

Comprehensive Failure Analysis and Lessons Learned in Hempoxies Processing

Technical Pitfalls, Stoichiometric Drift, and
Degradation Vulnerabilities

Organization: Landry Industries Inc.

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Table of Contents

1. Executive Overview and Strategic Positioning
2. Precursor Synthesis Vulnerabilities and Chemical Side Reactions
3. Stoichiometric Deviations and Network Topography Flaws
4. Industrial Processing and Rheological Failures
5. Thermal, Exothermic, and Kinetic Degradation Vectors
6. Scale-Up Delusions and Technology Readiness Level Overreach
7. Preventative Protocols and Process Parameters
8. Conclusions

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, unprocessed 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.

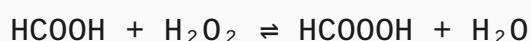
This enables self-healing, thermal thermoforming, and low-energy chemical recyclability, addressing the primary environmental and lifecycle constraints of modern composite engineering.

Critical Finding: Transitioning from petroleum-based thermosets to structural bio-vitrimer 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.

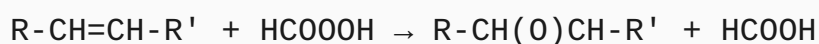
Precursor Synthesis Vulnerabilities and Chemical Side Reactions

The primary matrix monomer in the Hempoxies architecture is Epoxidized Hemp Seed Oil (EHSO), produced by converting unsaturated fatty acid double bonds 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 ($\Delta H \approx -200$ kJ/mol). Allowing the reaction temperature to exceed 60°C, or failing to manage localized thermal spikes, triggers a destructive side reaction.

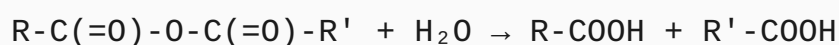
Thermal Runaway Risk: In the presence of the aqueous acid phase, elevated temperatures catalyze the nucleophilic ring-

opening of newly formed oxirane rings by water or formic acid, converting them to non-reactive diol structures that permanently destroy monomer crosslinking functionality.

Instead of yielding structural EHSO with an Oxirane Oxygen Content (OOC) above 6.5% and an Epoxy Equivalent Weight (EEW) of 185–195 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).

Moisture Contamination and Catalyst Poisoning

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 ($Zn(acac)_2$) or Zinc Acetate Dihydrate ($Zn(OAc)_2$).

Preventative Measure: All precursor feedstocks must be vacuum-dried at 60°C over 3 Å molecular sieves until moisture levels fall below 500 ppm. This is non-negotiable for vitrimeric functionality.

Sizing Solution Purification

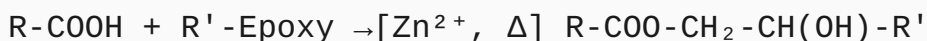
When synthesizing Quadruple-Function Modified Hemp Lignin (QF-MHL) or Epoxidized Lignin (EL) for the fiber-matrix interphase, technical Kraft or Organosolv lignins are reacted with epichlorohydrin under basic conditions (NaOH). Incomplete purification leaves residual sodium chloride (NaCl), unreacted 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 ($-\text{OH}$) 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*:



Stoichiometric Error Pattern: 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. These unreacted carboxylic acids act as internal plasticizers, attract

atmospheric moisture, and catalyze uncontrolled hydrolytic degradation of the ester backbone over time.

Hempoxies 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.

Empirical vs. Theoretical Titration

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.

Critical Formulation Parameters

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 (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 Zn^{2+} catalyst centers	Catalyst poisoning; complete loss of vitrimeric self-healing/flow
Catalyst Loading ($Zn(OAc)_2$)	10 mol% to carboxyl (3.5–4.5 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 ($>5000 \text{ mPa}\cdot\text{s}$ 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 ($800\text{--}1200 \text{ mPa}\cdot\text{s}$), the system integrates Hemp-Derived Furfuryl Glycidyl Ether (FGE) as an aromatic reactive diluent. However, processing parameters must be rigidly controlled:

Infusion Temperature Boundary

Resin temperature during infusion must be held at **$60^\circ\text{C} \pm 2^\circ\text{C}$** . Lowering the temperature below 55°C increases viscosity above $1500 \text{ mPa}\cdot\text{s}$, 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 Constraint

Vacuum pressure during degassing and infusion must not drop below 50 mbar. Applying deeper vacuum ($<10 \text{ mbar}$) 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.

Reinforcement Moisture and Interfacial Strength

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.

IFSS Collapse Risk: 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.

Biochar Dispersion and Pulverization Risk

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 rpm), after which the biochar is added at a lower mixing speed (≤ 1500 rpm).**

Gelation Phase Disturbance

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:

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

Exothermic Runaway: 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 210–220°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 180–200°C for topology establishment). Dwell steps allow reaction enthalpy to dissipate safely while the resin remains below its thermal degradation threshold.

Thermal Hierarchy and Processing Windows

To maintain structural integrity during service while retaining thermal reprocessability, Hempoxies systems must operate within a strict hierarchy of thermal transitions:

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

- **Service Temperature (T_{service}):** Must remain at least 40°C below T_g to prevent viscoelastic creep under structural loads
- **Glass Transition Temperature (T_g):** Tuned between 85°C and 115°C via FGE aromatic modulation
- **Topology Freezing Temperature (T_v):** Occurs between 165°C and 185°C, where melt viscosity drops to 10^{12} Pa·s
- **Processing and Healing (T_{process}):** Conducted between 170°C and 190°C to promote rapid transesterification
- **Degradation Threshold ($T_{\text{degradation}}$):** Above 210–220°C, thermal scission of the bio-derived backbone occurs

Thermo-oxidative Aging and Nitrogen Purging

Thermal remolding or self-healing performed in ambient air at elevated temperatures (180–200°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 Boundaries and Safe Operating Limits

Processing Boundary	Safe Operating Limit	Exceeded Limit Threshold	Primary Hazard / Structural Failure
VARI Resin Temperature	60°C ± 2°C	>70°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°C; IFSS collapses
Laminate Exotherm Core	≤ 190°C	>210°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	>220°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.

Nanothread Scale-Up and Optical Window Fouling

Advanced Hemproxies 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.

Feedstock Variability and Iodine Value Measurement

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 $\pm 15\%$ 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.

Mandatory Quality Control: 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 $\leq 60^{\circ}\text{C}$ ($55^{\circ}\text{C} \pm 2^{\circ}\text{C}$)	Prevents acid-catalyzed oxirane ring-opening into non-reactive diol sludge
Reinforcement Pre-Drying	Vacuum-dry at 105°C for ≥ 2 h (<0.5 wt% H_2O)	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 $60^{\circ}\text{C} \pm 2^{\circ}\text{C}$	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 ≤ 1500 rpm (after high-shear nano-dispersion)	Preserves biochar porous microstructure and prevents viscosity spikes
Laminate Core Temperature	Strictly $\leq 190^{\circ}\text{C}$ (Ramp rates $\leq 1.5^{\circ}\text{C}/\text{min}$)	Controls reaction exotherm ($\Delta H \approx 300$ 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		Prevents thermo-oxidative crosslinking, matrix

Manufacturing Parameter	Strict Operational Boundary	Primary Engineering Rationale
	Sealed, nitrogen-purged (N ₂) hot-press molds	darkening, and T _v elevation

Conclusions

The Hemproxies 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.

Key Takeaways

- **Chemical Precision:** Epoxidation temperature control ($55^{\circ}\text{C} \pm 2^{\circ}\text{C}$) is critical to prevent diol formation and resin sludge
- **Stoichiometric Accuracy:** Empirical EEW titration (ASTM D1652) is non-negotiable; theoretical values introduce 12% errors
- **Moisture Management:** Precursor drying (<500 ppm) and reinforcement pre-drying (<0.5 wt%) prevent catalyst poisoning and IFSS collapse

- **Processing Discipline:** VARI temperature ($60^{\circ}\text{C} \pm 2^{\circ}\text{C}$), vacuum level (≥ 50 mbar), and shear rates (≤ 1500 rpm for biochar) must be rigidly maintained
- **Thermal Control:** Multi-stage isothermal cure schedules with controlled ramp rates ($\leq 1.5^{\circ}\text{C}/\text{min}$) prevent exothermic runaway and thermal degradation
- **Feedstock Variability:** Agricultural biomass requires lot-by-lot quality verification (Iodine Value, EEW) due to seasonal and regional variations
- **Scale-Up Reality:** Laboratory formulations must be re-engineered for industrial heat dissipation, flow dynamics, and process robustness before TRL advancement

Document Classification: Technical Reference Material

Audience: Materials Engineers, Process Chemists, Composite Manufacturing Specialists

Reference: Landry Industries Inc. — Hempoxies Technical Monographs v.1-v.32