

DISE

DELAYED IN-SITU SUSPENSION POLYMERIZATION

A liquid-to-particle platform for deep fracture placement and high-conductivity support

TECHNICAL WHITE PAPER

Version 5.0 | September 2026

Dr Juan Martin

Project Lead

DISE

One formulation. One transformation pathway. One engineering objective.

PROJECT: **DISE**

INNOVATIVE MATERIALS FOR SUBSURFACE APPLICATIONS

DISE

Delayed *In-Situ* Emulsion Polymerization (*Suspension*)

Controlled *In-Situ* Formation of Discrete, Load-Bearing Microparticles That Preserve Flow Pathways

DISE is a low-viscosity liquid system that travels as a stable droplet dispersion and transforms in-place into spherical, high-strength microparticles only after reaching the target environment.



LOW-VISCOSITY TRANSPORT
≤10 cP liquid ensures easy pumping and placement



DELAYED ACTIVATION
25–75 min programmable activation window after placement



DISCRETE MICROPARTICLES
70–600 μm spherical particles with minimal agglomeration



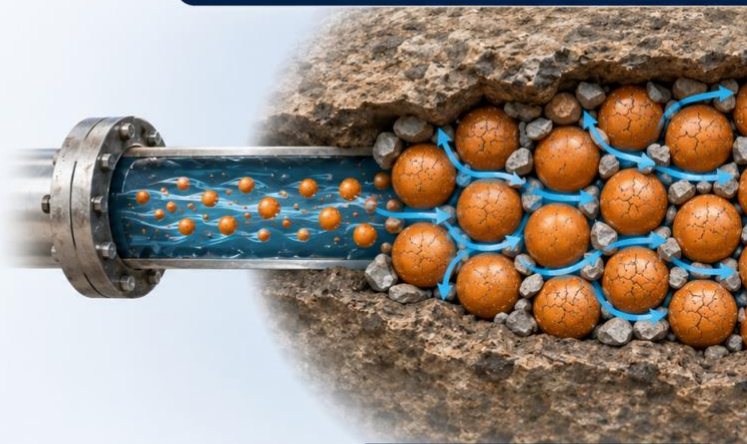
LOAD-BEARING STRENGTH
Withstands 4,500–6,000 psi at reservoir conditions



FLOW PATHWAYS PRESERVED
High permeability retention enables continued fluid transport

PROJECT OBJECTIVE

Deliver a novel material system that can be injected as a liquid, remain stable during transport, and transform in-situ into a microparticle pack that supports reservoir integrity while preserving flow.



DISE travels as a low-viscosity aqueous suspension of reactive droplets and transforms after placement into discrete load-bearing particles. Version 5 fixes the development chemistry as a TMPTA/DVB network and removes all alternative monomer families from the programme.

Contents

Executive Summary	4
1. The DISE proposition	5
2. Selected formulation: TMPTA/DVB	6
3. Droplet architecture and interfacial protection	7
4. Programmed thermal-dose activation	8
5. Transport rheology, density and thermal control	9
6. Particle formation and mechanical performance	10
7. Fracture conductivity and pack architecture	11
8. Field formulation, storage and deployment	12
9. Validation programme and performance gates	13
10. Evidence synthesis and competitive position	14
References	15

Executive Summary

DISE is a delayed in-situ suspension-polymerization platform designed to separate two functions that conventional proppant systems must perform simultaneously: easy hydraulic placement and high post-placement mechanical strength. During pumping, DISE is a water-dominated suspension of hydrophobic reactive droplets. After the required thermal exposure, each droplet becomes a microreactor and cures into a discrete particle. The aqueous phase remains non-structural, so the final architecture is particulate rather than a continuous polymer plug.

Version 5 selects one chemistry for development: trimethylolpropane triacrylate/divinylbenzene (TMPTA/DVB). The choice is anchored in the closest available published precedent. Ren et al. (2026) used TMPTA with DVB in a phase-changeable liquid for self-generated proppants and reported rapid post-trigger strength development, near-90% pellet formation, chemical resistance and only 3% crushing at 69 MPa. DISE's 6,000 psi closure condition is approximately 41 MPa. The study therefore places the selected network family in a mechanical regime above the DISE design requirement, while DISE adds controlled droplet templating, delayed activation and low-viscosity transport.

The selected system uses di-tert-butyl peroxide (DTBP) as the high-temperature initiator, a calibrated inhibitor reserve for induction control, partially hydrolysed PVA for steric stabilization and hydrophilically modified silica for Pickering reinforcement. These choices form one integrated formulation; development work optimizes their ratios rather than screening alternative chemistries.

Requirement	V5 response
≤10 cP transport	Water-dominated continuous phase and bounded droplet volume fraction.
25–75 min delay	DTBP thermal-dose kinetics plus calibrated inhibitor capacity.
70–600 μm particles	Pre-engineered droplets act as particle templates.
4,500–6,000 psi closure	TMPTA/DVB selected from direct 2026 proppant evidence at 69 MPa.
Flow preservation	Discrete particle pack rather than a continuous cured matrix.

1. The DISE proposition

DISE reverses the conventional proppant sequence. Instead of pumping the final solid through the wellbore and fracture network, it transports the future proppant as a liquid droplet and creates the solid only after placement. Recent in-situ generated proppant research establishes the feasibility of this liquid-to-solid strategy: Zhang et al. (2022) reported adjustable thermo-responsive transformation and field application in eight wells; Krishnan et al. (2024) describe in-situ generated proppants as an emerging class with reported stress resistance up to 80 MPa; and Bai et al. (2025) demonstrated temperature-regulated in-situ particle generation with high sphericity and aqueous-phase control of particle size.

1.1 Functional sequence

- Transport — stable O/W suspension with the aqueous phase governing bulk rheology.
- Delay — early radical production remains below the threshold for sustained network growth.
- Activation — accumulated thermal dose and declining inhibition permit rapid intradroplet polymerization.
- Particle formation — TMPTA/DVB crosslinking locks the droplet morphology into a solid particle.
- Fracture support — particles carry closure load while interparticle voids remain available for flow.

1.2 The key engineering distinction

The droplet is the transport unit, the chemical reactor and the particle template. DISE therefore defines the future particle population before pumping rather than relying on a bulk resin to fragment unpredictably during cure.

2. Selected formulation: TMPTA/DVB

V5 fixes the reactive network as TMPTA/DVB. Styrene/DVB, TMPTMA, TAIC and vinyl-ester branches are removed. Ren et al. (2026) provide the decisive evidence: the same TMPTA/DVB pairing was used for self-generated proppants, with rapid gel-effect-assisted strength development, near-90% pellet formation, strong chemical resistance and 3% crushing at 69 MPa.

2.1 TMPTA

TMPTA is the principal multifunctional network former. Its three acrylate groups support rapid branching and gelation once propagation begins. That behaviour is valuable after placement because the system can move quickly from the induction period into a mechanically coherent network.

2.2 DVB

DVB supplies aromatic rigidity and additional crosslinking functionality. It is deliberately treated as an optimized minority comonomer rather than maximized. Perez et al. (2025) showed in polymeric proppant materials that an intermediate DVB content gave the best balance of crosslink density and mechanical performance, reinforcing the principle that toughness and deformation resistance must be optimized together.

Component	Selected role
TMPTA	Principal multifunctional reactive monomer.
DVB	Aromatic crosslinking comonomer.
DTBP	Oil-soluble thermal initiator selected for high-temperature decomposition kinetics.
Phenolic inhibitor reserve	Calibrated induction control, distinct from supplier storage stabilization.

The chemistry is fixed, but V5 does not invent a final mass ratio before HPHT kinetic and rheological calibration. Component ratios are formulation-lock variables, not alternative formulations.

3. Droplet architecture and interfacial protection

Suspension polymerization is the physical foundation of DISE. Brooks (2010) describes an established free-radical bead-forming process in which final bead-size distribution commonly follows the polymerizing droplet distribution and where both water-soluble polymers and particulate solids can act as suspending agents.

3.1 PVA + silica interface

DISE selects partially hydrolysed PVA as the steric protective colloid and hydrophilically modified silica nanoparticles as the Pickering stabilizer. Lee et al. (2014) demonstrated mechanically stable silica/PVA interfacial layers and resistance to coalescence under saline conditions. Li et al. (2024) further showed that engineered silica Pickering systems can retain stability under high-salinity and elevated-temperature reservoir conditions.

3.2 Tack-phase protection

The most vulnerable morphology interval occurs after polymerization starts but before the network is fully load-bearing. PVA reduces collision efficiency through steric separation; the silica layer supplies a persistent physical barrier. The qualification endpoint is preservation of droplet individuality through the complete conversion trajectory, not simply bottle stability before heating.

Parameter	Target
Droplet envelope	70–600 μm
Development centre	D50 $\approx$ 200–300 μm
Fine fraction	Minimize <70 μm material
Doublets	<5% development target
End state	Predominantly discrete, near-spherical particles

4. Programmed thermal-dose activation

DISE uses accumulated thermal history rather than a step-function trigger because each fluid element experiences a transient temperature trajectory during surface preparation, tubing transit and fracture entry.

$$\Theta(t) = \int_0^t k_d[T(\tau)] d\tau \quad ; \quad k_d(T) = A \exp(-E_a/RT)$$

4.1 DTBP selection

DTBP is selected because published commercial kinetic data place its one-hour half-life at approximately 149–151°C. That aligns naturally with a 150°C target environment. The final induction time is then tuned by DTBP concentration and inhibitor capacity rather than by switching initiator chemistry.

4.2 Reaction sequence

Stage	Mechanism
1. Radical generation	DTBP undergoes thermal O–O homolysis inside the organic phase.
2. Induction	Early radicals are intercepted while inhibitor capacity remains sufficient to suppress sustained propagation.
3. Propagation / branching	Radicals add across TMPTA and DVB vinyl groups, increasing molecular weight and network connectivity.
4. Gelation / autoacceleration	Termination becomes diffusion-limited as viscosity rises; the Trommsdorff–Norris effect accelerates conversion.
5. Final cure	The network becomes increasingly immobile and mechanically stable as diffusion becomes restricted.

The 25–75 minute window is therefore measured for the complete formulation by calorimetry and HPHT conversion testing; it is not inferred from initiator half-life alone.

5. Transport rheology, density and thermal control

5.1 Dispersed-phase volume fraction

The reactive droplet volume fraction ϕ is the master variable linking chemical payload to viscosity, collision frequency, heat release and final particle population. DISE uses Krieger–Dougherty scaling for screening and HPHT rheology for qualification.

$$\eta_r = \eta_{\text{susp}} / \eta_c = (1 - \phi/\phi_m)^{-[\eta]\phi_m}$$

A ϕ range around 0.20–0.30 is a development window, not a fixed claim. The selected value is the highest loading that maintains ≤ 10 cP, acceptable pause stability, tack-phase separation and thermal margin.

5.2 Density evolution

Polymerization changes specific volume. DISE therefore uses measured conversion-dependent density $\rho_d(\alpha, T, P)$ rather than matching only the starting monomer density. Brine density is selected to minimize cumulative gravitational slip during transport, pump pauses and cure.

$$v_{\text{slip}} \approx 2 \Delta\rho(\alpha, T, P) g R^2 / 9\mu c$$

5.3 Exotherm control

The reactive inventory is divided among hundreds-of-micrometre droplets surrounded by a high-heat-capacity aqueous phase. Bounded ϕ limits heat generation per unit treatment volume, while the fracture wall provides additional thermal mass. Reaction calorimetry is coupled to the kinetic model to verify that self-heating remains inside the induction-time margin.

6. Particle formation and mechanical performance

The 2026 TMPTA/DVB study is the closest published mechanical precedent for V5. Ren et al. reported completion of the self-generated-proppant strength-growth process within approximately eight minutes after transformation began, near-90% pellet formation, chemical resistance and a 3% crushing rate at 69 MPa.

DISE's 6,000 psi upper closure condition is approximately 41 MPa. The 69 MPa literature result does not substitute for DISE qualification because particle geometry and formulation details differ, but it establishes that the selected network family is capable of operating in a stress regime above the design requirement. This is why V5 selects TMPTA/DVB and removes the alternative networks.

Qualification	V5 gate
Crush/fines	<10 wt% fines at the defined 6,000 psi protocol
Sustained HPHT loading	Stable pack height and conductivity over the qualification hold
DMA / hot mechanics	No service-limiting softening at 150°C
Chemical exposure	No functionally significant loss after defined brine/acid/hydrocarbon exposure

Mechanical success is assessed at particle-pack level. Proppant literature shows that crushing, creep, embedment and rock-particle interaction collectively determine fracture performance.

7. Fracture conductivity and pack architecture

DISE is designed to create a mechanically supported but hydraulically open fracture. The cured phase must therefore remain particulate. Connected interparticle voids provide the flow architecture that a continuous cured matrix would remove.

$$k \propto \epsilon^3 d_p^2 / (1 - \epsilon)^2$$

Kozeny–Carman is used only as directional scaling. Real fractures are rough, confined and stress dependent; the authoritative performance measurement is HPHT fracture conductivity under closure stress, supported by micro-CT imaging of particle distribution and connected void space.

- A narrow particle distribution limits fines that can occupy pore throats.
- Tack-phase stabilization prevents large clusters that can bridge prematurely.
- Particle size can be selected against the target fracture-aperture distribution.
- Micro-CT verifies that the cured phase remains discrete rather than forming a continuous matrix.

7.1 Hydraulic gate

The development target is $\geq 70\%$ retained conductivity/permeability relative to a defined reference condition under the same temperature and closure-stress protocol. The baseline is specified in advance so that the percentage is reproducible and auditable.

8. Field formulation, storage and deployment

DISE separates logistics stability from downhole timing. Raw monomers remain under supplier-qualified storage stabilization; the field activation package is introduced only during controlled preparation.

Pack	Composition	Function
A — Reactive	TMPTA/DVB with supplier-qualified storage stabilization	Stores the hydrophobic reactive phase without the thermal initiator.
B — Aqueous	Engineered brine + partially hydrolysed PVA + hydrophilically modified silica	Creates and protects the O/W droplet population.
C — Activation	DTBP + calibrated induction-control chemistry	Introduced close to deployment to establish the downhole reaction clock.

8.1 Field sequence

- Prepare Pack B and confirm brine composition, silica dispersion and continuous-phase viscosity.
- Meter Pack A into Pack B through qualified inline shear to establish D10/D50/D90.
- Introduce Pack C sufficiently close to pumping to minimize surface residence after activation chemistry is present.
- Verify bulk viscosity and droplet distribution before injection.
- Pump through the qualified pressure/shear envelope and allow reservoir thermal history to complete transformation.

DTBP is stored separately according to supplier temperature, packaging and SADT requirements. The downhole induction package is not used as a substitute for conventional monomer or peroxide storage safety.

9. Validation programme and performance gates

The V5 programme is a formulation-lock exercise, not a chemistry-screening programme. TMPTA/DVB remains fixed. Development optimizes component ratios, ϕ , droplet size, DTBP loading and induction capacity until the integrated operating envelope is achieved.

Work package	Experiment	Gate
WP1 • Months 1–3	HPHT rheology, calorimetry, conversion kinetics, morphology	≤ 10 cP; 25–75 min induction; discrete cure; controlled exotherm
WP2 • Months 4–6	10,000 psi circulation loop with restrictions, shear and pause/restart	$< 15\%$ D50 shift; no operational fouling; preserved post-loop cure
WP3 • Months 7–9	Fracture placement, in-situ cure, 6,000 psi closure, micro-CT and conductivity	< 10 wt% fines target; discrete pack; $\geq 70\%$ retained conductivity/permeability

9.1 Integrated pass condition

The formulation is accepted only where hydraulic, morphological, kinetic, gravitational, thermal and mechanical envelopes overlap. This prevents a gain in one variable—such as reactive loading—from being accepted if it compromises pumpability, morphology or conductivity.

10. Evidence synthesis and competitive position

V5 is deliberately narrower than the preceding white papers. It does not ask a reviewer to choose between several plausible networks. It selects the chemistry with the closest published precedent to the required function and builds the transport, activation and interface engineering around that chemistry.

Reviewer question	Evidence-led answer
Can liquid precursor become proppant in situ?	Yes: laboratory and field precedent exists, including eight-well application (Zhang et al., 2022).
Can particle generation be controlled?	Yes: Bai et al. (2025) report regulated solidification, sphericity ≥ 0.9 and aqueous-phase size control.
Why TMPTA/DVB?	Direct 2026 self-generated-proppant evidence reports 3% crushing at 69 MPa, above the ~41 MPa DISE closure target.
Can droplets become beads predictably?	Yes: suspension polymerization is an established bead-forming process in which bead distribution commonly follows droplet distribution.
Why PVA/silica?	Published work supports silica/PVA interfacial layers and silica Pickering stability under reservoir-relevant salinity and temperature.
What proves DISE itself?	Integrated HPHT transport-to-cure testing followed by stressed fracture conductivity and micro-CT.

10.1 Final technical position

The V5 hypothesis is precise: a TMPTA/DVB reactive droplet, protected by a PVA/silica interface and initiated by a DTBP-based thermal-dose system, can be transported in a water-dominated suspension and converted after placement into a mechanically competent particulate pack. Each element has a published precedent. The remaining engineering task is to integrate those precedents into one qualified DISE formulation under the challenge conditions.

References

Ten references were selected for direct relevance to formulation choice, in-situ proppant generation, droplet stabilization or mechanical qualification. Cite Them Right Harvard format.

- Ren, X., Li, Z., Chen, Y., Fu, X., Zhang, Y., Fang, D. and Chen, X. (2026) 'A specific strategy for accelerating strength-development rate of self-generated proppants: the gel effect related autoacceleration', *Fuel*, 417, 138620. doi: 10.1016/j.fuel.2026.138620.
- Bai, S., Yang, Y., Wang, L. and Yang, Z. (2025) 'On-demand in situ proppant generation via temperature-induced solidification of fracturing fluid', *Industrial & Engineering Chemistry Research*, 64(51), pp. 24333–24345. doi: 10.1021/acs.iecr.5c03553.
- Krishnan, M.R., Li, W., Alharbi, B. and Alsharaeh, E. (2024) 'Recent developments on in-situ generated proppants for hydraulic fracturing operations: a critical review', *Geoenvironment Science and Engineering*, 242, 213227. doi: 10.1016/j.geoen.2024.213227.
- Perez, C.J., Rueda, F., Pettarin, V., Tomba, J.P. and Carella, J.M. (2025) 'Styrene-divinylbenzene copolymers for high-performance proppant applications', *Polymer Engineering & Science*, 65(6), pp. 3247–3258. doi: 10.1002/pen.27211.
- Zhang, N., Luo, Z., Zhao, L., Zhu, R., Chen, W., Liu, G., Chen, X., Xie, Y. and Cheng, L. (2022) 'Innovative thermo-responsive in-situ generated proppant: laboratory tests and field application', *Journal of Petroleum Science and Engineering*, 208, 109514. doi: 10.1016/j.petrol.2021.109514.
- Li, D., Wang, Y., Liang, S., Bai, B., Zhang, C., Xu, N., Shi, W., Ding, W. and Zhang, Y. (2024) 'Synthesizing dendritic mesoporous silica nanoparticles to stabilize Pickering emulsions at high salinity and temperature reservoirs', *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 687, 133481. doi: 10.1016/j.colsurfa.2024.133481.
- Lee, G.J., Son, H.A., Cho, J.W., Choi, S.K., Kim, H.T. and Kim, J.W. (2014) 'Stabilization of Pickering emulsions by generating complex colloidal layers at liquid–liquid interfaces', *Journal of Colloid and Interface Science*, 413, pp. 100–105. doi: 10.1016/j.jcis.2013.09.015.
- Brooks, B.W. (2010) 'Suspension polymerization processes', *Chemical Engineering & Technology*, 33(11), pp. 1737–1744. doi: 10.1002/ceat.201000210.
- Luo, Z., Li, J., Zhao, L., Zhang, N., Chen, X., Miao, W., Chen, W. and Liang, C. (2021) 'Preparation and characterization of a self-suspending ultra-low density proppant', *RSC Advances*, 11, pp. 33083–33092. doi: 10.1039/D1RA05611E.
- Man, S. and Wong, R.C.-K. (2017) 'Compression and crushing behavior of ceramic proppants and sand under high stresses', *Journal of Petroleum Science and Engineering*, 158, pp. 268–283. doi: 10.1016/j.petrol.2017.08.052.