

Hempoxies — Fully Hemp-Sourced Matrix Chemistry (Corrected Section)

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Status and scope

Every carbon atom in the proposed Hempoxies matrix can be traced to hemp, but not every reagent. This is a TRL 1–2 research hypothesis; all performance figures elsewhere in the dossier are projected targets, not validated results.

"100% hemp-derived" is defined here as **100% hemp-derived carbon in the cured matrix**. Oxidants and mineral reagents (hydrogen peroxide, hydrogen chloride, ozone or air) are consumed in processing and are not hemp-sourced. Fibre reinforcement is outside this section's scope; see Corrections.

Matrix component	Hemp fraction	Route	Non-hemp inputs	Evidence status
Epoxidized hempseed oil (EHSO)	Seed oil	In situ peracetic acid epoxidation	H ₂ O ₂ , acid catalyst	Demonstrated on hemp oil
Acetic acid (peracid carrier)	Shive/hurd hydrolysate	Co-product of furfural pretreatment	Pretreatment catalyst	Demonstrated on hemp shives
Furfuryl glycidyl ether (FGE)	Shive hemicellulose + seed-oil glycerol	Furfural → furfuryl alcohol; glycerol → epichlorohydrin	Reducing agent, HCl, base	Furfural from hemp demonstrated; full hemp-traced FGE not shown
Citric acid (primary crosslinker)	Hurd sugars	<i>Aspergillus niger</i> fermentation	Pretreatment acid, nutrients	Shown on other lignocellulose; not on hemp
Azelaic acid (optional co-crosslinker)	Seed-oil fatty acids	Oxidative cleavage	O ₃ or H ₂ O ₂ /air + catalysts	Commercial on other oils; not on hempseed oil

Matrix component	Hemp fraction	Route	Non-hemp inputs	Evidence status
Lignin glycidyl ether (optional stiffener)	Hurd lignin	Glycidylation with epichlorohydrin	HCl, base	Shown on other lignins
Exchange catalyst	None	Catalyst-free β -hydroxyester exchange	None	Shown for soybean-oil analogue

Component 1 — Epoxy base

Epoxidized hempseed oil (EHSO) remains the backbone, and hemp oil epoxidation is already demonstrated. Its high polyunsaturated content gives many oxirane sites per triglyceride.

Feedstock. Hempseed oil is dominated by linoleic (~55%), α -linolenic (~16%) and oleic (~11%) acids ([J. Agric. Food Chem. 2014](#)). Across 21 Turkish samples, linoleic ranged 55.4–56.9% and α -linolenic 16.5–20.4% ([Kiralán et al. 2010](#)).

Epoxidation. Hemp oil has been epoxidized with peroxyacetic acid generated in situ from acetic acid and H_2O_2 over an acidic ion-exchange resin ([Cooney 2009](#); [Cooney et al. 2011](#)). The reported optimum was 1.0 mol C=C : 0.67 mol acetic acid : 1.0 mol H_2O_2 , with resin at 15 wt% of oil.

Hemp-sourcing the peracid carrier. Hemp shive hydrolysis yields 51.4 kg acetic acid per dry tonne alongside furfural ([Brazdausks 2019](#)). H_2O_2 stays external; it also bleaches crude oil during epoxidation ([ChemEngineering 2025](#)).

FGE reactive diluent. Hemp shives yield 67.8 kg furfural per dry tonne while retaining 99.7% of cellulose for later steps ([Brazdausks 2019](#)). Furfural is reduced to furfuryl alcohol, then glycidylated with epichlorohydrin.

Epichlorohydrin. Glycerol-based epichlorohydrin is commercial at 100% renewable carbon ([AGC EPINITY](#); [Solvay Epicerol](#)). Hempseed oil processing supplies glycerol; the chlorine comes from HCl. No hemp-traced FGE has been reported yet.

Lignin glycidyl ether (optional stiffener). Lignin's phenolic hydroxyls are glycidylation sites ([Green Chem. 2016](#)). A glycidylated methanol-soluble lignin has been cured using lignin itself as hardener ([Int. J. Biol. Macromol. 2015](#)). Hemp-hurd lignin was not among the

biomasses tested.

Component 2 — Polycarboxylic crosslinker

Citric acid stays the primary crosslinker, and fermenting it from hemp hurd sugars is plausible but undemonstrated. Sebacic acid is removed; azelaic acid is the hemp-compatible diacid.

Citric acid. Epoxidized soybean oil cured with aqueous citric acid, with no other catalyst or solvent, gave a fully bio-based network ([Altuna et al., Green Chem. 2013](#)). Industrial citric acid comes from *A. niger* fermenting sucrose feedstocks such as molasses ([Upton et al. 2022](#)).

Lignocellulosic route. *A. niger* on pretreated corn stover reached 100.04 g/L citric acid at 94.11% yield, comparable to sugar-based fermentation ([Zhou et al. 2017](#)). Hemp hurd hydrolysate has not been tested.

Azelaic acid (optional co-crosslinker). Novamont's commercial two-step oxidative cleavage converts oleic, linoleic and linolenic acids to azelaic acid, using H_2O_2 and air with recoverable tungsten and cobalt catalysts ([ACS ES&T Engineering](#)). Those three acids make up about 80% of hempseed oil. Yields and co-products from hempseed oil specifically are unreported.

Design note. Azelaic acid is difunctional, citric acid trifunctional. Partial substitution should lower crosslink density and T_g ; treat the ratio as a tuning variable.

Correction — sebacic acid. Commercial sebacic acid is made by alkaline cleavage of castor oil, not hemp ([Molecules](#)). Earlier text listing it as hemp-derivable should be withdrawn.

Component 3 — Exchange catalysis

The recommended baseline adds no catalyst. Epoxy-citric acid networks self-heal through β -hydroxyester transesterification without extrinsic catalysts ([Altuna et al. 2013](#)). Zinc acetate moves from formulation component to reference control.

Three options, ranked for a hemp-only claim.

1. **Catalyst-free (baseline).** Exchange relies on internal catalysis. Tertiary amines and abundant hydroxyls can drive it without additives ([Polym. Chem. 2021](#)). Expect slower relaxation than catalysed networks.

2. Zinc acetate from hemp acetic acid (control). Zinc is mined, but acetate carbon can come from shive hydrolysate. This keeps the hemp-carbon definition while not being a hemp-sourced catalyst. $\text{Zn}(\text{OAc})_2$ and TBD are the most studied epoxy-vitrimer catalysts ([Niu et al. 2019](#)).

3. Hemp ash (hypothesis only). Untested in any vitrimer; see below.

Loading. Epoxidized vegetable oil vitrimers need lower catalyst loading than conventional epoxy vitrimers ([R. Soc. Open Sci. 2025](#)). That favours option 1 or a low-dose option 2.

Why hemp ash is not a drop-in. Potassium-rich ash from herbaceous biomass is an established heterogeneous catalyst for biodiesel transesterification ([Processes 2024](#)). There, free molecules diffuse to the solid surface. In a crosslinked network they cannot, so the catalyst must be molecularly dispersed.

Mechanism mismatch. Zinc activates the ester by raising carbonyl electrophilicity ([RSC Appl. Polym. 2024](#)). Ash species act as bases. Agricultural-residue ash studies report calcium and potassium oxides as dominant phases, not zinc ([Biomass 2024](#)).

Hemp ash composition itself was not found in this review; it must be measured before any catalyst claim.

Network chemistry and expected limitations

The matrix is a β -hydroxyester covalent adaptable network, and its main risk is low stiffness, not chemistry. Acid ring-opening of epoxides leaves an ester beside a hydroxyl; heating drives transesterification between them, rearranging topology at constant link count ([US patent background](#); [Altuna et al. 2013](#)).

Hempseed-oil precedent. A room-temperature-curable hempseed-oil epoxy vitrimer with internally catalysed transesterification has been reported ([Zhang et al., ACS Sustain. Chem. Eng. 2020](#)). A fully bio-based EHSO vitrimer using vanillin-derived imine crosslinkers has also been presented ([Pittsburg State 2025](#)).

Stiffness ceiling. High T_g and strength remain hard for plant-oil vitrimers. Epoxidized soybean oil with a rigid rosin-derived triacid reached only T_g 65 °C and 16 MPa tensile ([Yang et al., Mater. Des. 2020](#)). Neat EHSO–citric acid should be projected in that range or below.

Rigidity levers. Lignin-derived epoxies have been structure-tuned to T_g 94 °C and 134 °C ([Green Chem. 2016](#)). Lignin glycidyl ether and FGE content are the hemp-sourced routes to raise T_g .

Tv. Dropping zinc acetate should raise relaxation temperatures or lengthen relaxation times. The earlier projected Tv of ~150–160 °C needs re-projection for the catalyst-free baseline.

Neat matrix vs composite. Tensile projections above 180 MPa in v17.2 assume fibre reinforcement. Report neat-matrix and composite targets separately.

Corrections to prior versions and claim language

Six earlier claims need correcting before the next release. The largest is the “100% bio-derived feedstocks” line in [v17.2](#), which specifies zinc acetate and PAN carbon fibre.

Earlier claim	Status	Correction
100% bio-derived feedstocks (v17.2)	Overstated	Zinc is mined. PAN comes from acrylonitrile, commercially made by propylene ammoxidation (Green Chem. 2018). Limit the claim to the matrix.
Infinite solid-state recycling; net-negative carbon (v17.2)	Unsupported at TRL 1–2	Restate as projected; needs cycling tests and an LCA.
Sebacic acid is hemp-derivable	Incorrect	Castor-derived; use azelaic acid.
Hemp ash (K_2CO_3 , CaO, Zn) catalyses vitrimer exchange	Unsupported	Biodiesel precedent only; label as hypothesis.
Ash species act as “Lewis bases”	Imprecise	The relevant contrast is mechanism: zinc activates the carbonyl, ash species act as bases.
Imidazole-like amines isolated from hemp waste	Unsupported	No literature found; remove or label speculative.

Bio-PAN outlook. Acrylonitrile from glycerol via acrolein has reached techno-economic study ([AIChE 2017](#)). A hemp-glycerol PAN route is conceivable but far beyond TRL 1–2.

Recommended claim language.

Hempoxies matrix (TRL 1–2 research hypothesis): all matrix carbon is designed to be hemp-traceable from seed oil and shives/hurd. Process oxidants and mineral reagents are external. All performance figures are projected, not validated.

Open questions to move toward TRL 3

The first experiment to run is a catalyst-free EHSO–citric acid cure with a zinc acetate control. Every other item depends on whether that baseline relaxes usefully.

- ☐ Epoxidize one hempseed oil lot; record iodine value and oxirane oxygen content.
- ☐ Cure EHSO with aqueous citric acid, no catalyst; run stress relaxation across temperature against a 1 wt% Zn(OAc)₂ control.
- ☐ Measure neat-matrix T_g and tensile strength; report separately from composite targets.
- ☐ Measure hemp-hurd ash composition (K, Ca, Mg, Si, Zn) before any catalyst claim.
- ☐ Test a water-soluble hemp-ash fraction as a dispersed catalyst against the zinc control.
- ☐ Ferment hemp hurd hydrolysate with *A. niger*; report citric acid titer and yield.
- ☐ Trial oxidative cleavage of hempseed oil to azelaic acid; report yield and co-products.
- ☐ Make FGE from hemp furfural and glycerol-based epichlorohydrin; confirm purity.
- ☐ Commission independent biobased-carbon testing of the cured matrix.

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