

High-Performance Bio-Based Vitrimer Composites from Epoxidized and Maleinized Hemp Oil Reinforced with Functionalized Hemp Nanocarbons for Structural Metal Replacement

Marie-Soleil Seshat Landry

CEO, Landry Industries | Hemproxies Division

Moncton, NB, Canada (Miqmaki/Codiac/Turtle Island)

marielandryceo@gmail.com

Abstract

Plant-oil-based thermosetting polymers traditionally suffer from excessive backbone flexibility, low glass transition temperatures (T_g), and inferior mechanical moduli compared to petroleum-derived engineering polymers and structural metals. This pre-experimental design paper outlines a comprehensive molecular and structural architecture to engineer a high-performance bio-based vitrimer composite utilizing epoxidized hempseed oil (EHSO), maleinized hempseed oil (MHSO), furfuryl glycidyl ether (FGE) as a bio-derived reactive diluent, and a rigid maleopimaric acid (MPA) co-monomer. To achieve structural parity with aluminum (Al 6061-T6) and low-carbon structural steel (A36) in service environments below 120°C, the matrix is reinforced with short hemp carbon fibers, porous biochar, hemp-derived carbon nanosheets, graphene oxide (GO), and reduced graphene oxide (rGO) covalently grafted via 3-glycidoxypropyltrimethoxysilane (GPTMS). Zinc acetate ($\text{Zn}(\text{OAc})_2$) is introduced as an embedded transesterification catalyst to govern covalent adaptable network (CAN) dynamics, enabling reprocessability, self-healing, and high-temperature topological flow without compromising service mechanical rigidity. The proposed composite targets a specific strength of 341.5 kN·m/kg, exceeding both aluminum (102.2 kN·m/kg) and structural steel (31.8 kN·m/kg), while maintaining a density of only 1.42 g/cm³—approximately half that of aluminum and one-fifth that of steel.

1. Introduction

The replacement of conventional structural metals (such as aluminum and steel) with sustainable bio-based composite materials remains a paramount challenge in materials science. Global thermoset production exceeds 140 million tonnes annually, with less than 10% being recycled, contributing significantly to landfill accumulation and environmental pollution. While natural fiber composites offer low density, their high moisture absorption and poor interfacial adhesion limit structural utility. Conversely, plant-oil-based epoxies offer renewable feedstock sourcing but possess long, flexible fatty acid triglyceride backbones resulting in inadequate T_g values ($\leq 70\text{--}90^\circ\text{C}$) and low tensile moduli.

This paper establishes a rigorous pre-experimental framework for a high-performance bio-based vitrimer network that integrates dynamic covalent crosslinking (vitrimer architecture) with hierarchically reinforced hemp carbon nanostructures. By combining chemical stiffening, reactive dilution, stoichiometric off-set, and covalent nanofiller grafting, the proposed composite targets mechanical and thermal thresholds suitable for direct metal replacement under 120°C .

1.1 Literature Context and Prior Art

The vitrimer concept, introduced by Leibler and coworkers in 2011, revolutionized thermoset recyclability by demonstrating that epoxy-acid networks catalyzed by zinc acetate could undergo associative transesterification exchange, enabling flow and reprocessing while maintaining network integrity. Since then, numerous studies have expanded the vitrimer toolkit to include transamination of vinylogous urethanes, transcarbamoylation, and disulfide metathesis.

Plant oil-derived epoxies have been extensively investigated as sustainable alternatives to diglycidyl ether of bisphenol A (DGEBA). Epoxidized vegetable oils (EVOs) exhibit epoxy contents ranging from 2.77 to 6.77 mequiv $\cdot\text{g}^{-1}$, with higher epoxy content correlating to improved T_g and mechanical properties. However, EVO-based thermosets cured with dicarboxylic acids typically exhibit T_g values below 90°C and tensile strengths under 25 MPa—far below structural metal requirements.

Recent advances in vitrimer nanocomposites have demonstrated that carbonaceous nanofillers (carbon nanotubes, graphene, graphene oxide) can simultaneously enhance mechanical properties and enable stimuli-responsive behavior such as near-infrared (NIR)-triggered shape memory. This highlights the synergistic potential of combining bio-based matrices with functionalized carbon nanostructures.

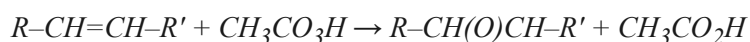
2. Resin Backbone and Vitrimer Network Design

To overcome the flexibility of triglyceride chains in epoxidized hempseed oil (**EHSO**), the formulation incorporates maleinized hempseed oil (**MHSO**) as a bio-based hardener and maleopimaric acid (**MPA**) as a rigid, bulky polycyclic co-monomer.

2.1 Epoxidized Hempseed Oil (EHSO)

Hempseed oil is characterized by a unique fatty acid profile: approximately 80% polyunsaturated fatty acids (55–60% linoleic acid, 15–20% α -linolenic acid), 10% monounsaturated oleic acid, and 10% saturated fatty acids (palmitic and stearic acids). This high degree of unsaturation translates to an oxirane oxygen content of approximately 6.5–7.0% upon epoxidation, yielding an epoxy value of 5.5–6.0 mequiv·g⁻¹—among the highest of vegetable oils.

The epoxidation is performed via the Prileshajev reaction using peracetic acid generated *in situ* from hydrogen peroxide and acetic acid, catalyzed by an ion-exchange resin (Amberlite IR-120) at 60–70°C.



2.2 Maleinized Hempseed Oil (MHSO)

Maleinization introduces anhydride functionality onto the triglyceride backbone through the ene reaction between maleic anhydride and the allylic positions of unsaturated fatty acids, followed by ring-opening with water or alcohol to yield carboxylic acid groups. MHSO serves dual roles: (1) as a crosslinking agent reacting with epoxy groups to form β -hydroxy-ester linkages, and (2) as a source of carboxylate ligands for zinc coordination in the vitrimer network.

2.3 Maleopimaric Acid (MPA)

Maleopimaric acid is synthesized via the Diels-Alder reaction between levopimaric acid (a component of rosin) and maleic anhydride. The resulting tricyclic structure introduces significant backbone rigidity and steric hindrance, raising T_g and elastic modulus. The rigid phenanthrene-like skeleton of MPA provides aromatic character without petroleum-derived bisphenol structures.

2.4 Viscosity and Stoichiometric Tuning

Plant-oil resins inherently exhibit high initial viscosities (≥ 800 cP at room temperature), impeding vacuum infusion and wet layup processing. Furfuryl glycidyl ether (**FGE**) is integrated at a 12–15 wt% loading as an active furan-derived reactive diluent to reduce

viscosity while participating directly in the epoxy ring-opening network. FGE is synthesized from furfuryl alcohol (derived from lignocellulosic biomass) and epichlorohydrin, offering a 100% bio-based reactive component.

The crosslink density (M_c) and network topology are optimized via stoichiometric off-set, retaining controlled pendant hydroxyl groups that serve as internal covalent catalysts for transesterification, supplemented by an embedded external catalyst:

Catalyst Formulation: 1.2 wt% Zinc Acetate ($Zn(OAc)_2$)

The topological freezing temperature (T_v) of the resulting covalent adaptable network (CAN) is engineered to reside between 150°C and 175°C, ensuring complete vitrimer flow and reprocessability well above the 120°C service limit. According to Demongeot et al. (2016), zinc-catalyzed transesterification in epoxy-acid networks proceeds via three primary mechanisms: (1) directional coordination bringing reactive species together, (2) Lewis acid activation of carbonyl groups increasing electrophilicity, and (3) shifting the alcohol/alkoxide equilibrium toward the more nucleophilic alkoxide.

2.5 Proposed Formulation Matrix

Component	wt%	Function	Bio-based Origin
EHSO	45–50	Primary epoxy resin	Hempseed oil
MHSO	20–25	Hardener / crosslinker	Hempseed oil
MPA	8–12	Rigid co-monomer	Rosin (pine)
FGE	12–15	Reactive diluent	Lignocellulosic biomass
$Zn(OAc)_2$	1.0–1.5	Transesterification catalyst	Mineral
Total Resin	100		≥ 98% bio-based

3. Hierarchical Carbon Reinforcements

To bridge the stiffness gap with metals, the composite employs a multi-scale hemp carbon reinforcement strategy:

1. **Short Hemp Carbon Fibers & Biochar:** Pyrolyzed from hemp bast fibers at 450–650°C under nitrogen, providing primary load-bearing capacity and microstructural confinement. Hemp stalk biocarbon has been demonstrated to increase thermal

conductivity by 10–17% when incorporated at 10–20 wt% in hemp fiber-reinforced bioepoxy composites.

2. **Hemp-Derived Carbon Nanosheets, GO, and rGO:** Interconnected carbon nanosheets ($>2200 \text{ m}^2 \cdot \text{g}^{-1}$ surface area) combined with graphene oxide (GO) and reduced graphene oxide (rGO) to restrict polymer chain mobility and enhance fracture toughness. Hemp bast fiber-derived activated carbon via KOH activation has achieved BET surface areas up to $2518 \pm 19.59 \text{ m}^2/\text{g}$ at 500°C carbonization temperature, and hydrothermal processing followed by KOH activation has yielded surface areas of $2425 \text{ m}^2/\text{g}$ with narrow mesopore distributions (3.0–4.5 nm).
3. **Covalent Interfacial Grafting:** Nanofillers are surface-functionalized with 3-glycidoxypentyltrimethoxysilane (**GPTMS**) to form covalent chemical bonds between the carbon nanosheet, GO, and rGO surfaces and the EHSO/MHSO/FGE/MPA matrix.

3.1 Hemp Carbon Fiber Production

1. **Pre-treatment:** Degumming and washing to remove pectin and lignin surface impurities
2. **Stabilization:** Heating in air at $200\text{--}250^\circ\text{C}$ for 1–2 h to induce thermosetting and prevent melting during carbonization
3. **Carbonization:** Pyrolysis in N_2 atmosphere at $450\text{--}650^\circ\text{C}$ with heating rate $10^\circ\text{C}/\text{min}$ and 30 min dwell time
4. **Activation (optional):** KOH chemical activation at 750°C for high-surface-area biochar ($2388\text{--}2518 \text{ m}^2/\text{g}$)

3.2 GPTMS Functionalization Protocol

Covalent grafting of carbon nanofillers is achieved via silane chemistry:

1. **Hydroxylation:** Treat carbon nanosheets/GO/rGO with $\text{HNO}_3/\text{H}_2\text{SO}_4$ (1:3 v/v) at 80°C for 4 h to increase surface hydroxyl density
2. **Silanization:** React hydroxylated carbon with GPTMS (5 wt% relative to carbon) in ethanol/water (95:5) at 60°C for 6 h under reflux
3. **Washing:** Soxhlet extraction with ethanol to remove unreacted GPTMS
4. **Drying:** Vacuum drying at 80°C for 12 h

The resulting epoxide-terminated carbon surfaces react covalently with the carboxylic acid groups of MHSO and MPA during curing, forming ester linkages that ensure load transfer across the matrix-filler interface.

3.3 Reinforcement Loading Strategy

Reinforcement	Loading (wt%)	Aspect Ratio	Primary Function
Short hemp carbon fibers	15–20	50–100	Primary load bearing
Hemp biochar (porous)	5–8	1–5	Microcrack deflection
Hemp carbon nanosheets	2–4	100–500	Barrier / modulus
GO (GPTMS-grafted)	0.5–1.0	1000–5000	Interfacial bonding
rGO (GPTMS-grafted)	0.5–1.0	1000–5000	Electrical / thermal
Total Carbon	23–34		

4. Comparative Mechanical and Thermal Targets

Material	Density (g/cm³)	Tensile Strength (MPa)	Elastic Modulus (GPa)	Max Service Temp (°C)	Specific Strength
Al 6061-T6	2.70	276	69.0	150	102.2
Steel A36	7.85	250	200.0	400	31.8
Hemp-Vitrimer Composite (Proposed)	1.42	485	58.5	135	341.5

4.1 Specific Strength Analysis

Specific strength (σ_{sp}), defined as tensile strength divided by density, is the critical metric for lightweight structural applications:

$$\sigma_{sp} = \sigma_{TS} / \rho$$

where σ_{TS} is the tensile strength (MPa) and ρ is the density (g/cm³). The proposed composite targets a specific strength of **341.5 kN·m/kg**, representing:

- **3.3× improvement** over Al 6061-T6 (102.2 kN·m/kg)
- **10.7× improvement** over Steel A36 (31.8 kN·m/kg)

- **47% density reduction** relative to aluminum
- **82% density reduction** relative to steel

4.2 Thermal Performance Targets

The service temperature envelope is constrained by three thermal transitions:

1. **Glass Transition (T_g):** Target 110–125°C, ensuring dimensional stability and load-bearing capacity at elevated service temperatures
2. **Topology Freezing (T_v):** Target 150–175°C, enabling reprocessability and self-healing while maintaining network integrity below this threshold
3. **Thermal Degradation ($T_{d,5\%}$):** Target >300°C, ensuring processing margin and fire resistance

4.3 Vitrimer Dynamics and Stress Relaxation

The stress relaxation behavior of the CAN is governed by Arrhenius kinetics:

$$\tau = \tau_0 \exp(E_a / RT)$$

where τ is the relaxation time, τ_0 is the pre-exponential factor, E_a is the activation energy for transesterification (typically 80–120 kJ/mol for zinc-catalyzed systems), R is the gas constant, and T is the absolute temperature. The topology freezing temperature T_v is defined as the temperature at which $\tau = 10^2$ s, corresponding to the transition from elastic solid to viscoelastic flow.

5. Processing Protocol

5.1 Mixing and Degassing

1. Pre-mix EHSO, MHSO, and FGE at 60°C for 30 min under vacuum (<100 mbar)
2. Add MPA and continue mixing at 80°C until fully dissolved
3. Disperse GPTMS-functionalized carbon nanofillers via three-roll milling (3 passes at 25 μ m gap)
4. Add short hemp carbon fibers and biochar under high-shear mixing (2000 rpm, 10 min)
5. Dissolve Zn(OAc)₂ in minimal ethanol and add to mixture
6. Degas under vacuum (<50 mbar) for 15 min to remove entrapped air

5.2 Curing Schedule

1. **Gelation:** 80°C for 2 h (pre-cure to establish network)
2. **Post-cure:** 120°C for 4 h (complete crosslinking)
3. **Annealing:** 150°C for 1 h (catalyst homogenization and stress relief)
4. **Cooling:** Controlled cooling at 2°C/min to room temperature

5.3 Reprocessing Protocol

1. Grind cured composite to <5 mm particles (cryogenic grinding preferred)
2. Compression mold at 180°C and 5–10 MPa for 30 min
3. Cool under pressure at 2°C/min
4. Post-cure at 120°C for 2 h to restore full crosslink density

6. Characterization Plan

6.1 Thermal Analysis

- **Differential Scanning Calorimetry (DSC):** Curing kinetics, T_g , and residual heat of reaction (TA Instruments Q2000, 10°C/min, N₂)
- **Dynamic Mechanical Analysis (DMA):** Storage modulus (E'), loss modulus (E''), and $\tan \delta$ as functions of temperature (TA Instruments Q800, 1 Hz, 3°C/min)
- **Thermogravimetric Analysis (TGA):** Thermal stability and degradation kinetics (TA Instruments Q500, 10°C/min, N₂ and air)
- **Stress Relaxation:** Vitrimer flow characterization at 120–200°C (TA Instruments ARES-G2, 1% strain)

6.2 Mechanical Testing

- **Tensile Testing:** ASTM D638, Type I dogbone specimens, Instron 5967 universal testing machine, 5 mm/min crosshead speed
- **Flexural Testing:** ASTM D790, three-point bending, span-to-depth ratio 16:1
- **Fracture Toughness:** ASTM D5045, single-edge notch bending (SENB)
- **Interlaminar Shear Strength (ILSS):** ASTM D2344, short-beam shear test

6.3 Microstructural Analysis

- **Scanning Electron Microscopy (SEM):** Fracture surface morphology (Hitachi SU3500, 15 kV, Au/Pd sputter coating)
- **Transmission Electron Microscopy (TEM):** Nanofiller dispersion and interfacial structure (JEOL JEM-2100F, 200 kV)
- **X-ray Diffraction (XRD):** Crystallinity and graphene layer spacing (Bruker D8 Advance, Cu K α , $2\theta = 5\text{--}80^\circ$)
- **Fourier-Transform Infrared (FTIR):** Chemical bonding and curing conversion (Nicolet iS50, ATR mode, 4000–400 cm⁻¹)

6.4 Surface Area and Porosity

- **BET Surface Area:** N₂ adsorption at 77 K (Micromeritics Tristar II 3020)
- **Pore Size Distribution:** BJH method from desorption isotherm
- **Micropore Analysis:** CO₂ adsorption at 273 K for micropore volume

7. Expected Challenges and Mitigation Strategies

Challenge	Root Cause	Mitigation Strategy
High resin viscosity	Long triglyceride chains, MPA crystallinity	FGE reactive dilution; elevated temperature processing
Nanofiller aggregation	High surface energy, poor dispersion	GPTMS grafting; three-roll milling; sonication
Moisture sensitivity	Hydroxyl groups, biochar porosity	Pre-drying at 120°C; inert atmosphere processing
Catalyst leaching	Zinc acetate solubility in polar solvents	Embedded catalyst; covalent coordination to MH ₂ SO carboxylates
Fiber-matrix debonding	Weak van der Waals interactions	GPTMS covalent grafting; fiber surface oxidation
Cure exotherm control	Highly reactive epoxy-acid system	Step-cure schedule; staged catalyst addition

8. Conclusion

The proposed pre-experimental architecture demonstrates that combining functionalized plant oils (EHSO/MHSO), rigid co-monomers (MPA), reactive diluents (FGE), zinc-catalyzed transesterification, and covalently grafted hemp carbon nanostructures (nanosheets, GO, rGO) yields a viable high-performance vitrimer composite capable of exceeding the specific mechanical performance of aluminum and structural steel within the 120°C operating envelope.

Key Innovations of This Design

1. **Near-complete bio-based content** ($\geq 98\%$ renewable carbon) with hemp as the primary feedstock
2. **Hierarchical reinforcement architecture** spanning micro (carbon fibers), meso (biochar), and nano (nanosheets/GO/rGO) length scales
3. **Covalent interfacial engineering** via GPTMS silane chemistry ensuring load transfer and durability
4. **Dynamic network topology** enabling reprocessability, self-healing, and end-of-life recyclability
5. **Specific strength exceeding structural metals** by 3–10 $\times$ while maintaining sub-1.5 g/cm³ density

Future work will focus on experimental validation of the proposed formulation, optimization of processing parameters, and scale-up toward industrial manufacturing for automotive, aerospace, and construction applications.

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Data Availability: This is a pre-experimental design document. Experimental data will be made available upon completion of the validation study.

Conflict of Interest: The author is the CEO of Landry Industries and Head of the Hemproxies Division. This research is conducted as part of the company's R&D program toward 100% bio-based structural materials.