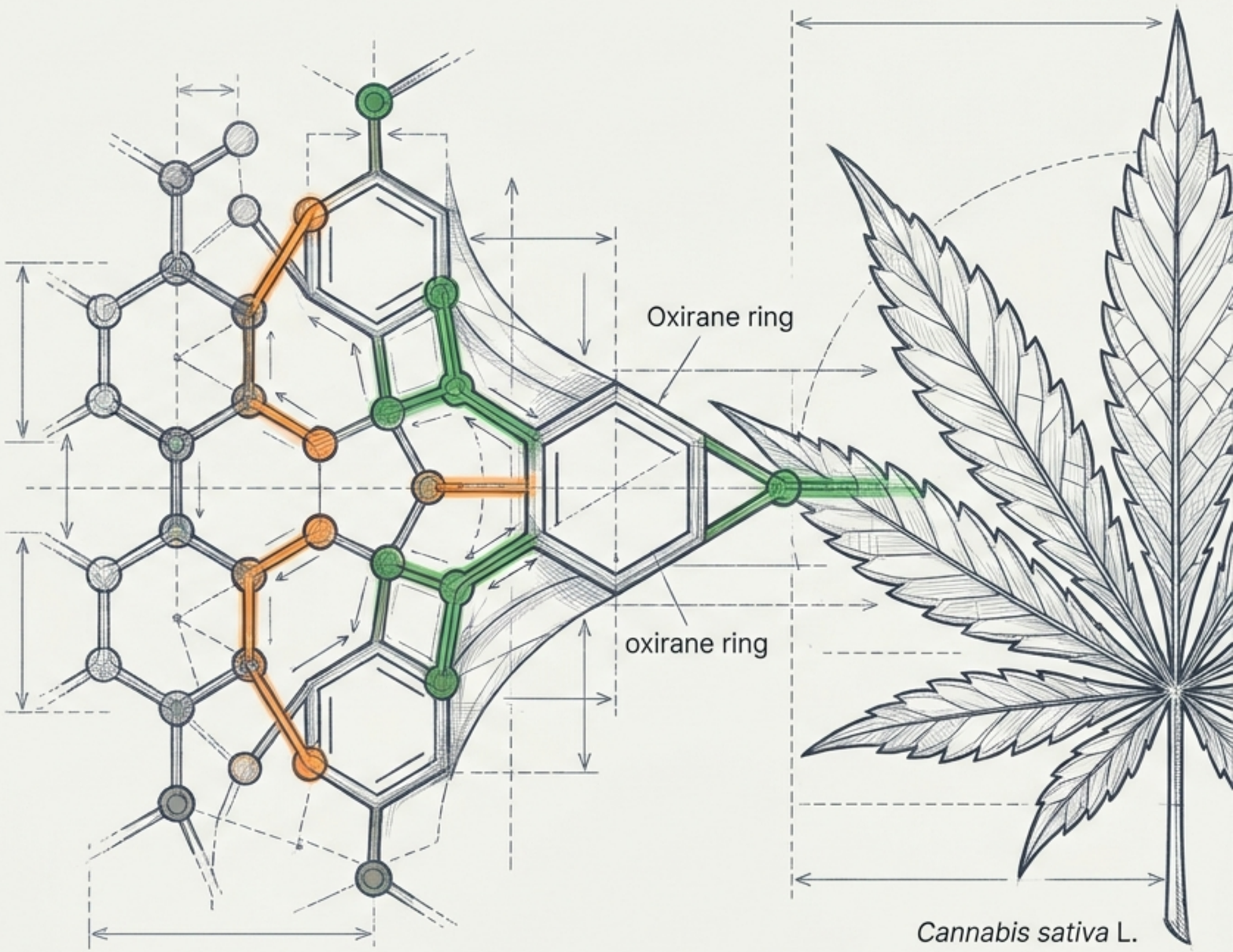
Hempoxies: A Fully Bio-Based Vitrimer Nanocomposite System

Design, Synthesis, and Characterization of Dynamic Covalent Networks for Recyclable High-Performance Applications

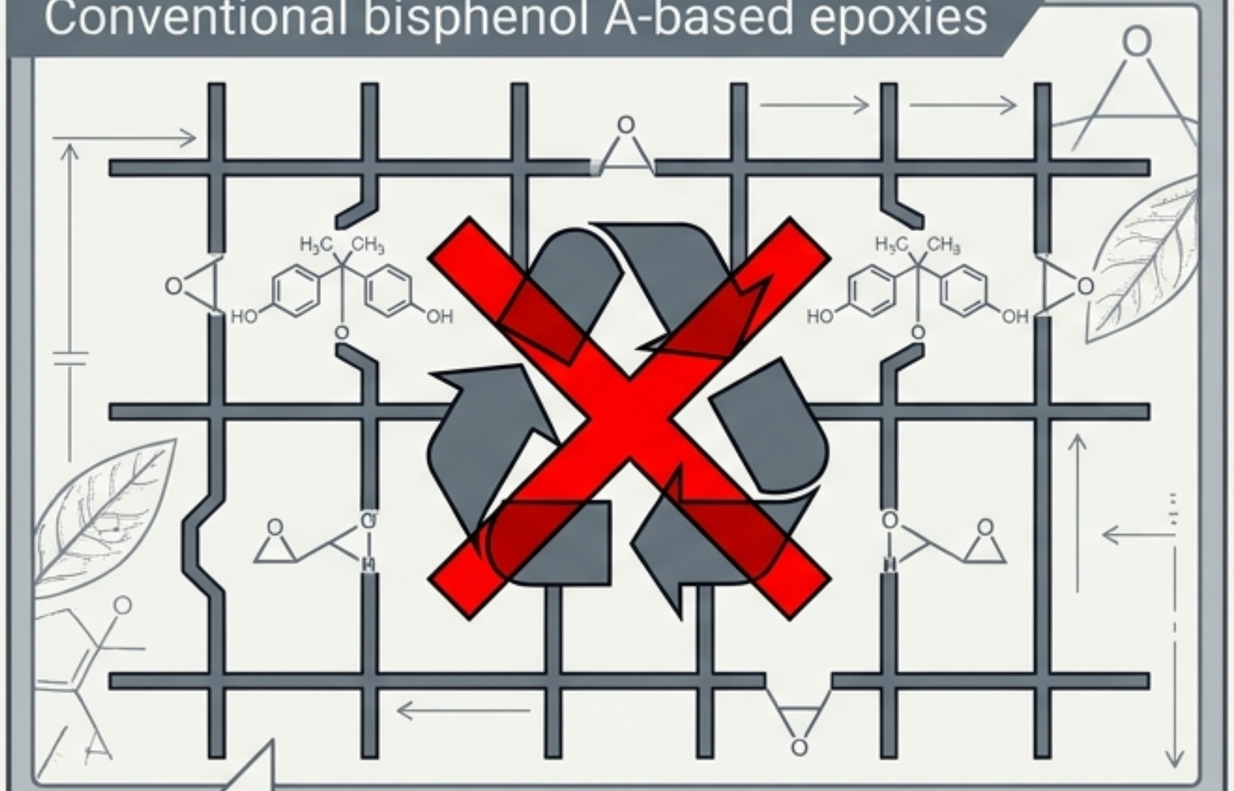
Author: Marie-Soleil Seshat Landry
(Landry Industries Inc.)



Gemini Notebook

The permanent covalent bonds of conventional thermosets create an irreversible **environmental liability.**

Conventional bisphenol A-based epoxies



Conventional bisphenol A-based epoxies form permanent crosslinks. Excellent dimensional stability, but fundamentally non-recyclable. End-of-life disposal relies exclusively on incineration or landfilling.



3.5+ Million Tonnes

Annual global production of synthetic thermoset resins.



Irreversible Loss

Embodied energy lost permanently upon disposal.



Fossil-Derived

Petroleum feedstocks release volatile organic compounds during processing.

Gemini Notebook

Hempoxies resolves the recyclability paradox by engineering a high-performance vitrimer entirely from industrial hemp.

A fully bio-based (95–100% carbon content) covalent adaptable network (CAN).

Matrix & Diluent

Extracted from hempseed oil (rich in linoleic and α-linolenic acids).

Vitrimer Engine

Synthesized via sebacic acid and dynamic catalysts.



Compatibilizer

Sourced from lignin-rich processing residues.

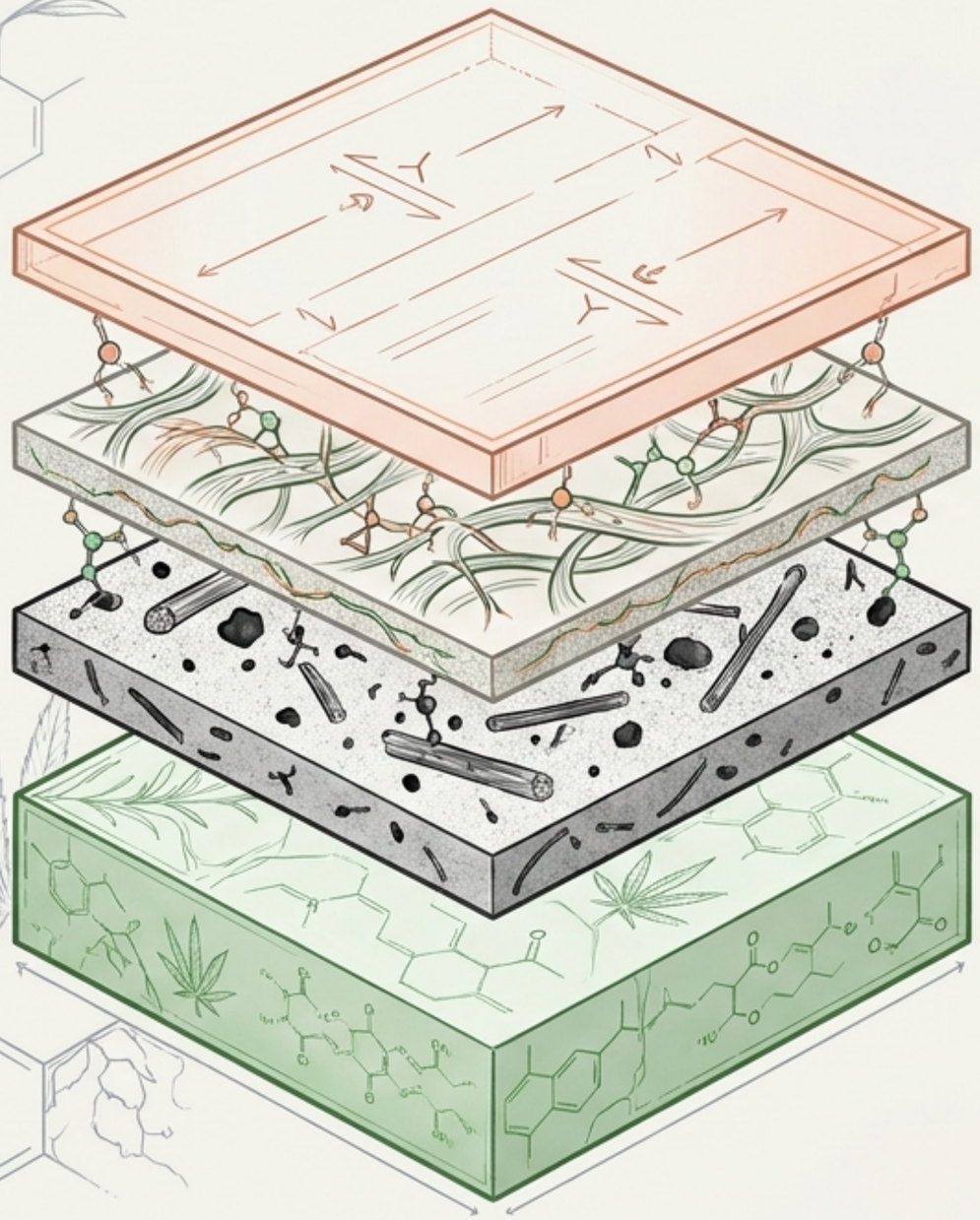
Reinforcement

Multi-scale carbon derived from hemp hurd and bast fiber.

Agronomic Advantage: Rapid 90–120 day growth cycle, nitrogen-fixing roots, minimal pesticide requirement, high carbon fixation (~22 tonnes CO_2/ha/year).

Gemini Notebook

The Formulation Stack: Deconstructing the bio-composite layer by layer.



Layer 4: Vitrimer Engine

Sebacic Acid (40–55 PHR) + $Zn(acac)_2$ Catalyst (2–5 PHR)

Function: Ester former and dynamic exchange trigger.

Layer 3: Interfacial Bridge

Epoxidized Lignin (5–15 PHR)

Function: Covalent integration between filler and matrix.

Layer 2: Reinforcement

Multi-Scale Hemp Carbon (3–16 PHR total)

Function: Hierarchical mechanical and thermal enhancement.

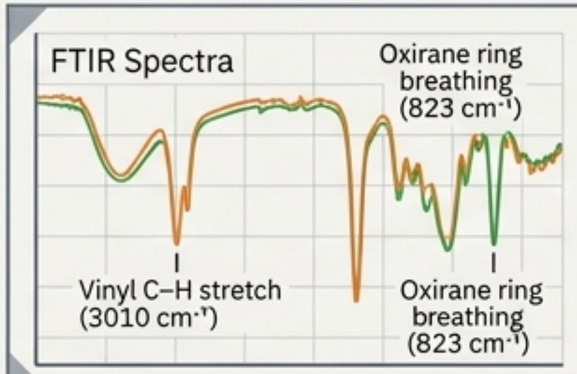
Layer 1: Base Matrix

Epoxidized Hempseed Oil (EHO, 100 PHR) + Furfuryl Glycidyl Ether (FGE, 15–25 PHR)

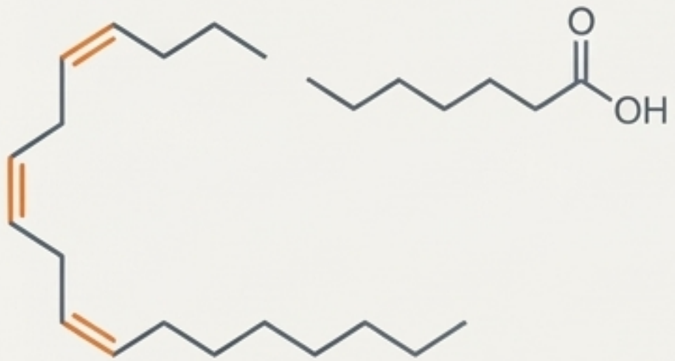
Function: Primary resin and reactive diluent for viscosity control.

Gemini Notebook

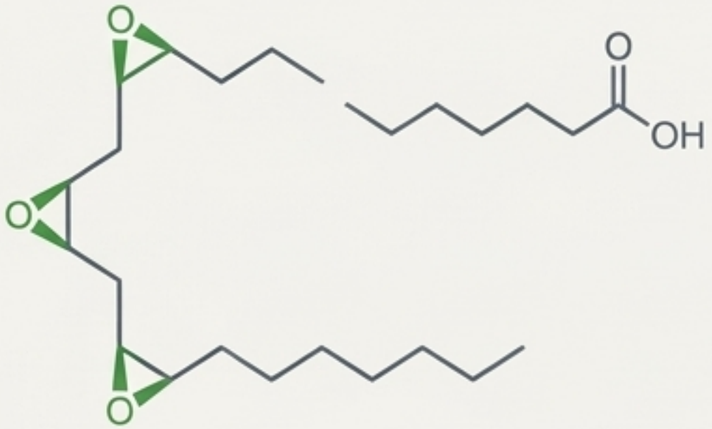
Controlled *in situ* epoxidation functionalizes polyunsaturated hempseed oil



FTIR Inset: Disappearance of the vinyl C–H stretch at 3010 cm^{-1} and the emergence of the oxirane ring breathing band at 823 cm^{-1} confirms complete functionalization.







Process Detail: Swern-type epoxidation utilizes formic acid and H_2O_2 (30%) at 50°C to generate an in situ peroxyformic acid. This electrophilically attacks the C=C double bonds of the fatty acids.

Yield Specification: Achieves an Epoxide Oxygen Content (EOC) of 5.8–7.2%.

Gemini Notebook

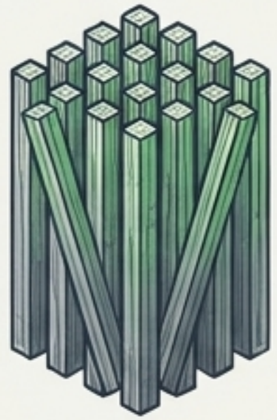
Hierarchical carbon reinforcements dictate thermal, stiffness, and conductivity parameters.

Micro — Nano



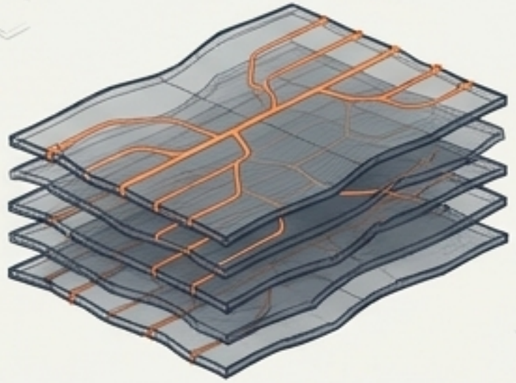
Biochar
(Micro-scale)

Source: Pyrolyzed hemp hurd (600°C).
Geometry: Particulate / Spherical.
Properties: High surface area (600–900 m^2/g activated).
Composite Role: Thermal conductivity for uniform heat distribution during reprocessing.



Cellulose Nanocrystals / CNCs
(Nano-rod)

Source: Acid-hydrolyzed hemp bast fiber.
Geometry: High aspect ratio rods (L: 200–400 nm, D: 10–20 nm).
Properties: Highly crystalline (75–82%), ~150 GPa filler modulus.
Composite Role: Primary longitudinal stiffness and stress transfer.



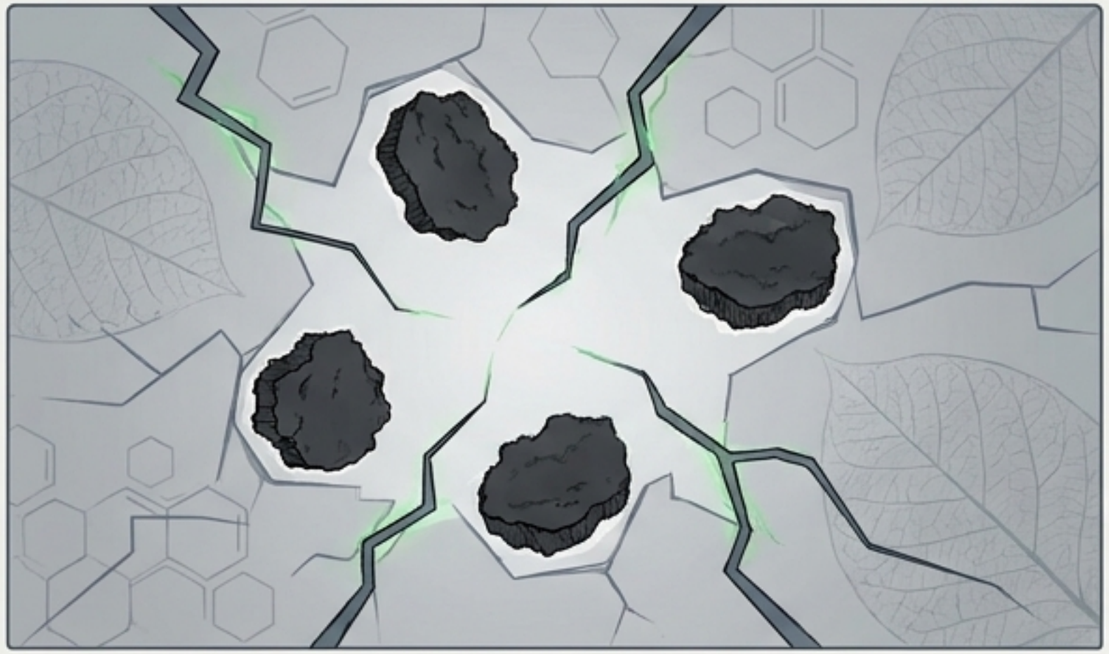
Carbonized Fiber Nanosheets / CFN
(Nano-sheet)

Source: Carbonized (1000°C) and ball-milled fiber.
Geometry: Lateral sheets (1–5 µm wide, 5–20 nm thick).
Properties: Partially graphitic structure, electrically conductive (15–45 S/m).
Composite Role: Electrostatic discharge dissipation via percolation pathways.

Gemini Notebook

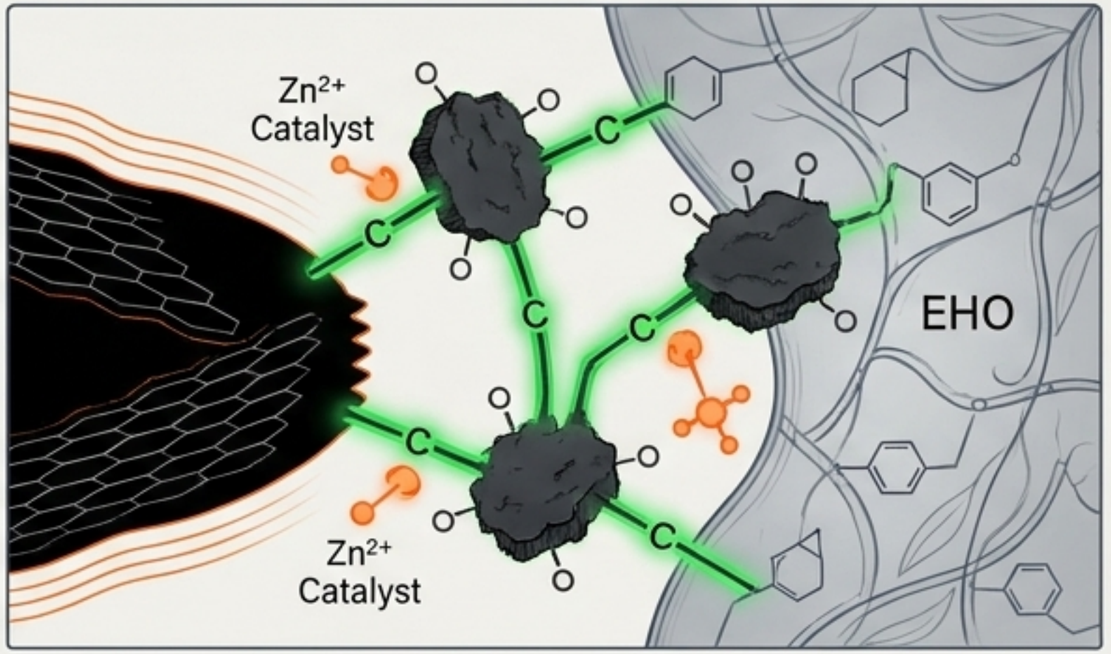
Epoxidizing lignin transforms an incompatible additive into a critical interfacial bridge

Static Network



The Lignin Problem: Technical kraft lignin typically causes phase separation and mechanical embrittlement in conventional epoxies due to poor interfacial adhesion.

Dynamic Network

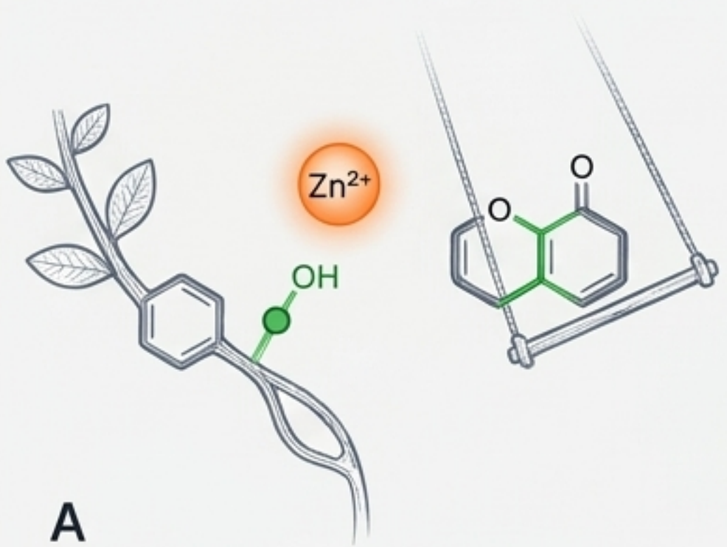


The Hempoxies Solution: Reacting lignin with epichlorohydrin (ECH) generates oxirane-functional groups (0.8–1.2 mmol/g).

The Macro-Result: The lignin acts as a reactive co-monomer, covalently linking the carbon fillers to the EHO matrix. This eliminates the weak interface that causes cohesive failure, directly enhancing fracture toughness.

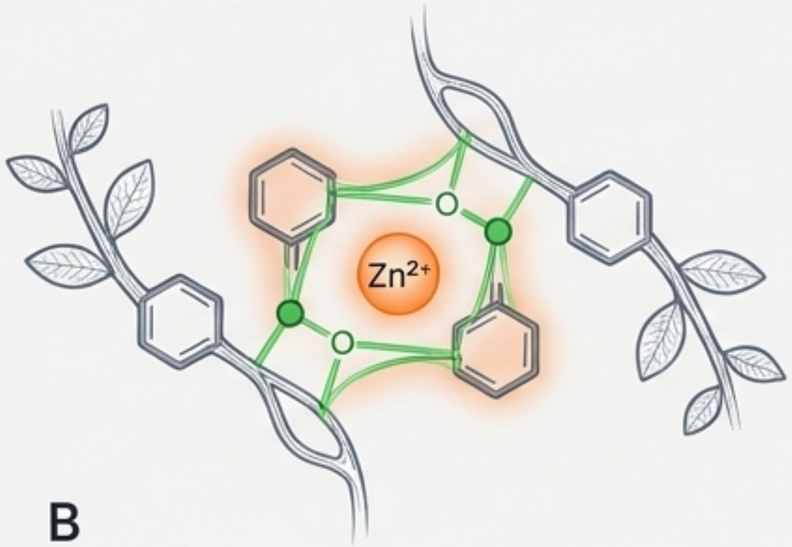
Gemini Notebook

The Vitrimer Engine: Zinc-catalyzed transesterification enables topology reconfiguration without degradation



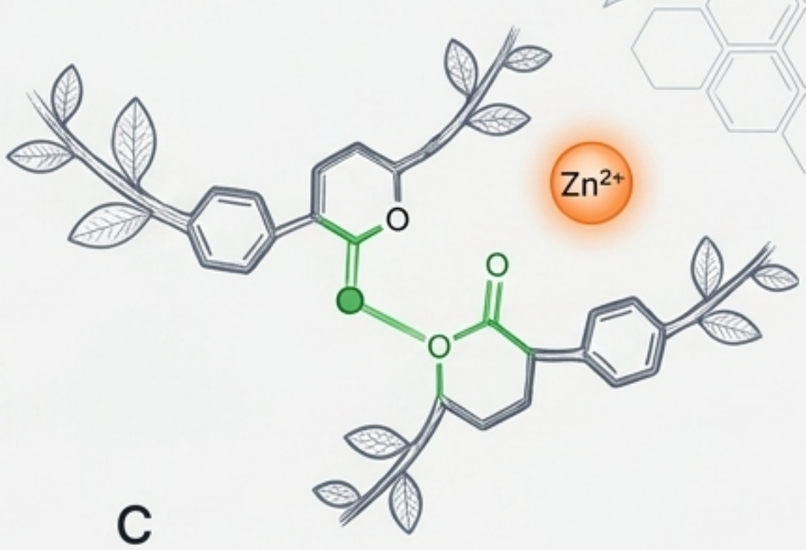
A

State A: Pendant hydroxyl group and Zn^{2+} catalyst approach ester linkage.



B

State B: Intermediate: Simultaneous bonding with thermal activation (Zn^{2+}-catalyzed).

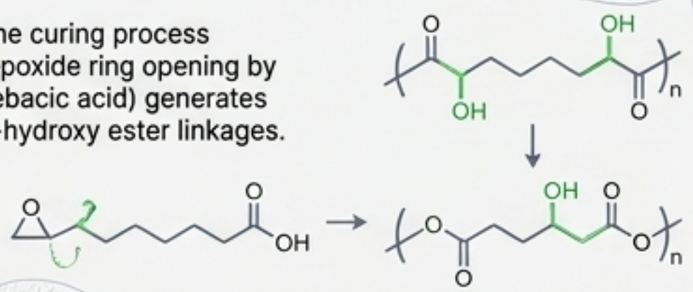


C

State C: New bond formed, original bond released. Topology reconfigured.

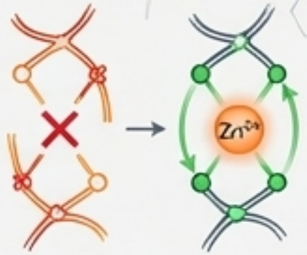
The Mechanism

The curing process (epoxide ring opening by sebacic acid) generates β-hydroxy ester linkages.



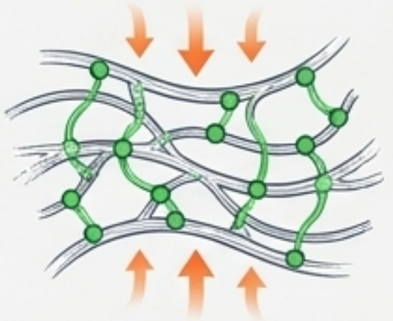
Associative Exchange

Unlike dissociative networks that break bonds before forming new ones (losing structural integrity), this network utilizes Zn^{2+}-catalyzed transesterification. A pendant hydroxyl group attacks an adjacent ester bond, exchanging partners dynamically.



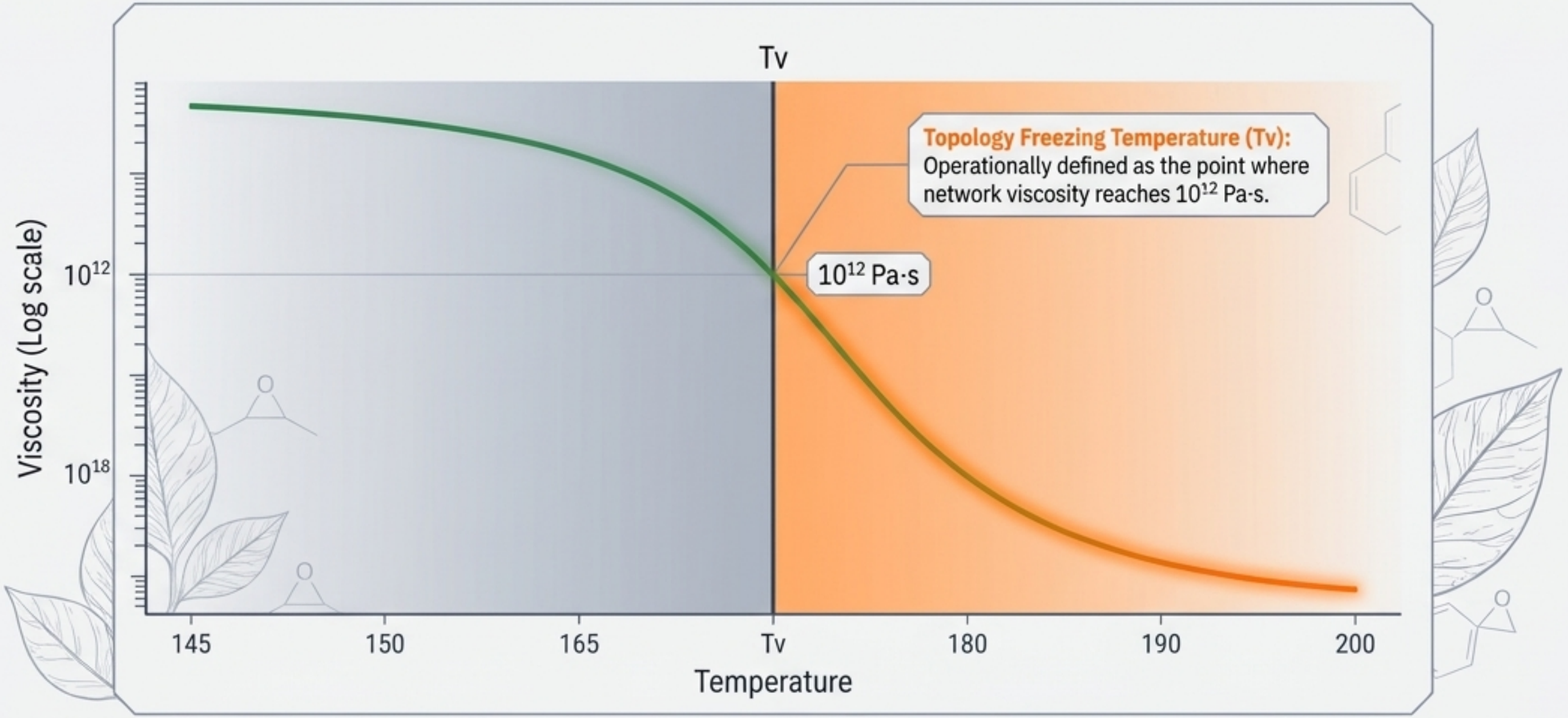
The Result

The total number of crosslinks is strictly conserved. The material flows like a viscous liquid under heat but never loses its crosslink density.



Gemini Notebook

Arrhenius kinetics dictate a strict boundary between rigid service and viscous self-healing.



Service Window (< Tv)

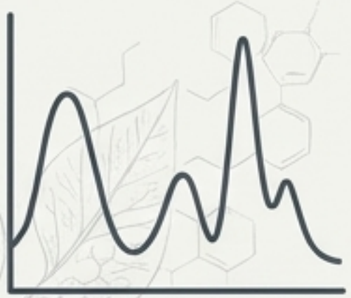
Projected at temperatures below 145–165°C. Exchange kinetics are exponentially slow. The network is permanently locked, creep-resistant, and behaves as a rigid structural thermoset.

Reprocessing Window (> Tv)

At 180°C, the activation energy (E_a = 90–110 kJ/mol) is overcome. Characteristic relaxation time (τ^*) drops to 8–25 minutes. The network topology unfreezes, enabling autonomous self-healing and complete molding.

Gemini Notebook

A comprehensive characterization matrix verifies molecular structure and macroscopic behavior.



Spectroscopic Verification (FTIR & Raman)

Tracks the disappearance of **oxirane rings** (**cure completion**) and characterizes **carbon morphology** via **D/G band** analysis.



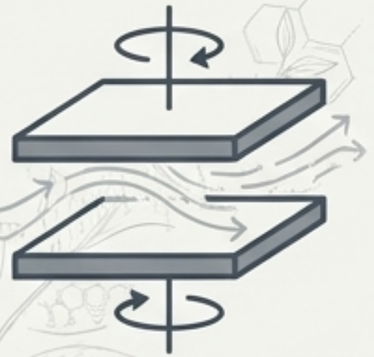
Dynamic Mechanical Analysis (DMA)

Captures storage modulus (**E'**), **Tg** (tan δ peak), and computes effective network **crosslink density (n_e)** through rubber elasticity theory.



Thermal Stability (TGA & DSC)

Determines $T_{d5\%}$ decomposition limits, char yield (600°C), and confirms complete network formation (residual cure enthalpy < 5 J/g).

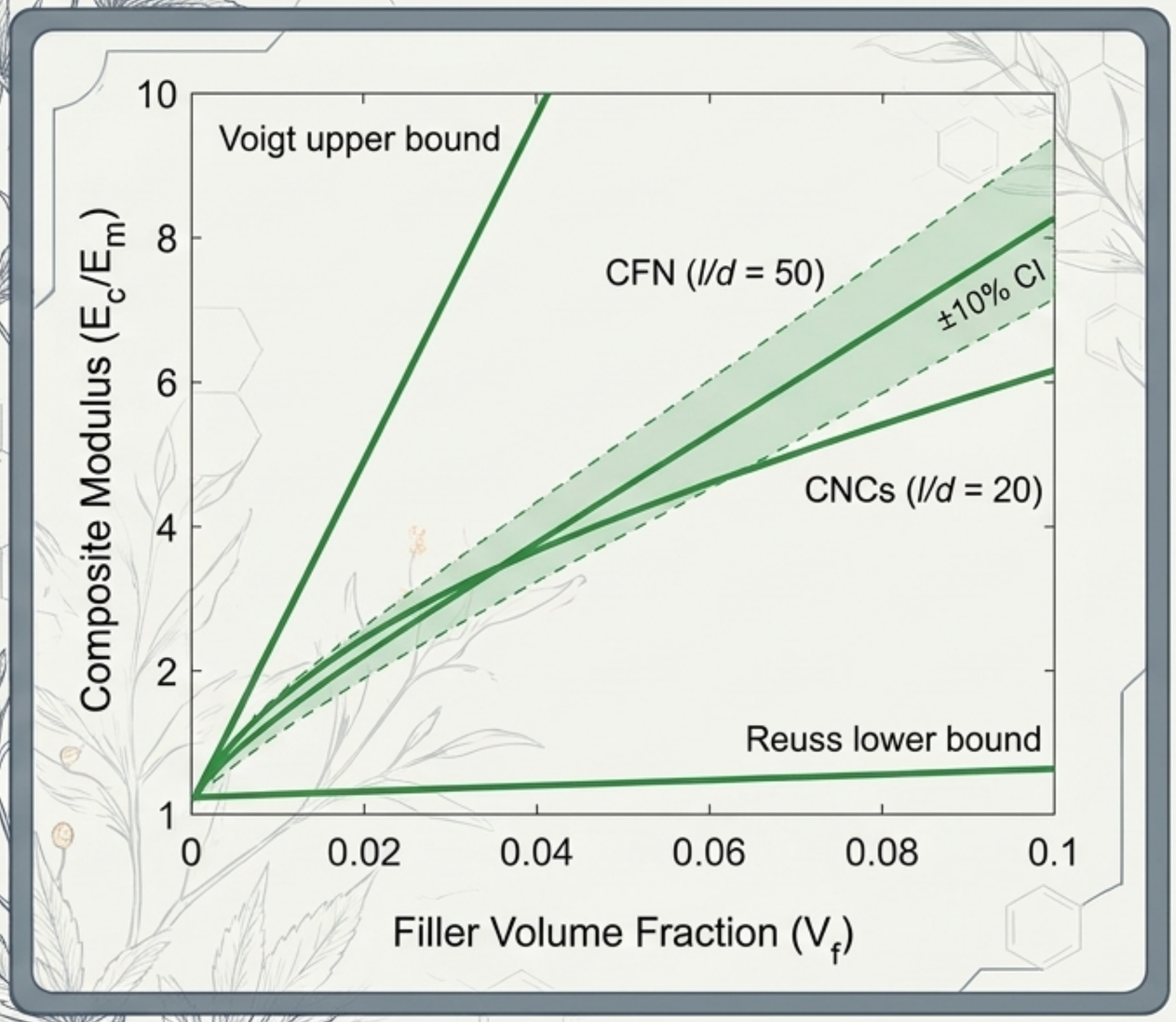


Stress-Relaxation Rheometry

Extracts relaxation time (τ*) and activation energy (E_a) to mathematically plot the Arrhenius vitrimer behavior.

Gemini Notebook

Semi-empirical modeling projects aerospace-grade stiffness via nanoscale reinforcement



The Model:

The Halpin-Tsai semi-empirical model is applied to account for the non-continuous nature and high aspect ratios of the hemp nanofillers.

Performance Projection:

At CNC loadings of just 3–5 wt%, the model predicts a Young's modulus of 1.8–2.8 GPa.

Matrix Enhancement:

This represents a 5x to 8x magnitude improvement over the unfilled EHO control matrix (0.3–0.6 GPa).

Gemini Notebook

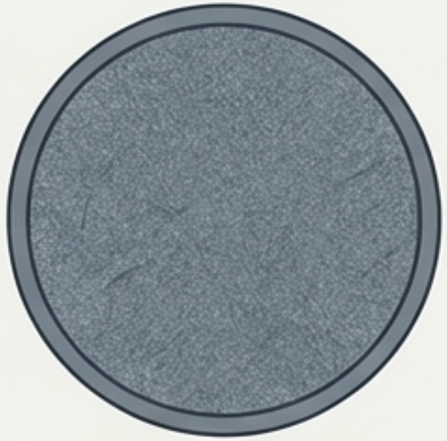
Hempoxies matches synthetic aerospace epoxies in strength while achieving 100% recyclability.

The Performance & Sustainability Matrix

	Hempoxies (Target)	EHO Control	DGEBA (Synthetic)
Young's Modulus (GPa)	**1.8–2.8**	0.3–0.6	2.5–3.5
UTS (MPa)	**35–60**	8–15	55–90
Glass Transition T_g (°C)	**65–95**	-10–15	120–180
Healing Efficiency (%)	**>85%**	~40%	0% - Non-healable
Bio-based Content (%)	**~95–100%**	~100%	<5%

Gemini Notebook

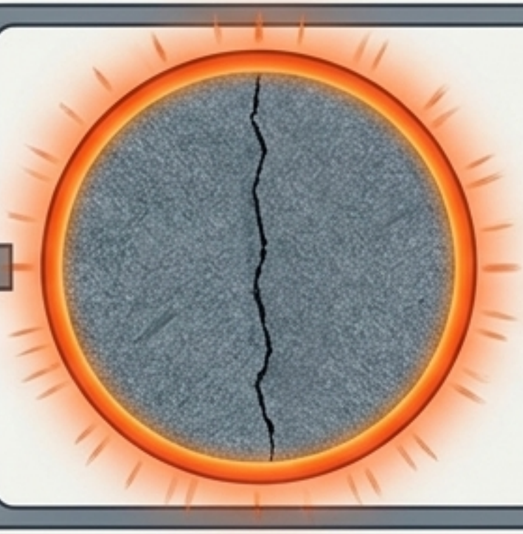
Dynamic network mobility above T_v enables autonomous structural recovery.



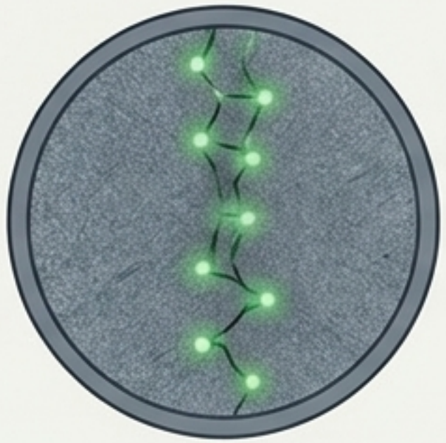
1. Damage Initiation: Specimen sustains critical mid-gauge micro-cracking and fracture.



2. Interface Contact: Cut surfaces are brought together under minimal pressure (0.1 MPa).



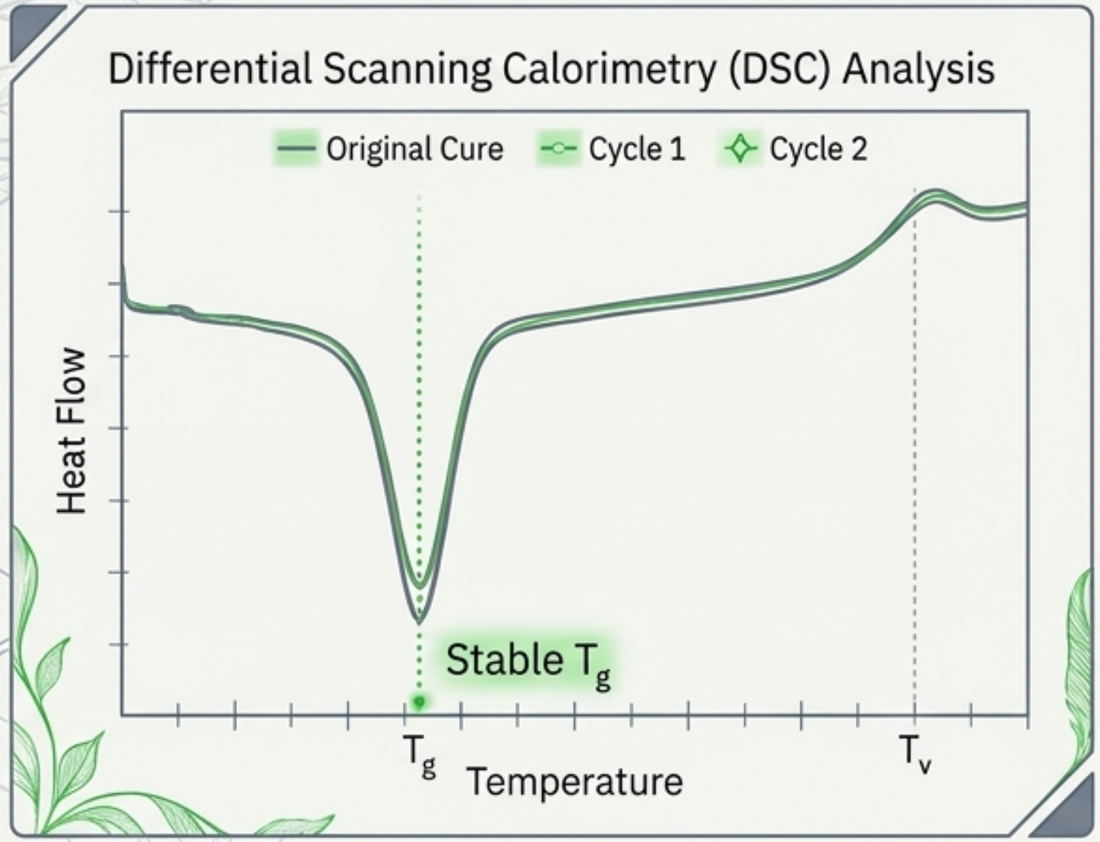
3. Thermal Annealing: Application of 180°C heat for 30 minutes unfreezes the network topology.



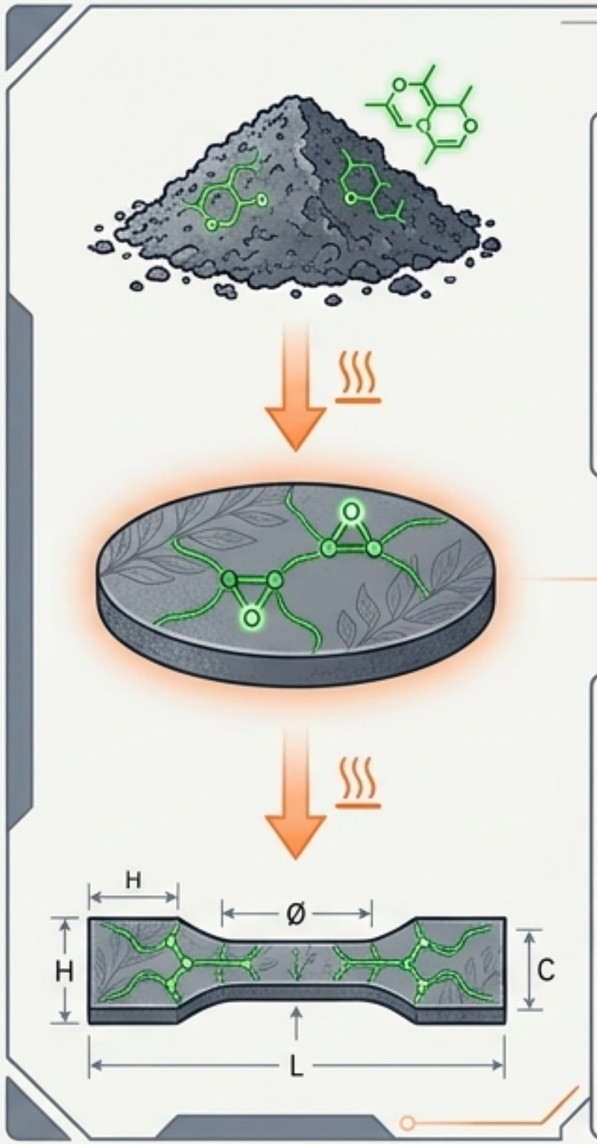
4. Strength Recovery: Associative exchange bridges the fracture, yield a healing efficiency (η_{heal}) of >85% of original Ultimate Tensile Strength.

Gemini Notebook

Complete chemical recyclability: remolding without loss of crosslink density.



Network Integrity: Differential Scanning Calorimetry (DSC) analysis confirms that the glass transition temperature (T_g) and thermal stability remain constant across multiple reprocessing cycles.



Reprocessing Protocol: At end-of-life, the composite can be ground into powder and hot-pressed above T_v (180°C).

The Result: The reformed matrix retains its original mechanical modulus, proving the vitrimer network avoids the degradation typical of dissociative polymers.

Gemini Notebook

A paradigm shift for advanced manufacturing: the closed-loop bio-composite lifecycle

Feedstock Phase

Industrial hemp cultivation achieves ~22 tonnes CO_2/ha/year carbon fixation, offsetting processing energy

Synthesis Phase

Formulation of the ~95–100% bio-based CAN utilizing every anatomical component of the plant



End-of-Life

Complete elimination of thermoset waste via 180°C thermal reprocessing. Zero landfill contribution.

Service Phase

Aerospace and automotive applications demanding high strength and creep resistance.

Gemini Notebook

The Iterative Horizon: Validating and scaling the Hempoxies framework



Formulation & Catalyst Optimization

Tuning the **FGE:EHO ratio** to balance **modulus** against toughness. Exploring **alternative catalysts** (e.g., TBD, guanidine) to lower T_v and **accelerate exchange rates**.



Accelerated Aging & Life Cycle Assessment

Conducting 1000-hour **hydrolytic stability tests** (**85°C/85% RH**) on the **ester network**. Executing formal ISO 14040 Life Cycle Assessment to quantify **net greenhouse gas emissions**.



Scale-Up & Certification

Advancing from **laboratory-scale (10g)** synthesis to **pilot-scale (1kg)** utilizing **high-shear mixing**, followed by rigorous **ASTM/ISO certification testing** for commercial aerospace and automotive sectors.

Gemini Notebook



The future of high-performance manufacturing is grown, engineered, and infinitely reformed.

Hempoxies establishes a rigorous theoretical and experimental framework for a next-generation sustainable thermoset platform, entirely derived from *Cannabis sativa* L.

Research by Marie-Soleil Seshat Landry | Landry Industries Inc. | Concept Framework 2026

Gemini Notebook