasibility requires cartridge stability, pressure delivery, nozzle output, recovery, cure through the printed geometry and final-part testing. Product labels cannot replace that route-specific work.

13. Geometry, properties, throughput, safety and change control

Nominal nozzle diameter is an input, not resolution. Minimum positive filament, negative gap, channel, corner radius, wall, span, overhang, enclosed cavity and interface must be measured separately. The cross-section can change through swell, drawdown, compression, wetting, drying, cure and support removal. A finer nozzle can produce a smaller nominal strand while increasing pressure variation or filler blockage. A geometric artefact programme should include the actual material age, build time and post-process.

Measurement uncertainty must be compatible with tolerance. Soft surfaces can deform under contact probes. Transparent or glossy elastomers can bias optical edge detection. Hydrogels can dehydrate during measurement. Computed tomography can lack contrast between similar polymers or introduce resolution limits. Mass and dimensions should be linked to conditioning time and environment. ISO/ASTM 52902 and 52927 can organise artefacts and characteristic/test-method selection [6,7], but the production component still needs feature-specific acceptance.

Properties require printed dimensions and orientation. A tensile or conductive specimen must state filament direction, intersections, interfaces, cure, conditioning, support contact and extraction location. ISO/ASTM 52924 can structure polymer-property classes [5], while ISO 17295 controls coordinate and orientation language [8]. A property from a moulded coupon, bulk-cured slug or single printed direction cannot be assigned to every feature. Functional testing at the component level is needed when geometry participates in performance.

Print speed is not throughput. A theoretical volumetric deposition rate can be written as 'Q', but accepted factory output includes conditioning, loading, priming, purging, calibration, building, cure or drying, bath/support removal, cleaning, inspection, rejects, maintenance and changeover. The useful measure is:

$$\text{Effective cell throughput} = \text{accepted components} / \text{elapsed time from released feedstock to final acceptance}$$

DIW can avoid mould tooling, place multiple materials and process specialist feedstocks at moderate temperature. It can also carry high labour for cartridge preparation, cleaning, support removal and inspection; low volumetric rate through fine nozzles; expensive waste from purging and expired reactive material; and nonlinear downtime from blockage. The correct comparison includes the explicit alternative—moulding, casting, dispensing, coating, machining, FFF, VPP, inkjet or no-build—and the required production volume.

NIOSH states that additive-manufacturing hazards depend on technology, materials and environment [26]. ER-144 does not convert that broad guidance into one DIW exposure limit. Hazards can include reactive monomers or oligomers, catalysts, solvents and vapours; fine particles, fibres or dried residues; pressure injection and line release; hot surfaces or exotherm; UV or visible-light sources; moving equipment; sharp needles; cleaning chemicals; biological materials where used; and contaminated support or waste. Each formulation requires a current SDS, chemical inventory, task analysis and applicable legal controls.

Engineering controls should favour enclosure, local capture where justified, pressure-rated hardware, guarded motion and radiation interlocks, closed material transfer, spill containment and compatible cleaning. A pressure line must be isolated and depressurised before opening. Wipes, purge, failed parts, baths, solvents, cartridges, mixer tips and contaminated PPE require defined segregation and disposal. 'Water-based', 'bio', 'silicone' or 'solvent-free' does not mean harmless or drain-disposable.

Change control must capture material revision or lot strategy, filler supplier or surface treatment, mix order, cartridge or seal, tubing length, mixer, nozzle, pressure hardware, software, toolpath, ambient temperature/humidity, bath formulation, cure source, post-process and measurement method. Seemingly small changes can alter residence, shear, cure, wetting or residue. Requalification depth should follow a documented equivalence and risk assessment, not a visual comparison.

14. Qualification architecture, selection gate and conclusions

ISO/ASTM 52920:2023 frames industrial additive manufacturing as a controlled process and production site [2]. For DIW, that system includes material genealogy, conditioning, loading, air control, pressure or displacement generation, tubing and connectors, independent A/B metering where applicable, mixer and nozzle state, environment, toolpath, substrate or bath, conversion, support removal, conditioning, measurement and disposition. A printer name and a paste datasheet describe only fragments.

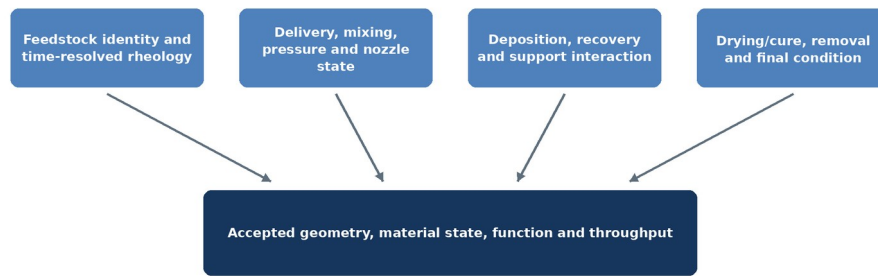


Figure 2. Coupled DIW production window

Table 2. Mechanism-to-defect and evidence matrix

Mechanism or change	Possible visible result	Possible hidden consequence	Minimum evidence
Sedimentation, bleeding or air	Pulsing, streaks, bubbles or interrupted line	Composition drift, voids and local property loss	Cartridge-position samples, density/solids/air checks, delivered-mass trend
Rheology or temperature drift	Changed width, sag or unstable pressure	Recovery/cure shift and non-uniform interfaces	Time/temperature-conditioned rheology and line/stack challenge
Metering or mixing error	Colour or cure variation, soft/tacky regions	Stoichiometric gradient and incomplete conversion	Independent stream mass/flow, mixed-state uniformity and conversion map
Nozzle wear, blockage or slip	Width change, roughness, curling or flow loss	Fibre/particle segregation and pressure uncertainty	Nozzle identity/inspection, pressure–flow response and outlet composition
Start-stop/corner mismatch	Blobs, gaps, thin starts and overfilled corners	Stress concentrators, leaks or functional discontinuity	Transient artefacts under production acceleration and pause states
Inadequate recovery or conversion	Spreading, collapse, sag or layer movement	Enclosed distortion, poor fusion or property gradients	Time-resolved line/stack/span geometry and state-specific conversion
Bath/support incompatibility	Drag, displaced paths, swelling or surface marks	Cure inhibition, trapped residue and chemistry transfer	Ink–bath compatibility, path-density challenge, removal and residue test
Drying/cure gradient	Warp, cracks, skinning or colour change	Residual solvent, internal under-cure and ageing drift	Mass/conversion/temperature history and section-sensitive final tests

The route-selection gate proceeds from the delivered component:

1. Define geometry, surface, material identity, softness/stiffness, environmental exposure, cleanliness, function, durability, regulatory boundary, throughput and cost in the final conditioned state.
2. Classify the feedstock and transition: colloidal/yield-stress, one-part reactive, two-part reactive, photo/thermal cure, hydrogel physical/secondary network, solution/drying, highly filled composite or another declared route.
3. Decide whether unsupported, local support, embedded bath, sacrificial core, mould-assisted deposition or a different AM/conventional process can create and release the required geometry.
4. Qualify feedstock genealogy, dispersion, air, time/temperature state, rheology protocol and conversion kinetics across the planned production window.
5. Qualify the complete delivery path: cartridge, seals, pump/pressure system, tubing, valves, A/B metering, mixer, nozzle, dead volume, residence, priming, purging and cleanout.
6. Map flow, pressure, path speed, nozzle height, starts/stops, corners, line spacing, layer delay, recovery and cure/dry trigger using line, intersection, stack, span and representative-feature artefacts.
7. Validate bath/support behaviour, path-density disturbance, cure compatibility, access, removal, cleanliness and dimensional change where support is used.
8. Demonstrate final conversion, conditioning, geometry, surface, interfaces, anisotropy, function, durability and measurement uncertainty on printed representatives and the component.
9. Establish repeatability across lots, cartridges, nozzles, operators, machines, baths, shifts and maintenance intervals; define alarms, rejects and requalification triggers.
10. Compare accepted-component throughput, yield, labour, material/support/purge waste, maintenance, safety controls and full cost against the declared alternative, then issue a go/no-go decision.

Table 3. Minimum industrial qualification record

Record block	Minimum controlled content	Release question
Material genealogy	Grade/revision, lot, composition or controlled surrogate, storage/open age, conditioning, particles/fibres, rheology and cure/dry state	Was the exact material state released for this route?
Delivery path	Cartridge/reservoir, piston/seals, pump or pressure system, tubing, fittings, valves, mixer, nozzle and temperatures	Did every product-contact element remain within its qualified state?
Metering and residence	A/B or multimaterial ratios, flow/mass, pressure, dead volume, residence distribution, starts/stops, prime and purge	Was delivered composition controlled through the complete run?
Deposition and support	Toolpath/version, speed/flow, gap, line/layer spacing, substrate or bath, recovery, conversion timing and environmental state	Was geometry built inside the qualified placement and support window?

Record block	Minimum controlled content	Release question
Conversion and removal	Drying/cooling/cure irradiance/temperature/humidity, support/bath washing, cleaning and conditioning	Did the printed intermediate reach the declared final state without hidden residue or under-conversion?
Final acceptance	Geometry, surface, voids, interfaces, properties, function, durability, cleanliness and measurement uncertainty	Is the tested object the specified delivered component?
Factory and change	Cell time, yield/rejects, waste, exposure controls, maintenance, deviations, equivalence and requalification decisions	Can every accepted component be traced to an unchanged qualified route?

The evidence base contains defined materials, equipment and research systems. It does not provide universal viscosity, yield-stress, recovery, modulus, nozzle, pressure, speed, layer-height, pot-life, cure, drying, span, resolution or property settings. The author's 90-minute/24-hour/0.3-mm silicone project example is not a validated parameter set for ER-144. Commercial page descriptions identify families and category boundaries but do not independently close performance claims.

The following conclusions control industrial use:

1. DIW and paste extrusion are state-transition manufacturing routes, not viscosity classes or syringe attachments.
2. Shear thinning can reduce delivery resistance but is not sufficient for filament formation, recovery, fusion, shape retention or final conversion.
3. Pressure, flow, nozzle geometry, mixer residence, path speed and material age must be measured as one delivery system.
4. Nozzle diameter, CAD line width and layer height do not by themselves establish realised resolution or accepted geometry.
5. Unsupported and embedded writing exchange different risks; the better route depends on geometry, compatibility, removal, cleanliness and final condition.
6. One-part, two-part, moisture-, thermal- and photo-cure silicones require distinct evidence; silicone-like vat photopolymers are another category.
7. Hydrogel print success does not establish biological acceptance, and highly filled green-body success does not establish dense ceramic or metal properties.
8. Fillers can create rheology and function while also creating dispersion, wear, anisotropy, void and conversion burdens that must be tested in the printed state.
9. Drying, cure, cooling, support removal and conditioning are manufacturing operations inside the qualification boundary.
10. Effective throughput counts accepted components after the complete route; there is no universal technology winner.

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