

Comprehensive Failure Analysis and Lessons Learned in Hempoxies Processing: Technical Pitfalls, Stoichiometric Drift, and Degradation Vulnerabilities

Executive Overview and Strategic Positioning

The development of Hempoxies—a bio-derived composite platform utilizing *Cannabis sativa* L. feedstocks (utilizing processed derivatives such as carbonized bast fibers, biochar, nanosheets, and extracted biomolecules, while strictly excluding raw, un-processed fibers) and dynamic Covalent Adaptable Networks (CANs)—represents a major effort to resolve the thermodynamic non-recyclability of conventional Carbon Fiber Reinforced Polymers (CFRPs). Standard aerospace and structural composites rely on petroleum-derived Bisphenol-A diglycidyl ether (DGEBA) cured with static amine or acid hardeners. These systems lock polymer chains into permanent three-dimensional covalent networks that cannot be melted, dissolved, or reprocessed without complete backbone cleavage.

Hempoxies replace static thermosets with vitrimeric matrices governed by associative bond-exchange mechanisms, primarily zinc-catalyzed transesterification, dynamic imine formation, or disulfide metathesis. At service temperatures below their glass transition, these materials exhibit the mechanical rigidity, thermal stability, and creep resistance characteristic of classical structural thermosets. Above the Topology Freezing Transition Temperature (T_v), thermally activated exchange reactions allow the network topology to rearrange dynamically without reducing overall crosslink density. This enables self-healing, thermal thermoforming, and low-energy chemical recyclability, addressing the primary environmental and lifecycle constraints of modern composite engineering.

However, transitioning from petroleum-based thermosets to structural bio-vitrimers introduces severe chemical vulnerabilities, stoichiometric sensitivities, rheological constraints, and scale-up exotherm risks. Uncontrolled synthesis or processing can cause catastrophic material failures—such as complete oxirane ring destruction, resin sludge formation, premature gelation, internal delamination, or permanent loss of vitrimeric malleability. A comprehensive synthesis of technical data across the Hempoxies development iterations (v.1 through v.32) establishes the critical failure modes, stoichiometric errors, temperature boundaries, moisture constraints, and scale-up pitfalls that must be strictly avoided during manufacturing.

Precursor Synthesis Vulnerabilities and Chemical Side Reactions

The primary matrix monomer in the Hempoxies architecture is Epoxidized Hemp Seed Oil (EHSO), produced by converting the unsaturated fatty acid double bonds (π -bonds of linoleic,

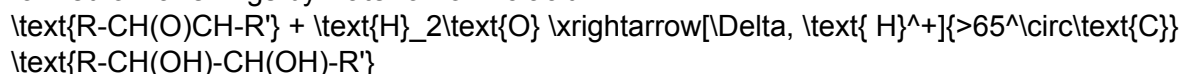
(α -linolenic, and oleic acids) into three-membered oxirane rings via *in situ* performic or peracetic acid pathways. The performic acid synthesis relies on an equilibrium reaction between formic acid and hydrogen peroxide:



The resulting performic acid transfers an oxygen atom to the alkene double bonds of the triglyceride chains:

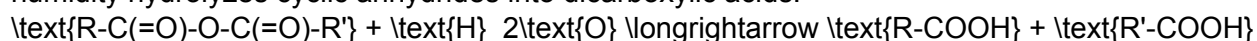


This epoxidation process is intensely exothermic, releasing substantial heat ($\Delta H \approx -200 \text{ kJ/mol}$). Allowing the reaction temperature to exceed 60°C , or failing to manage localized thermal spikes, triggers a destructive side reaction. In the presence of the aqueous acid phase, elevated temperatures catalyze the nucleophilic ring-opening of newly formed oxirane rings by water or formic acid:



Accumulation of these diol structures permanently destroys the monomer's crosslinking functionality. Instead of yielding structural EHSO with an Oxirane Oxygen Content (OOC) above 6.5% and an Epoxy Equivalent Weight (EEW) of $185\text{--}195 \text{ g/eq}$, uncontrolled thermal runaways convert the precursor into a viscous, non-curing sludge. This sludge cannot achieve the crosslink density required for structural applications, causing a total collapse of Young's modulus and glass transition temperature (T_g).

In formulations utilizing Maleinized Hemp Seed Oil (MHSO) or bio-derived cyclic anhydrides as hardeners, moisture contamination introduces immediate stoichiometric instability. Ambient humidity hydrolyzes cyclic anhydrides into dicarboxylic acids:



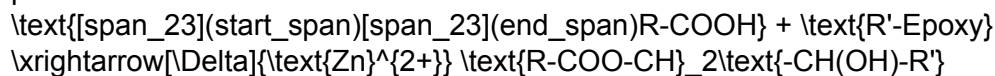
This hydrolysis alters the pre-calculated Acid Equivalent Weight (AEW) and causes premature crystallization within the liquid resin blend. Moisture also deactivates Lewis acid transesterification catalysts, such as Zinc Acetylacetonate ($\text{Zn}(\text{acac})_2$) or Zinc Acetate Dihydrate ($\text{Zn}(\text{OAc})_2$). Water molecules coordinate strongly to the electrophilic zinc metal center, blocking the coordination sites required to promote associative exchange between ester carbonyl oxygens and pendant hydroxyl groups. When the catalyst is poisoned, the bond-exchange rate ($k(T)$) drops toward zero, causing the cured composite to behave as a static, brittle thermoset that lacks self-healing and thermal reprocessability. All precursor feedstocks must be vacuum-dried at 60°C over $3 \text{ \AA}$ molecular sieves until moisture levels fall below 500 ppm .

When synthesizing Quadruple-Function Modified Hemp Lignin (QF-MHL) or Epoxidized Lignin (EL) for the fiber-matrix interphase, technical Kraft or Organosolv lignins are reacted with epichlorohydrin under basic conditions (NaOH). Incomplete purification leaves residual sodium chloride (NaCl), unreacted epichlorohydrin, or free alkali. Ionic impurities (Na^+ , Cl^-) interfere with catalyst activity during curing and increase the overall water absorption capacity of the interphase. Subsequent water ingress causes plasticization and premature hydrolytic cleavage of ester linkages. Sizing solutions must be washed with deionized water until silver nitrate (AgNO_3) titration confirms zero residual chloride ions.

Stoichiometric Deviations and Network Topography Flaws

Standard epoxy engineering targets a strict 1:1 stoichiometric balance between epoxide rings

and reactive hardener sites to maximize network crosslink density. However, applying an equimolar 1:1 ratio to zinc-catalyzed transesterification vitrimers represents a fundamental design error. Transesterification vitrimers require secondary hydroxyl groups (-OH) to act as nucleophiles that attack ester linkages during dynamic bond exchange. Ring-opening esterification of an epoxide by a carboxylic acid generates these ester and secondary hydroxyl pairs *in situ*:



If a system is formulated with an equimolar ratio (1:1) or an excess of carboxylic acid, unreacted carboxyl groups remain trapped within the network. Unreacted carboxylic acids act as internal plasticizers, attract atmospheric moisture, and catalyze uncontrolled hydrolytic degradation of the ester backbone over time. Conversely, Hemposies v.17 mandates a target Epoxy-to-Carboxyl ratio of 1:0.8, corresponding to a 1.51:1.00 operational ratio when accounting for the steric hindrance of bulky triglyceride chains. This 20% molar surplus of epoxide groups guarantees complete consumption of carboxylic acid hardeners (such as citric acid or sebacic acid) while providing the free volume and hydroxyl density necessary for dynamic bond exchange.

Formulating matrix batches using theoretical Epoxy Equivalent Weights rather than empirical titration data introduces significant stoichiometric drift. Assuming a theoretical EHSO EEW of 174 g/eq based on idealized fatty acid structures—instead of measuring the empirical value of 185–195 g/eq via peracid titration (ASTM D1652)—introduces a 12% error in crosslinker calculation. This error shifts the Topology Freezing Transition Temperature (T_v) outside the safe processing window (165–185°C), raising it above the thermal degradation threshold of the bio-based resin backbone (>220°C). Consequently, attempting to thermally reprocess or self-heal the composite causes thermal degradation of the matrix and interphase before bond exchange can occur.

Formulation Parameter	Ideal Operational Target	Deviated / Incorrect Value	Direct Failure Mechanism	Macroscopic Consequence
Epoxy : Carboxyl Ratio	1.0 : 0.8 (System 1.51:1.0)	1.0 : 1.0 (Equimolar)	Unreacted carboxyl accumulation; insufficient free volume.	Elevated moisture uptake, T_g drop of up to 30°C, severe creep.
EHSO EEW Basis	Empirical titration (185–195 g/eq)	Theoretical assumption ([span_29](start_span)[span_29](end_span)174 g/eq)	12% stoichiometric deficit in crosslinking agent.	T_v shifts above 220°C; thermal degradation during remolding.
Epoxidation Temperature	55°C ± 2°C	>65°C	Acid-catalyzed ring-opening by aqueous formic acid.	Formation of non-reactive diols; loss of resin curing capacity.
Precursor Moisture Content	<500 ppm	>2000 ppm	Water coordinates to [span_32](start_span)[span_32](end_span)	Catalyst poisoning; complete loss of vitrimeric self-healing/flow.

Formulation Parameter	Ideal Operational Target	Deviated / Incorrect Value	Direct Failure Mechanism	Macroscopic Consequence
			Zn^{2+} catalyst centers.	
Catalyst Loading ($\text{Zn}(\text{OAc})_2$)	10 mol% to carboxyl (3.5 phr) (4.5 phr)	<2 mol% OR >15 mol%	Under-loading stalls exchange; over-loading causes premature gelation.	Stalled stress relaxation OR loss of pot-life (<30 min at 60°C).

Industrial Processing and Rheological Failures

Unmodified Epoxidized Hemp Seed Oil exhibits a high room-temperature dynamic viscosity (>5000 mPa·s at 25°C) due to intermolecular hydrogen bonding and steric hindrance from long aliphatic triglyceride chains. Attempting Vacuum-Assisted Resin Infusion (VARI) or Resin Transfer Molding (RTM) at room temperature causes incomplete fiber wetting, dry fiber tows, and macro-void levels exceeding 5%. To reduce dynamic viscosity to the required infusion window (800–1200 mPa·s), the system integrates Hemp-Derived Furfuryl Glycidyl Ether (FGE) as an aromatic reactive diluent. However, processing parameters must be rigidly controlled:

- **Infusion Temperature Limit:** Resin temperature during infusion must be held at 60°C ± 2°C. Lowering the temperature below 55°C increases viscosity above 1500 mPa·s, stalling the fluid flow front across long preforms. Heating above 70°C accelerates the transesterification reaction, shortening the pot life from 4 hours to under 45 minutes and causing premature gelation before the mold is filled.
- **Vacuum Degassing Limit:** Vacuum pressure during degassing and infusion must not drop below 50 mbar. Applying deeper vacuum (<10 mbar) causes the low-boiling FGE reactive diluent to vaporize. Volatilization alters the Epoxy-to-Carboxyl ratio, releases gas bubbles into the resin line, and creates structural voids.

In accordance with the Hemproxies architecture, raw hemp fibers are strictly excluded in favor of processed derivatives, including Hemp-Derived Carbon Fiber (HDCF, produced via thermal stabilization and carbonization of bast fibers), Cellulose Nanocrystals (CNCs), and micro-porous Hemp Biochar (HDB). Nevertheless, processed carbon preforms and cellulosic nano-fillers can retain absorbed micro-porous or surface moisture (8–12 wt%) under ambient conditions. During the curing cycle, as the processing temperature passes 100°C and reaches the initial 120°C gelation step, trapped moisture vaporizes into high-pressure steam. This expanding steam creates micro-cavities at the reinforcement-matrix boundary, decoupling the reinforcement from the surrounding matrix. Consequently, Interfacial Shear Strength (IFSS) drops from an optimal 45–55 MPa to below 20 MPa, leading to early delamination under flexural loading. Processed fiber preforms and fillers must be dried under vacuum at 105°C for at least 2 hours to lower moisture content below 0.5% immediately prior to processing.

Micro-porous Hemp Biochar (HDB) is added to the matrix to improve dimensional stability, enhance thermal conductivity, and reduce creep. While high-shear mixing (>3000 rpm) is required to disperse nano-graphene agglomerates, applying these same shear rates to biochar

pulverizes its porous honeycomb structure. Crushing the biochar converts structured porous particles into fine carbon dust, which sharply increases resin viscosity, reduces crack-tip blunting performance, and degrades dimensional stability. Nano-graphene and carbon nanosheets must be dispersed in the resin first at high shear ($>3000 \text{ rpm}$), after which the biochar is added at a lower mixing speed ($\leq 1500 \text{ rpm}$).

Furthermore, mechanical vibration or mold movement during the initial 120°C gelation phase disrupts network formation as the resin transitions from a liquid to a rubbery gel.

Disturbance during gelation causes entrained micro-bubbles to coalesce, creating structural defects. Tooling consumables must also be selected carefully: standard polyester peel plies melt and decompose during the 200°C post-cure required for vitrimeric topology establishment, permanently fusing to the composite surface. Only high-temperature Polyamide 66 (Nylon) or PTFE-coated glass fabrics should be used.

Thermal, Exothermic, and Kinetic Degradation Vectors

The ring-opening addition of carboxylic acid crosslinkers to epoxidized triglycerides releases substantial heat ($\Delta H \approx 300 \text{ J/g}$). Because polymers exhibit low thermal conductivity ($\kappa \approx 0.2 \text{ W/m}\cdot\text{K}$), heat removal from thick composite sections is inherently slow. The internal temperature profile of a curing laminate is governed by the heat conduction equation with a non-linear reaction generation term:

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + \rho \Delta H \frac{d\alpha}{dt}$$

In composite parts thicker than 10 mm , internal heat generation can significantly outpace surface dissipation. Core temperatures can spike more than

50°C above the oven setpoint. If the core temperature exceeds $210\text{--}220^\circ\text{C}$, the triglyceride backbone and ester linkages undergo thermal cleavage, releasing volatile gases that produce internal voids and severe delamination. To prevent exothermic runaway, cure schedules must use controlled heating rates ($\leq 1.5^\circ\text{C/min}$) combined with multi-stage isothermal dwell steps (such as 80°C for gelation, 120°C for primary curing, 150°C for vitrification, and $180\text{--}200^\circ\text{C}$ for topology establishment). Dwell steps allow reaction enthalpy to dissipate safely while the resin remains below its thermal degradation threshold.

To maintain structural integrity during service while retaining thermal reprocessability,

Hempoxies systems must operate within a strict hierarchy of thermal transitions:

$$T_{\text{service}} < T_g < T_v < T_{\text{process}} < T_{\text{degradation}}$$

The service temperature (T_{service}) must remain at least 40°C below T_g to prevent viscoelastic creep under structural loads. The Glass Transition Temperature (T_g) is tuned between 85°C and 115°C via FGE aromatic modulation. The Topology Freezing Temperature (T_v), where melt viscosity drops to $10^{12} \text{ Pa}\cdot\text{s}$, occurs between 165°C and 185°C . Processing and healing (T_{process}) are conducted between 170°C and 190°C to promote rapid transesterification. Operating near or above the degradation threshold ($T_{\text{degradation}} > 210\text{--}220^\circ\text{C}$) induces thermal scission of the bio-derived backbone.

Additionally, thermal remolding or self-healing performed in ambient air at elevated temperatures ($180\text{--}200^\circ\text{C}$) exposes the aliphatic chains of the hempseed oil

backbone to atmospheric oxygen. Thermo-oxidative aging induces radical-mediated crosslinking across unreacted double bonds, darkening the matrix and restricting chain mobility. This reduces the dynamic bond-exchange rate, elevating T_v with each processing cycle and progressively degrading the material's self-healing efficiency. Thermal thermoforming and reprocessing must therefore be conducted in sealed, nitrogen-purged (N_2) environments.

Processing Boundary	Safe Operating Limit	Exceeded Limit Threshold	Primary Hazard / Structural Failure
VARI Resin Temperature	$60^{\circ}\text{C} \pm 2^{\circ}\text{C}$	$>70^{\circ}\text{C}$	Accelerated transesterification; pot-life collapses from 4 h to <45 min.
Degassing Vacuum Level	50 mbar	<10 mbar (Deep Vacuum)	Volatilization of FGE reactive diluent; stoichiometric shift and macro-voids.
Reinforcement Moisture	<0.5 wt%	>1.0 wt%	Residual moisture vaporizes into steam at $>100^{\circ}\text{C}$; IFSS collapses.
Laminate Exotherm Core	≤ 190°C (start_span_1 16)(end_span_1 16)	$>210^{\circ}\text{C}$	Exothermic runaway; thermal cleavage of ester bonds and internal delamination.
Biochar Dispersion Shear	≤ 1500 rpm	>3000 rpm	Pulverization of porous biochar structure; extreme viscosity spike.
Post-Cure Temperature	200°C (start_span_58 58)(end_span_58 58)	$>220^{\circ}\text{C}$	Thermal degradation of bio-based matrix and processed reinforcement interphase.

Scale-Up Delusions and Technology Readiness Level Overreach

A major non-technical risk in advanced bio-composite engineering is conflating benchtop chemical validation (Technology Readiness Level 2–3) with industrial manufacturing readiness (TRL 6–7). Laboratory synthesis of 50 g test samples in glass beakers does not encounter the heat dissipation limits, fluid flow resistance, or stochastic feedstock variations present in industrial manufacturing. Formulations that perform well in thin laboratory coupons can fail when scaled to large structural parts if exotherm mitigation, fluid rheology, and degassing protocols are not re-engineered for larger volumes.

Advanced Hempoxies variants (such as v.14 and v.15) attempt to incorporate ultra-high-stiffness 1D Oxygenated Carbon Nanothreads (OCNs) synthesized from furan precursors under extreme pressure. Early laboratory synthesis relied on Diamond Anvil Cells (DACs) at static pressures exceeding 8 GPa, which yielded only nanogram quantities per compression

cycle. To scale production, the Landry Cycle 5 GPa Pivot introduced a Piston-Laser Hybrid system utilizing Tungsten Carbide (WC) piston-cylinders driven by Resonant Two-Photon Absorption (TPA) femtosecond lasers (450 nm). However, this scale-up approach introduces severe operational vulnerabilities:

- **Optical Window Carbon Fouling:** Deposition of carbonized species onto the internal optical entry window attenuates laser intensity during the TPA cycle. Energy attenuation prevents full volumetric polymerization, leaving unreacted liquid furan pockets inside the nanothread matrix that collapse under shear loading.
- **Pressure Volatility and Amorphous Phase Shift:** Minor pressure fluctuations below the 5 GPa threshold shift the reaction away from sp³-bonded crystalline nanothreads, producing brittle amorphous carbon black instead.

Unlike petroleum feedstocks produced to rigid chemical specifications, agricultural biomass exhibits natural seasonal and regional variations. Raw hemp seed oil unsaturation levels can vary by up to 15% depending on weather conditions, soil quality, and crop cultivar. Unsaturation levels directly determine the Iodine Value (IV), which governs the final Oxirane Oxygen Content (OOC) and Epoxy Equivalent Weight (EEW) after epoxidation. Formulating batches using fixed recipe weights without measuring the EEW of each new oil lot guarantees stoichiometric imbalance. Every incoming lot of raw oil must undergo Iodine Value testing (ASTM D1959), and every epoxidized batch must be titrated for EEW (ASTM D1652) to recalculate hardener mass balances accurately.

Preventative Protocols and Process Parameters

To ensure successful manufacturing without triggering chemical, thermal, or mechanical failure, production protocols must enforce the non-negotiable processing boundaries outlined below:

Manufacturing Parameter	Strict Operational Boundary	Primary Engineering Rationale
Epoxidation Reaction Temperature	Strictly 60°C $\pm 2^{\circ}\text{C}$ (55 $^{\circ}\text{C}$ to 60 $^{\circ}\text{C}$)	Prevents acid-catalyzed oxirane ring-opening into non-reactive diol sludge.
Reinforcement Pre-Drying	Vacuum-dry at 105 $^{\circ}\text{C}$ for 2 h (<0.5 wt% H ₂ O)	Prevents steam expansion from absorbed moisture in processed preforms/fillers, micro-voiding, and IFSS collapse.
Stoichiometric Target Balance	Strictly 1:0.8 Epoxy:Carboxyl (1.51:1.0 operational)	Eliminates unreacted carboxyl groups that cause plasticization and creep.
VARI Infusion Temperature	Strictly 60°C $\pm 2^{\circ}\text{C}$	Maintains viscosity at 800–1200 mPa·s while preserving a 4-h pot-life.
Degassing Vacuum Level	Strictly 50 mbar	Prevents volatilization of FGE reactive diluent and stoichiometric drift.
Biochar Mixing Shear	Strictly $\leq 1500\text{ rpm}$ (after high-shear)	Preserves biochar porous microstructure and prevents

Manufacturing Parameter	Strict Operational Boundary	Primary Engineering Rationale
	nano-dispersion)	viscosity spikes.
Laminate Core Temperature	Strictly $\leq 190^{\circ}\text{C}$ (Ramp rates $\leq 1.5^{\circ}\text{C/min}$)	Controls reaction exotherm ($\Delta H \approx 300 \text{ J/g}$) and prevents ester cleavage.
Post-Cure Consumables	Polyamide 66 (Nylon) or PTFE glass fabric	Prevents thermal melting and permanent part fusion during 200°C post-cure.
Thermoforming Atmosphere	Sealed, nitrogen-purged (N_2) hot-press molds	Prevents thermo-oxidative crosslinking, matrix darkening, and T_g elevation.

Conclusions

The Hempoxies platform demonstrates that structural, circular composites can be derived successfully from agricultural biomass. However, achieving mechanical performance comparable to petrochemical composites requires strict adherence to chemical and processing constraints. By eliminating stoichiometric errors, controlling precursor moisture, managing reaction exotherms, and enforcing precise processing boundaries, materials engineers can overcome the historical performance limitations of bio-based composites. Adhering to these protocols ensures the production of robust vitrimeric composites that deliver reliable structural performance during service while enabling full circularity at end-of-life.

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