

Neat Hemp-derived Vitrimers

A Ranked Review of Routes to an Unfilled Hempseed-Oil Vitrimer Epoxy

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Scope and honesty statement. “Neat” means an unfilled matrix: no fiber, CNC, biochar or nanosheets. The ranking below is a *structured judgement* built from published evidence found by live search on 29 September 2026. It is not a measurement. Scores can move as new data appear, and differences under about 0.3 points should be read as ties.

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1 Executive summary

Published, peer-reviewed evidence for hemp-derived vitrimers is thin. Only one route has a full hemp-specific peer-reviewed demonstration of vitrimer behavior. The remaining routes are either shown on other vegetable oils (soybean, canola, linseed, castor) or exist only as preprints, poster abstracts, or self-published proposals.

1. **Rank 1: Hemp glycidyl-ester epoxy (HOEP) + aliphatic amine, optionally with a rigid co-epoxy.** Best evidenced, room-temperature curable, demonstrated stress relaxation and repairability. Not fully bio-based as published, because the rigid co-epoxy was bisphenol-A based.
2. **Ranks 2–3: Epoxidized hemp oil (EHO) with polyacid (2) or anhydride (3), Zn(II)-catalyzed.** Strong precedent on other oils and a good review base, but no peer-reviewed hemp-specific dataset located. Polyacid networks tend to have low Tg; anhydride networks reach higher Tg.
3. **Ranks 4–8: imine (vanillin) hardeners, an all-hemp polyacid/glycidyl-ester pairing, UV cationic cure, disulfide/dual-dynamic networks, and self-catalyzing hardeners.**

Practical recommendation. Run Rank 1 as the anchor experiment, and Ranks 2 and 3 as head-to-head comparators against it, using the stoichiometric discipline in Section 4.

2 Background: what a neat hemp vitrimer must do

A vitrimer is a covalent network with associative bond exchange. In epoxy–acid and epoxy–anhydride systems the exchange is dynamic transesterification (DTER), which needs both ester groups and free hydroxyl groups in the network. Exchange becomes fast above the topology-freezing temperature T_v , while the network remains a solid thermoset below it.

Hemp oil is rich in polyunsaturated fatty acids, which epoxidation converts to internal oxirane groups (EHO/EHSO). Two consequences matter:

- Internal oxiranes are less reactive than terminal glycidyl groups, so cures are slower and need catalysts or elevated temperature.
- Flexible triglyceride backbones give low Tg. This is the central weakness of neat vegetable-oil vitrimers, and it drives most of the design choices below.

3 Ranking method

Each route is scored 1–5 on five criteria, then combined with fixed weights.

Criterion	Weight	What a 5 means
H: Hemp-specific evidence	0.30	Peer-reviewed hemp data including vitrimer behavior
T: Tg / structural potential	0.20	Credible path to Tg well above ambient
V: Vitrimer evidence overall	0.20	Stress relaxation and reprocessing shown (any oil)
B: Bio-based content	0.15	Fully bio-derived feedstocks
P: Processability / simplicity	0.15	One-pot, commodity reagents, mild cure

Table 1: Ranked results (weighted score out of 5)

Rank	Route	H	T	V	B	P	Score
1	HOEP + aliphatic amine (+ rigid co-epoxy)	5	3	5	3	5	4.30
2	EHO + polyacid + Zn(II)	2	2	4	5	4	3.15
3	EHO + anhydride + Zn(II)	2	4	3	4	3	3.05
4	EHO + vanillin imine hardener	3	3	3	4	2	3.00
5	All-hemp polyacid + hemp glycidyl ester	3	3	2	5	2	2.95
6	UV cationic cure + phosphate catalyst	1	2	3	4	4	2.50
7	Disulfide / dual-dynamic hardeners	1	3	4	3	2	2.45
8	Self-catalyzing hardeners (amine, lignin)	1	3	2	4	3	2.35

Reading the table. Rank 1 leads by a wide margin mainly because it is the only hemp route with peer-reviewed vitrimer data. Ranks 2–5 sit within about 0.2 points of one another and should be treated as a cluster, not a strict order. Ranks 6–8 are speculative for hemp.

Evidence tiers used. **Tier 1:** peer-reviewed, hemp-specific. **Tier 2:** peer-reviewed, other vegetable oil or petro analog. **Tier 3:** dissertation, patent, poster abstract. **Tier 4:** self-published proposal (Zenodo), not peer-reviewed and not experimentally validated.

4 Design rules that apply to every route

1. **Calculate in equivalents, not mass.** For any component, the equivalents are the mass divided by its equivalent weight (EEW for epoxides). Measure the EEW of your EHO by titration; do not rely on nominal values.
2. **Deliberately off-stoichiometric acid or anhydride.** The 2025 Royal Society Open Science review on epoxidized-vegetable-oil vitrimers discusses how the epoxy-to-curing-agent ratio governs free hydroxyl availability, and notes an industrial epoxy/anhydride ratio of roughly 1:0.8 to 1:0.9. A carboxyl-to-epoxy ratio near 0.8–0.9 is therefore a sensible screening center.
3. **Keep catalyst loading modest.** The same review reports that EVO-based vitrimers reportedly need lower catalyst loading than conventional epoxy vitrimers. Screen low first.
4. **Always run an EHO-only control** cured by the same route, so any Tg gain is attributable.
5. **Prove the vitrimer claim, do not assume it.** Show stress relaxation at several temperatures, fit an Arrhenius plot, then show reprocessing over several cycles with retained gel fraction and properties.
6. **Report replicates.** At least $n = 5$ specimens, mean $\pm$ SD, and raw traces.

5 Ranked routes

5.1 Rank 1 (score 4.30): Hemp glycidyl-ester epoxy + aliphatic amine

Chemistry. Zhang and co-workers converted hemp fatty acids to a triglycidyl-ester epoxy (HOEP), blended it with a bisphenol-A diglycidyl ether (DER), and cured with an aliphatic amine (diethylenetriamine, DETA). The network contains many ester bonds and hydroxyl groups, so DTER operates at elevated temperature. Glycidyl esters are terminal and far more reactive than internal epoxides, which is why the cure works at room temperature.

Evidence (Tier 1). ACS Sustainable Chemistry & Engineering 2020, 8, 14964. Reported: room-temperature-cured coatings with Tg above 40 °C, scratch hardness 5H, gouge hardness 6H, adhesion 5B, good solvent resistance, and renewable HOEP up to 67.5 wt% of the composition. Stress relaxation rate increased with temperature, and reparability was demonstrated.

Strengths. Only hemp route with peer-reviewed vitrimer behavior; ambient cure; compatible with commercial epoxy practice.

Weaknesses. The published system uses a petro-derived bisphenol-A co-epoxy and a petro-derived amine, so it is not fully bio-based. HOEP is not simply epoxidized hemp oil: it requires converting fatty acids to glycidyl esters, an extra synthesis step. Coating-grade Tg (above 40 °C) is well below structural targets.

Neat-matrix variants worth testing.

- HOEP / DER ratio sweep, as in the original work.
- Replace DER with a bio-aromatic epoxy to raise renewable content.
- Post-cure sweep to examine the effect on stress relaxation.

5.2 Rank 2 (score 3.15): EHO + polyacid + Zn(II) catalyst

Chemistry. Epoxy-carboxylic acid ring-opening gives β -hydroxy esters, providing both ester and hydroxyl for DTER. Candidate acids: citric, succinic, tartaric, adipic, sebacic, lactic. Catalysts: Zn acetate, Zn(acac)₂, TBD.

Evidence (Tier 2 for other oils).

- Epoxidized canola oil cured with lactic acid and Zn acetate or ZnAl layered double hydroxide at 1–2 wt% showed vitrimer behavior, with T_v between about 195 and 235 °C.
- Epoxidized soybean oil with citric acid gave a fully bio-based vitrimer with stress relaxation and self-healing, but Tg of about 25 °C and very low tensile strength (about 0.6 MPa).
- Epoxidized linseed oil with tartaric acid gave a catalyst-free vitrimer with Tg near 50 °C and activation energies of 49–71 kJ/mol, with full stress relaxation within a few hundred seconds at 200 °C.

Hemp-specific: your v17.2 and HERA-75 concepts sit here (Tier 4, unvalidated).

Strengths. Fully bio-derived, simple, commodity reagents, and the strongest cross-oil precedent.

Weaknesses. Low Tg and low strength are the recurring result on other oils. Citric acid solubility and dispersion in oil can limit homogeneity (your Hemproxies 56 proposal addresses this with an ethanol processing aid, again unvalidated). Water release and moisture sensitivity must be controlled.

Test plan. Acid-type sweep at fixed carboxyl/epoxy ratio 0.8; Zn acetate vs Zn(acac)₂ at 0.25–1.0 wt%; a catalyst-free tartaric-acid arm as a reference.

5.3 Rank 3 (score 3.05): EHO + anhydride + Zn(II) catalyst

Chemistry. Anhydride opening by hydroxyl produces a monoester acid, which then opens the epoxide. Rigid cyclic anhydrides raise crosslink rigidity. Maleinized hemp oil is a hemp-derived anhydride-type option.

Evidence.

- (Tier 2) Curing epoxy resin E51 with a phthalic anhydride/sebacic acid mixture and TBD catalyst, Tg rose from 79 to 143 °C as anhydride content increased, with T_{d5} of 322 °C for one composition.
- (Tier 2) A bio-based triepoxy cured with an anhydride and a zinc catalyst reached Tg of 187 °C with self-healing by DTER.

- (Tier 2) Aminoglycidyl epoxies cured with anhydride showed high Tg and efficient stress relaxation, because tertiary amines also catalyze the exchange.
- (Tier 4) A hemp platform record proposes $\text{Zn}(\text{acac})_2$ as a dual catalyst for cure and exchange.

Strengths. Highest Tg ceiling among the polyester routes; the best-established route to structural-grade vitrimers.

Weaknesses. Common anhydrides (phthalic, hexahydrophthalic) are petro-derived; bio-derived options are fewer. Hemp-specific data are missing. Anhydrides are moisture sensitive.

Test plan. Anhydride/acid split sweep in the EHO matrix, mirroring the E51 study, to map Tg against anhydride fraction.

5.4 Rank 4 (score 3.00): EHO + vanillin-based imine hardener

Chemistry. Dynamic imine (Schiff-base) crosslinkers from vanillin and aliphatic diamines cure the epoxide through amine groups; imine exchange provides topological rearrangement.

Evidence. (Tier 3, hemp) A Pittsburg State graduate research abstract (Advisor: Dr. Ram Gupta, 2025) describes EHSO cured with vanillin-imine crosslinkers, evaluated by rheology, stress relaxation and mechanical tests. (Tier 2, soybean) A vanillin Schiff-base hardener with soybean oil epoxy, where only 30 wt% added commercial epoxy improved thermo-mechanical properties while keeping reprocessability.

Strengths. Vanillin is lignin-derived; imine exchange is fast and can operate without a metal catalyst.

Weaknesses. Multi-step hardener synthesis; imine hydrolysis sensitivity; results for hemp exist only as an abstract.

5.5 Rank 5 (score 2.95): All-hemp polyacid + hemp glycidyl ester

Chemistry. A 2018 Washington State dissertation converted hemp fatty acids into polycarboxylic acids, then into a hempseed-oil-based curing agent (HO-polyacid) and epoxy monomer (HO-EP), with terminal reactive groups and shorter spacing between functional groups. Pairing the two gives a fully hemp-derived ester network.

Evidence (Tier 3). The dissertation reports significantly improved mechanical and thermal properties versus conventional epoxidized vegetable oil. Vitrimer behavior for this pairing was not shown in the material located.

Strengths. Highest genuine hemp content; higher functional density than EHO.

Weaknesses. Extra synthetic steps; no vitrimer demonstration. This route is a research opportunity rather than an established method.

5.6 Rank 6 (score 2.50): UV cationic cure with phosphate catalyst

Epoxidized castor oil with a cationic photoinitiator and dibutyl phosphate as transesterification catalyst formed UV-cured networks that underwent thermally activated bond exchange, avoiding long thermal cures. This is a Tier 2 result on castor oil; I found no hemp precedent. Thick-section cure depth and photoinitiator residues are open concerns.

5.7 Rank 7 (score 2.45): Disulfide and dual-dynamic hardeners

Catalyst-free epoxidized-soybean-oil vitrimers have been made with a disulfide diamine hardener. A vanillin-cystamine epoxy combined imine and disulfide exchange with fast stress relaxation. Both are Tier 2 with no hemp precedent. Disulfides add oxidation sensitivity and odor concerns, and sulfur compounds may conflict with a strictly bio-based claim.

5.8 Rank 8 (score 2.35): Self-catalyzing hardeners

Tertiary amines within a hardener can both accelerate cure and catalyze DTER, as shown for aminoglycidyl epoxy–anhydride networks (Tier 2, petro-based). The dual-lignin proposal (maleinated plus Mannich lignin with EHSO) applies this idea to hemp, but it is a Tier 4 pre-experimental proposal. It scores lowest only because it is untested, and its upside, avoiding metal catalysts, is real.

6 Cross-route comparison of dynamic chemistry

Route	Exchange type	Catalyst need	Tg outlook
HOEP + amine	Transesterification	Internal (hydroxyl/amine)	Modest, coating grade
EHO + polyacid	Transesterification	Zn(II) or none (tartaric)	Low to modest
EHO + anhydride	Transesterification	Zn(II), TBD, or amine	Highest ceiling
EHO + imine	Imine exchange	Often none	Modest
UV cationic	Transesterification	Phosphate	Low to modest
Disulfide	S–S exchange	None or mild	Modest
Self-catalyzing	Transesterification	Internal	Unknown for hemp

7 Recommended first-year experimental program

1. **Characterize the feedstock.** EEW (epoxide titration), residual iodine value, acid value, water content of every EHO lot.
2. **Baseline A: EHO + citric/succinic acid + Zn acetate** at carboxyl/epoxy 0.8, with a catalyst-free control.
3. **Baseline B: EHO + anhydride + Zn(II)**, with anhydride/acid fraction sweep.
4. **Anchor: HOEP/co-epoxy + amine**, reproducing the published system before modifying it.
5. **Vitrimer proof for every matrix:** DMA or rheometer stress relaxation at three or more temperatures; Arrhenius fit; three reprocessing cycles with gel fraction.
6. **Publish measured data** (raw traces plus summary) before any filler work.

8 Pitfalls specific to hemp oil

- **Incomplete epoxidation.** Residual double bonds oxidize and darken during cure; check with NMR or titration.
- **Oxirane ring-opening during epoxidation** lowers functionality; report measured EEW.
- **Lot-to-lot variation** in a natural oil: use one characterized lot per experimental series.
- **Water.** It quenches anhydrides, complicates acid cures, and can hydrolyze imines.
- **Equivalent-counting errors.** Convert everything to equivalents before mixing.
- **Overclaiming.** Do not use “vitrimer,” “recyclable” or “carbon-negative” without the evidence listed in your claim–evidence table.

9 What would change the ranking

- A peer-reviewed hemp dataset for Routes 2 or 3 would raise their H score by up to 3 points, moving them close to Rank 1.
- A bio-derived rigid co-epoxy in Route 1 would raise its bio-based score and remove its main weakness.
- Demonstrated vitrimer behavior in the all-hemp pairing (Rank 5) would raise both V and H.

Source list

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