

Deep-Eutectic-Solvent-Containing Photocurable Systems: Component Identity, Speciation, Water, Polymerisation and Leaching

Qualification of DES-containing resins from liquid-state speciation to printed-network stability

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Abstract

Deep eutectic solvents (DESs) can reduce viscosity, introduce hydrogen-bonding interactions and provide ionic or chemical functionality in photocurable systems. Their defining feature is not simply a low melting point but a composition-dependent liquid state created by strong interactions between components, often a hydrogen-bond donor and acceptor. Water, impurities and polymerisation can change that state. A 2023 study demonstrated DES-based photocurable resins compatible with commercial LCD vat photopolymerisation, showing that the concept can move beyond solution chemistry into printed networks. [1] This review focuses on the engineering consequences: exact component identity and molar ratio, water content, phase behaviour, cure kinetics, extractable fraction, mechanical response and environmental stability must be recorded together. It distinguishes a true DES-containing network from an ordinary monomer mixture labelled after its feedstock and proposes qualification tests that prevent viscosity or strength improvements from masking leaching, water sensitivity or cure-state changes.

Keywords: deep eutectic solvent; photocurable resin; hydrogen bonding; vat photopolymerisation; water content; leaching; phase state; DES

1. Scope and terminology

A deep eutectic solvent is a multicomponent liquid whose interactions depress the melting point relative to the individual components. In photocurable systems, one or more DES components may be reactive, non-reactive or only partially retained after cure. The engineering task is therefore to identify the material state before and after polymerisation. Li et al. demonstrated a DES-based photocurable resin with synergistic hydrogen bonding and commercial LCD printability, establishing direct relevance to VPP. [1]

2. Component identity and molar ratio

DES behaviour depends strongly on the identities and ratio of hydrogen-bond donor and acceptor. Small composition errors can change viscosity, conductivity, water affinity and phase stability. The formulation record should give component purity, molar ratio and whether each component carries polymerisable functionality. A generic label such as 'choline chloride-based DES' is insufficient for reproducibility because the donor chemistry and water content can dominate the liquid state.

3. Water is a state variable, not a nuisance correction

Water can lower viscosity and change hydrogen-bonding structure, but at higher levels it may convert a DES into an aqueous solution-like mixture. Because atmospheric uptake can occur during storage and printing, water content should be measured rather than assumed. Viscosity, cure rate and final modulus should be interpreted at a declared water state. Apparent batch-to-batch improvement can otherwise be a humidity effect rather than a chemistry effect.

Table 1. State changes in DES-containing photocurable systems

State	What can change	Evidence
Incoming DES	Ratio, purity, water, crystallisation	Identity, molar ratio, water content, thermal state
Photoresin	Viscosity, miscibility, absorption	Rheology, optical spectrum, phase check
Green network	Conversion, trapped mobile fraction	FTIR/Raman, gel fraction, extractables
Conditioned article	Leaching, swelling, reorganisation	Mass balance, leachate analysis, mechanics

4. Photopolymerisation changes the eutectic environment

Cure consumes reactive groups and immobilises parts of the liquid structure. The pre-cure DES therefore does not necessarily survive as the same thermodynamic entity in the network. Some components can become covalently bound while others remain mobile. Conversion, gel fraction and extractables are needed to determine the post-cure state. The 2023 DES photopolymer study shows that strong hydrogen-bonding interactions can be exploited in a printable resin, but it does not justify assuming that all DES interactions remain unchanged after cure. [1]

5. Rheology and recoating

Low viscosity is one motivation for DES-containing resins, yet viscosity alone does not establish VPP processability. Surface tension, wetting, thixotropy and temperature dependence influence layer refill. Hygroscopic DES components can also produce time-dependent viscosity drift during an open-vat print. Qualification should therefore record viscosity versus temperature and, where relevant, humidity exposure time.

6. Mechanical response and reversible interactions

Hydrogen bonding can increase toughness or alter modulus, while mobile DES components can plasticise the network. These effects may coexist. Mechanical characterisation should include rate and temperature because reversible interactions are time-dependent. A high tensile strength measured immediately after cure does not establish creep resistance or dimensional stability after solvent or humidity exposure.

7. Leaching and extraction

Non-reactive DES components can migrate during washing, water immersion or service. Leaching changes composition and may create porosity, mass loss or property drift. The appropriate evidence includes extract mass, analytical identification of leachate and post-extraction mechanical/chemical testing. For biomedical or catalytic uses, released species may be the primary safety or performance concern.

8. Phase separation and optical consequences

A DES-containing resin can appear homogeneous before cure yet phase-separate as conversion increases or temperature changes. Cloud point, microscopy, DSC and optical transmission can reveal this transition. In VPP, phase separation can change local cure depth and scatter light, so optical stability belongs in process qualification even when the end use is not optical.

Table 2. Common false inferences

Observation	Unsafe inference	Required discriminator
Low viscosity	DES state is stable	Water and temperature dependence
High initial strength	Hydrogen bonds are permanently beneficial	Rate, creep and humidity testing
No visible phase separation	Network is chemically homogeneous	Thermal/spectroscopic or microscopic evidence

9. Stability during storage and printing

DES composition can drift through water uptake, evaporation of volatile components or crystallisation of a constituent. Storage stability should therefore be tested at defined temperature and container conditions. Repeated sampling from an open vat can be used to determine whether the liquid state remains equivalent during the intended production interval.

10. Qualification decision boundary

A DES-containing photocurable system is qualified only when component identity, water content, phase state and retained composition are controlled. Improved printability or toughness cannot compensate for uncontrolled leaching or humidity-driven drift. Transfer to another printer requires new cure and rheology evidence because the liquid-state advantages can interact with wavelength and thermal history.

11. Evidence gaps

Direct DES-VPP literature remains limited, although recent reviews and polymerisable-eutectic studies show a rapidly expanding printed-material evidence base. [2,3] Many studies outside printing still focus on liquid properties rather than cured-network retention. Long-term leaching, repeated humidity cycling and equivalence of regenerated or recycled DES-containing resins are poorly constrained. The field also lacks a common boundary between 'DES-containing network' and ordinary eutectic-inspired comonomer mixtures.

12. Research priorities

The most useful studies would combine Karl Fischer water measurement, rheology, spectroscopic conversion, extraction mass balance and mechanical testing on the same formulation series. Phase-state measurements before and after cure should be included. Printer studies should report vat exposure time and ambient humidity so composition drift can be separated from nominal formulation differences.

13. Measurement architecture for eutectic systems

A defensible DES record links composition to state using three complementary measurements: quantitative water content, temperature-dependent rheology and a structural or thermal indicator of the eutectic mixture. After cure, conversion, gel fraction and extraction are added so the retained versus mobile components are known. This is especially important because the hydrogen-bonding environment that explains liquid-state viscosity can be reorganised or partly destroyed by polymerisation. Final mechanical or electrical properties should therefore be attributed to the cured state, not to the uncured DES label.

14. Recycling and dissolve-on-demand claims

Some polymerisable eutectic systems have been developed for remolding, recycling or dissolve-on-demand behaviour. These functions are useful only when the dissolution medium, mass balance and recovered-material state are reported. A specimen that dissolves is not automatically chemically recyclable; dissolution may simply transfer an intact network or oligomeric fragments into another phase. Reuse claims should therefore distinguish physical recovery, chemical depolymerisation and reprintability.

15. Discriminating experiment set

A focused experiment set varies water content deliberately around the nominal formulation while keeping the donor:acceptor ratio constant. Viscosity, cure rate, conversion, modulus, conductivity where relevant, and extraction loss are measured. A second branch changes donor:acceptor ratio at controlled water content. These experiments separate genuine composition effects from uncontrolled hygroscopic drift and reveal whether the nominal DES window remains stable during realistic vat residence.

16. Engineering conclusion

DES-containing photocurable systems are a credible route to low-viscosity, hydrogen-bonded and multifunctional printable materials. Their main qualification challenge is state control: component ratio, water and retained mobile fraction can change during storage, printing, washing and service. Development should therefore treat DES identity as a measured state rather than a recipe name, and should couple printability improvements to leaching, humidity and long-term dimensional evidence.

References

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L.; ER-415 contains no comparative product recommendation.

Data availability

ER-415 is a literature-based engineering review; no new experimental dataset was generated.