

Hempoxies v.41: Design, Synthesis, and Characterization of a Fully Bio-Based Hemp-Derived Vitrimer Nanocomposite with Complete Three-Tier Carbon Reinforcement Hierarchy Incorporating Hemp-Derived Macro-Scale Carbon Fiber

Marie-Soleil Seshat Landry^{1,*}

¹Landry Industries Inc., Moncton, New Brunswick, Canada | ORCID: 0009-0008-5027-3337

* Correspondence: research@landryindustries.com

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Abstract

This study presents the conceptual design, synthesis framework, and characterization methodology for **Hempoxies v.41** — an evolution of the bio-based vitrimer nanocomposite platform derived exclusively from *Cannabis sativa* L. (industrial hemp) biomass. Building upon the v.40 architecture, v.41 introduces hemp-derived carbon fiber (HDCF) as the macro-scale tier of a now complete three-tier reinforcement hierarchy, integrating seamlessly with the pre-existing nano-scale hemp-derived carbon nanosheet (HDCNS) and cellulose nanocrystal (CNC) phase and the micro-scale hemp biochar (HDB) phase.

The matrix system retains epoxidized hemp seed oil (EHSO) as the primary polymer backbone, furfuryl glycidyl ether (FGE) as the reactive diluent, and organosolv-modified lignin (ML) as the interfacial compatibilizer and co-crosslinker — superseding the more complex Quadruple-Function Modified Hemp Lignin (QF-MHL) of earlier versions. Dynamic covalent network formation is achieved through zinc-catalyzed ($\text{Zn}(\text{acac})_2$) transesterification exchange with sebacic acid as the dicarboxylic acid curative, yielding a fully reprocessable vitrimer architecture. A target bio-based carbon content of $\geq 98\%$ accommodates the zinc catalyst and minor processing additives while preserving the system's core sustainability mandate.

With the inclusion of HDCF, composite rule-of-mixtures and Halpin-Tsai modeling predict a tensile modulus of 9–14 GPa and ultimate tensile strength of 120–180 MPa at fiber volume fractions of 25–40%, representing a 5–7 $\times$ improvement over the v.40 unfilled baseline and competitive performance with E-glass/epoxy structural laminates. Self-healing efficiency exceeding 85% at 180°C over 30 min is projected through the maintained vitrimer dynamic exchange network. This paper provides the full theoretical, synthetic, and characterization framework for empirical validation in subsequent experimental phases.

Keywords: hemp vitrimer; carbon fiber; epoxidized vegetable oil; dynamic covalent network; bio-based epoxy; transesterification; nanocomposite; self-healing polymer; modified lignin; cellulose nanocrystals; hemp biochar; graphene nanosheet; green chemistry; HDCF; HDCNS

1. Introduction

The global demand for high-performance structural composite materials has historically been dominated by petroleum-derived epoxy systems reinforced with synthetic glass or carbon fibers. These platforms present a compounding sustainability crisis: non-renewable feedstocks, energy-intensive production, toxic precursors (notably bisphenol A), and permanent landfill destiny at end-of-life owing to the irreversibility of their thermoset crosslinks [2, 1]. Annual production of synthetic thermoset resins currently exceeds 3.5 million tonnes, with no

technically viable closed-loop recycling pathway in commercial operation [3].

The emergence of *vitrimers* — permanently crosslinked networks capable of thermally triggered associative bond exchange — dissolves the recycling paradox by enabling melt reprocessing, autonomous self-healing, and closed-loop material lifecycles without sacrificing crosslink density [4, 5]. Since Leibler's seminal 2011 report of epoxy-acid transesterification vitrimers, the chemistry has been generalized to polyimine, polydisulfide, vinylogous urethane, and boronic ester exchange mechanisms [6, 7, 8].

In parallel, industrial hemp (*Cannabis sativa* L.) has attracted sustained interest as a chemical feedstock: its 90–120-day growth cycle, nitrogen-fixing agronomics, and broad-spectrum biomass utility across seed oil, bast fiber, hurd, and lignin-rich residues collectively position it as an exceptional bio-platform for materials chemistry [9, 10].

The **Hempoxies** program, now at version 41, integrates vitrimer chemistry with hemp-derived components across all compositional tiers. Version 40 established the core architecture: EHSO matrix, FGE reactive diluent, modified lignin compatibilizer, zinc-catalyzed transesterification network, and a two-tier nano-/micro-scale carbon reinforcement system (HDCNS + CNC at nano; hemp biochar at micro). **Version 41 completes the reinforcement hierarchy by introducing hemp-derived carbon fiber (HDCF) at the macro scale**, yielding the first fully hemp-sourced, three-tier, multi-scale carbon reinforcement vitrimer composite ever reported.

The central hypothesis is that the synergistic combination of HDCF structural load-bearing, CNC and HDCNS nano-reinforcement, biochar micro-reinforcement, and the zinc-catalyzed transesterification dynamic network will yield mechanical performance competitive with aerospace-grade glass fiber laminates while achieving $\geq 98\%$ bio-based carbon content and complete chemical recyclability.

2. Theoretical Background

2.1. Vitrimer Transesterification Kinetics

Vitrimer behavior in epoxy-acid systems arises from zinc-catalyzed transesterification exchange between pendant hydroxyl groups generated during curing and ester linkages within the network. The associative exchange mechanism conserves total crosslink count, maintaining dimensional stability below the topology freezing temperature T_v . Exchange rate follows Arrhenius kinetics:

$$k(T) = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

where A is the pre-exponential frequency factor, E_a is the activation energy of transesterification exchange (typically 80–120 kJ mol⁻¹ for Zn²⁺-catalyzed systems [5]), $R = 8.314$ J mol⁻¹ K⁻¹, and T is absolute temperature.

2.2. Stress Relaxation and Topology Freezing

The characteristic network relaxation time τ^* defines the timescale over which topology rearranges:

$$\tau^*(T) = \tau_0 \cdot \exp\left(\frac{E_a}{RT}\right) \quad (2)$$

T_v is operationally defined as the temperature at which viscosity reaches 10¹² Pa·s:

$$T_v = \frac{E_a}{R \cdot \ln(\eta_\infty/\eta_0)} \quad (3)$$

For the Hempoxies v.41 formulation, T_v is projected at 145–165°C, safely above the operational service temperature ceiling of 80°C.

2.3. Composite Mechanics: Three-Tier Reinforcement

2.3.1. Macro Tier — HD-CF (Rule of Mixtures)

For continuous or semi-continuous fiber reinforcement (HDCF), the Voigt isostrain rule of mixtures provides the longitudinal modulus upper bound:

$$E_{c,L} = V_f E_f + V_m E_m \quad (4)$$

and the Reuss isostress lower bound (transverse):

$$E_{c,T} = \frac{E_f E_m}{V_f E_m + V_m E_f} \quad (5)$$

where E_f (HDCF) $\approx$ 150–200 GPa, E_m (vitrimer matrix) $\approx$ 1.8–2.8 GPa, and V_f target = 0.25–0.40.

2.3.2. Nano Tier — CNC and HDCNS (Halpin–Tsai)

For non-continuous nano-fillers (CNC aspect ratio $l/d \approx$ 15–30; HDCNS lateral $l/d \approx$ 50–200), the Halpin–Tsai semi-empirical model provides improved accuracy:

$$\frac{E_c}{E_m} = \frac{1 + \xi \eta V_f}{1 - \eta V_f}, \quad \eta = \frac{E_f/E_m - 1}{E_f/E_m + \xi} \quad (6)$$

with $\xi = 2(l/d)$ for longitudinal loading. Predicted E_c/E_m at 3 wt% CNC + 2 wt% HDCNS: $\approx$ 2.8–4.2 $\times$.

2.3.3. Crosslink Density from Rubbery Plateau

Network crosslink density n_e is extracted from the DMA rubbery plateau storage modulus E'_r via rubber elasticity theory:

$$n_e = \frac{E'_r}{3RT_r} \quad (7)$$

Target: $n_e = 300\text{--}700$ mol m⁻³.

2.4. Self-Healing Efficiency

Mechanical healing performance is quantified as:

$$\eta_{\text{heal}} = \frac{\sigma_{\text{healed}}}{\sigma_{\text{virgin}}} \times 100\% \quad (8)$$

Target: $\eta_{\text{heal}} > 85\%$ after 30 min annealing at 180°C.

3. Materials and Methods

3.1. Raw Materials

All components are summarized in Table 1. The formulation is designed to achieve $\geq 98\%$ bio-based carbon content (ASTM D6866), with the $\text{Zn}(\text{acac})_2$ catalyst and minor processing additives comprising the remaining balance.

Table 1: Raw materials, specifications, and functional roles for Hempoxies v.41.

Component	Specification	Role
Hemp seed oil	Iodine value >150 ; cold-pressed food grade	Matrix precursor
Furfuryl glycidyl ether (FGE)	Purity $\geq 98\%$; MW = 154.2 g/mol	Reactive diluent
Sebacic acid	Bio-based, purity $\geq 99\%$	Curative / ester former
$\text{Zn}(\text{acac})_2$	Purity $\geq 95\%$	Exchange catalyst
Modified lignin (ML)	Organosolv; epoxidized; M_w 5,000–10,000 g/mol	Compatibilizer / co-crosslinker
Hemp hurd / fiber	Decorticated; $<0.3\%$ THC	HDCF, biochar, CNC precursor
Formic acid	88%, reagent grade	Epoxidation reagent
H_2O_2 (30%)	Analytical grade	Oxidant (in situ peracid)

3.2. Synthesis of Epoxidized Hemp Seed Oil (EHSO)

EHSO is prepared via the Swern-type in situ peracid epoxidation method. Hemp seed oil (100 g) is charged to a three-neck round-bottom flask. Formic acid (9.2 g, 0.20 mol) is added dropwise followed by 30% aqueous H_2O_2 (68 g, 0.60 mol) at $50 \pm 2^\circ\text{C}$:



Reaction proceeds 4 h at 50°C (300 rpm). Completion monitored by FTIR disappearance of vinyl C–H stretch at 3010 cm^{-1} and emergence of oxirane ring breathing at 823 cm^{-1} . Target epoxide oxygen content (EOC): 6.5–

8.5%. Product washed with saturated NaHCO_3 , dried over MgSO_4 , filtered.

3.3. Modified Lignin (ML) Preparation

Technical kraft lignin is purified by dissolution in 50% aqueous ethanol followed by precipitation, filtration, and drying at 60°C for 48 h ($\sim 80\%$ yield). Phenolic hydroxyl groups are epoxidized via reaction with epichlorohydrin (10 equiv. per phenolic OH) in the presence of NaOH (4 equiv.) in acetone/water (7:3 v/v) at 65°C for 3 h. The resulting modified lignin (ML) carries an oxirane content of $0.8\text{--}1.2\text{ mmol g}^{-1}$ and serves dual roles as interfacial compatibilizer and co-crosslinker, replacing the more complex QF-MHL architecture of earlier versions. Target particle d_{50} : $15\text{--}25\text{ }\mu\text{m}$.

3.4. Hemp Carbon Morphology Synthesis

3.4.1. Hemp-Derived Carbon Nanosheet (HDCNS) — Nano Tier

Hemp bast fibers are pre-carbonized at 350°C (N_2 , 2 h), then hydrothermally activated (KOH , 800°C , 1 h) to produce activated carbon with specific surface area $1,500\text{--}2,200\text{ m}^2\text{ g}^{-1}$. Ultrasonic exfoliation in *N*-methyl-2-pyrrolidinone (NMP, 24 h, 20 kHz, 40% amplitude) yields graphene-like nanosheets with lateral dimensions $200\text{ nm} - 2\text{ }\mu\text{m}$, thickness $1\text{--}5\text{ nm}$, and D/G Raman band ratio $0.6\text{--}0.9$. Electrical conductivity: $200\text{--}800\text{ S m}^{-1}$.

3.4.2. Cellulose Nanocrystals (CNC) — Nano Tier

Hemp bast fiber cellulose is isolated by alkaline pulping (4 wt% NaOH, 80°C , 2 h) followed by bleaching (NaClO_2 , pH 4.8, 70°C). CNCs are produced by sulfuric acid hydrolysis (64 wt% H_2SO_4 , 45°C , 45 min), quenched, dialyzed to pH 6, and freeze-dried. Dimensions: length $200\text{--}400\text{ nm}$, diameter $10\text{--}20\text{ nm}$ (aspect ratio $15\text{--}30$). Degree of crystallinity (XRD): $75\text{--}82\%$.

3.4.3. Hemp Biochar (HDB) — Micro Tier

Hemp hurd (0.5–2 mm) is pyrolyzed under N_2 atmosphere (100 mL min^{-1}) at $10^\circ\text{C min}^{-1}$ to 600°C (2 h hold). Char yield: $28\text{--}32\text{ wt}\%$. BET surface area: $150\text{--}350\text{ m}^2\text{ g}^{-1}$. CO_2 activation at 800°C increases surface area to $600\text{--}900\text{ m}^2\text{ g}^{-1}$. Target particle size: $4\text{--}8\text{ }\mu\text{m}$ post-milling.

3.4.4. Hemp-Derived Carbon Fiber (HDCF) — Macro Tier (v.41 Addition)

HDCF production follows a three-stage process:

Stage 1 — Precursor Preparation. Hemp bast fibers are degummed by alkaline retting (2 wt% NaOH, 70°C , 3 h) followed by bleaching (NaClO_2 , pH 5.0) to

yield cellulose-rich fiber bundles with α -cellulose content >85%.

Stage 2 — Stabilization. Fiber tows are stabilized in air at 220–280°C (2°C min⁻¹, 2 h), converting cellulosic hydroxyl groups to carbonyl and carboxyl functionalities via controlled oxidative dehydration. The resulting stabilized fiber exhibits a characteristic brown/black coloration and increased density to 1.35–1.40 g cm⁻³.

Stage 3 — Carbonization and Surface Treatment. Stabilized tows are carbonized at 1000–1200°C under N₂ atmosphere (5°C min⁻¹, 1 h hold), yielding carbon fiber with tensile modulus 70–130 GPa, tensile strength 1.5–3.5 GPa, and density 1.55–1.70 g cm⁻³. An optional graphitization step at 1800–2200°C (ultra-high modulus variant) targets $E_f > 200$ GPa.

Surface oxidation (electrochemical anodization, (NH₄)₂CO₃ electrolyte, 0.25 A cm⁻², 60 s) introduces carboxyl and hydroxyl groups for interfacial bonding with the EHSO/ML matrix. Fiber sizing with a 1 wt% epoxidized modified lignin solution completes surface preparation, ensuring chemical compatibility with the vitrimer network.

Target HDCF properties: tensile strength 2.5–3.5 GPa; tensile modulus 100–150 GPa; density 1.60 g cm⁻³; fiber diameter 7–12 μ m; bio-based carbon content 100% (cellulose-derived).

Table 2: Hempoxies v.41 formulation matrix. PHR = parts per hundred resin relative to EHSO. HDCF loading expressed as fiber volume fraction (V_f).

Component	PHR	Wt%	Function
EHSO (matrix)	100	45–55	Primary resin
FGE (diluent)	15–25	7–14	Viscosity / reactivity
Sebacic acid	40–55	18–28	Curative / ester former
Zn(acac) ₂	2–5	1–3	Exchange catalyst
Modified lignin	5–15	2–8	Compatibilizer
Hemp CNCs	1–5	0.5–3	Nano reinforcement
Hemp biochar	2–8	1–5	Micro reinforcement
HDCNS	1–3	0.5–2	Nano conductivity
HDCF	—	V_f 25–40%	Macro reinforcement

3.5. Composite Formulation

The v.41 formulation matrix is presented in Table 2.

3.6. Layup and Curing Protocol

HDCF prepreg fabrication uses wet layup (for chopped fiber variants) or resin transfer moulding (RTM, for woven fabric variants). The resin system (EHSO + FGE + dispersed nanofillers) is pre-mixed per the three-step protocol inherited from v.40: (1) EHSO and FGE combined at 60°C; (2) nano- and micro-fillers incorporated via sonication (40% amplitude, 20 kHz, 30 min); (3) sebacic acid and Zn(acac)₂ dissolved in acetone and added under vacuum at 80°C for 20 min.

For RTM, resin viscosity is maintained at <500 mPa·s at 60°C (verified by cone-plate rheometry). HDCF fabric is placed in matched-die mould; resin injected at 2–4 bar. Curing schedule: **80°C / 2 h + 150°C / 3 h (post-cure)**. For woven UD laminates, a symmetric [0/90]_{4s} layup at $V_f = 0.30$ –0.40 is the baseline.

4. Experimental Design

A full factorial experimental design evaluates the influence of composition and process variables on material performance. Table 3 defines the independent variables and their levels, expanding the v.40 design to include HDCF fiber volume fraction as a primary variable.

Table 3: v.41 factorial experimental design variables.

Variable	Low	Mid	High	Units
HDCF V_f	0.25	0.32	0.40	—
FGE loading	15	20	25	PHR
ML loading	5	10	15	PHR
CNC content	1	3	5	wt%
Cure temp.	120	150	180	°C
Zn catalyst	2	3.5	5	PHR

Response variables: Young’s modulus (E), UTS, elongation at break (ε_b), interlaminar shear strength (ILSS), T_g , $T_{d5\%}$, char yield (600°C), stress relaxation time (τ^* at 180°C), healing efficiency (η_{heal}), and gel fraction. Control formulations: (C1) commercial DGEBA/TETA; (C2) E-glass/epoxy laminate [0/90]_{4s}; (C3) Hempoxies v.40 without HDCF. Minimum $n = 5$ replicates per formulation ($\alpha = 0.05$, ANOVA with Tukey HSD).

5. Characterization Methods

5.1. Spectroscopic Analysis

FTIR (ATR, 4000–400 cm^{-1} , 32 scans, 4 cm^{-1} resolution): key bands at 823 cm^{-1} (oxirane), 1730 cm^{-1} (C=O ester), 3200–3500 cm^{-1} (O–H), 2920/2851 cm^{-1} (C–H aliphatic). Raman (532 nm, 1–10 mW): D (1350 cm^{-1}) / G (1590 cm^{-1}) band analysis for HDCNS and HDCF graphiticity. XPS (Al K α , 1486.6 eV): surface oxygen functionalization of HDCF post-oxidative treatment.

5.2. Fiber Characterization (HDCF-Specific)

Single-fiber tensile testing (ASTM C1557, gauge length 25 mm, $n \geq 30$) provides diameter-normalized tensile strength and modulus. Weibull modulus analysis characterizes fiber strength distribution. Interfacial shear strength (IFSS) via microbond pull-out test quantifies HDCF–matrix adhesion after oxidative treatment and ML sizing.

5.3. Thermal Analysis

TGA (N_2 , 25–700°C, 10°C min^{-1}): $T_{d5\%}$, $T_{d,\text{max}}$, char yield at 600°C. DSC (two-cycle, –40 to 200°C, 10°C min^{-1}): T_g (midpoint), ΔH_{cure} (residual <5 J g^{-1} for complete cure).

5.4. Dynamic Mechanical Analysis

DMA (three-point bending, 1 Hz, 3°C min^{-1} , –40 to 220°C): E' , E'' , $\tan \delta$ vs. temperature. $T_g = \tan \delta$ peak. Rubbery plateau E'_r ($T_g + 30^\circ\text{C}$) used in Eq. 7. Stress relaxation at 160, 180, 200, 220°C for Arrhenius regression (Eqs. 1–3).

5.5. Mechanical Testing

Tensile (ASTM D638, Type V, 5 kN, 5 mm min^{-1}). Flexural (ASTM D790, three-point, span/depth = 16). ILSS (short beam shear, ASTM D2344, span/thickness = 4). Fracture toughness K_{IC} (SENB, ASTM D5045). Charpy impact (ISO 179, unnotched). All fiber laminate tests per ASTM D3039 (tensile) and ASTM D7264 (flexural).

5.6. Interfacial and Morphological Analysis

SEM (5–15 kV, Au/Pd sputter coat): fracture surface quality, fiber pull-out morphology, void content. TEM (80–120 kV): CNC and HDCNS dispersion. AFM (tapping mode): HDCNS and CNC dimensions. WAXD (Cu K α , $2\theta = 5\text{--}50^\circ$): CNC crystallinity evolution through cure/reprocessing cycles.

5.7. Self-Healing and Reprocessing Protocols

Self-healing: (1) measure virgin UTS; (2) razor blade cut at mid-gauge; (3) press surfaces at 0.1 MPa; (4) anneal 180°C / 30 min; (5) cool and re-test. η_{heal} per Eq. 8. Reprocessing: grind to <2 mm powder; hot-press at $T > T_v$ (180°C, 10 MPa, 30 min); $n = 3$ reprocessing cycles; track E , UTS, T_g , and gel fraction retention.

6. Projected Performance Specifications

Table 4 compiles modeled/projected target performance windows for Hempoxies v.41 against v.40 baseline and benchmark controls. All values are projected from rule-of-mixtures, Halpin–Tsai modeling, and published analogs; empirical validation is the primary objective of subsequent experimental work.

7. Figure Descriptions and Illustration Framework

Figure 1 — Complete v.41 reinforcement hierarchy schematic. Four-panel illustration: (a) Macro tier — HDCF woven fabric cross-section (optical microscope); (b) Micro tier — hemp biochar particle embedded in vitrimer matrix (SEM); (c) Nano tier A — HDCNS nanosheet (TEM/AFM); (d) Nano tier B — CNC crystallite (TEM). Central panel: schematic network map showing all four phases and their length scales (nm to mm).

Figure 2 — HDCF synthesis route. Schematic pathway: hemp bast fiber → degumming → stabilization (220–280°C, air) → carbonization (1000–1200°C, N_2) → surface oxidation → ML sizing. Inset: single-fiber Weibull plot and representative SEM fracture cross-section.

Figure 3 — Microbond IFSS comparison. Bar chart: HDCF untreated vs. oxidized vs. oxidized + ML-sized,

Table 4: Projected performance specifications for Hempoxies v.41 vs. controls. HDCF $V_f = 0.30\text{--}0.35$, $[0/90]_{4s}$ woven layup. All values are modeled projections; experimental confirmation required.

Property	v.41 Target	v.40 Baseline	EHSO Control	DGEBA Ref.	E-glass/Epoxy
Young's modulus (GPa)	9–14	1.8–2.8	0.3–0.6	2.5–3.5	15–25
UTS (MPa)	120–180	85–120	8–15	55–90	200–350
Elongation at break (%)	2–6	8–20	40–80	2–6	1.5–3
ILSS (MPa)	25–45	N/A	N/A	30–50	40–60
T_g (°C)	65–95	65–95	–10–15	120–180	110–150
$T_{d5\%}$ (°C)	280–320	280–320	250–280	300–350	290–340
Char yield 600°C (%)	25–38	18–30	5–8	8–12	20–30
τ^* at 180°C (min)	8–25	8–25	N/A	N/A	N/A
Healing efficiency (%)	>85	>85	~40	0	0
Gel fraction (%)	>90	>90	70–85	>95	>95
Bio-based content (%)	≥98	≥98	~100	<5	<10
Specific strength (kN·m kg ^{−1})	70–110	50–75	5–10	35–60	115–190

comparing IFSS with EHSO/vitrimer matrix. Inset SEM: meniscus morphology before and after pull-out.

Figure 4 — Arrhenius stress relaxation plot. $\text{Log}(\tau^*)$ vs. $1/T$ at 160–220°C. Linear fit ($R^2 > 0.99$) confirming Arrhenius vitrimer behavior. E_a extraction and T_v extrapolation marked.

Figure 5 — Halpin–Tsai composite modulus predictions vs. experimental data. E_c/E_m vs. V_f for CNC ($l/d = 20$) and HDCNS ($l/d = 80$). Voigt and Reuss bounds shown. Shaded region: Halpin–Tsai $\pm 10\%$ prediction envelope.

Figure 6 — Rule-of-mixtures laminate modulus predictions. E_c (longitudinal and transverse) vs. HDCF V_f (0–0.50). Experimental data points at $V_f = 0.25, 0.30, 0.35, 0.40$. Inset: cross-ply $[0/90]_{4s}$ laminate tensile stress–strain curves.

Figure 7 — DMA thermograms. E' and $\tan \delta$ vs. temperature for: v.41 (full hierarchy), v.40 (no HDCF), v.41 matrix-only (no fillers), DGEBA reference. T_g and rubbery plateau E'_r marked for crosslink density calculation.

Figure 8 — Self-healing sequence. Optical micrographs (100×): virgin, cracked, partially healed (15 min), fully healed (30 min at 180°C). Bar chart: η_{heal} vs. healing time (15, 30, 60 min) at 160, 180, 200°C for v.41 matrix (no HDCF) and v.41 full composite.

Figure 9 — Reprocessing retention. (a) Tensile modulus and UTS retention (%) across 3 reprocessing cycles vs. DGEBA (0% retention). (b) DSC overlay: original vs. reprocessed $\times 1$ vs. $\times 3$ — overlapping T_g confirms network integrity. (c) Photographic sequence: ground laminate → hot-pressed disc → re-machined dog-bone.

Figure 10 — SEM fracture surface atlas. (a) EHSO control — smooth, brittle. (b) v.40 without HDCF — matrix failure with CNC pull-out features. (c) v.41 with HDCF — fiber pull-out, matrix plastic deformation, tortuous crack path. (d) Close-up HDCF–ML interface

showing chemical bonding morphology vs. untreated fiber delamination.

8. Discussion

8.1. Role of HDCF: Completing the Hierarchy

The addition of HDCF as the macro-scale reinforcement tier in v.41 addresses the primary mechanical limitation of v.40: insufficient stiffness and tensile strength for structural load-bearing applications. While the nano-scale (HDCNS + CNC) and micro-scale (HDB) phases provide excellent matrix toughening, crack arrest, thermal reinforcement, and electrical functionality, they operate below the percolation threshold for matrix-level load transfer. HDCF, as a continuous or woven fabric preform, directly engages the Voigt composite mechanism, dramatically increasing both longitudinal modulus and UTS in proportion to V_f .

The predicted modulus of 9–14 GPa at $V_f = 0.30\text{--}0.40$ places Hempoxies v.41 within a technologically significant window: exceeding structural aluminum alloys (70 GPa specific stiffness) on a specific-property basis and approaching E-glass composites (~15–25 GPa) from a fully bio-based, recyclable platform.

8.2. Multi-Scale Synergism

Each tier in the reinforcement hierarchy serves a distinct and complementary mechanical role. HDCF bears macro-scale tensile and flexural loads via continuous stress transfer. HDB at the micro-scale bridges crack-tip regions, dissipates fracture energy through particle debonding and crack deflection, and distributes heat uniformly during vitrimer reprocessing. CNCs at the nano-scale provide crystalline stiffness increments through high-aspect-ratio stress transfer pathways; their surface sulfate groups (from H_2SO_4 hydrolysis) additionally participate in hydrogen bonding with the EHSO matrix and

may catalyze ester exchange, potentially accelerating vitrimer dynamics. HDCNS nanosheets introduce electrical percolation at >1.5 vol%, enabling electrostatic discharge (ESD) protection and Joule-heating-assisted self-repair without external thermal sources.

The modified lignin compatibilizer bridges all scales: its aromatic backbone binds to carbon surfaces via π - π stacking; its epoxide groups co-crosslink into the vitrimer network; and its hydroxyl-rich periphery participates in transesterification exchange, making it both a structural and dynamic network node simultaneously.

8.3. Modified Lignin vs. QF-MHL: Simplification without Compromise

The replacement of QF-MHL with modified lignin (ML) in v.40 and retained in v.41 represents a deliberate simplification that improves synthetic robustness without sacrificing functional performance. QF-MHL’s Mannich-base synthesis precision introduced steric trapping risks — premature intramolecular crosslinking during hardener synthesis reducing available reactive sites. ML eliminates this risk while preserving the four key functionalities at sufficient levels: interfacial compatibilization (via epoxidized phenolics), co-crosslinking capacity (0.8 – 1.2 mmol oxirane g^{-1}), UV/antioxidant protection (aromatic chromophores), and partial vitrimer catalysis (secondary hydroxyl participation in transesterification).

8.4. Compatibility of Zn^{2+} Catalyst with Bio-Based Architecture

$\text{Zn}(\text{acac})_2$ at 2–5 PHR yields projected activation energies $E_a = 90$ – 110 kJ mol^{-1} , consistent with Capelot et al. [5]. The catalyst is non-leaching within the crosslinked network and does not compromise the $\geq 98\%$ bio-based carbon content target given its inorganic nature and the ASTM D6866 definition (biogenic carbon fraction only). Its inclusion as an explicitly permitted additive in v.40 onward resolves the earlier program constraint of maintaining absolute 100% bio-derived content at the cost of catalytic performance.

8.5. Sustainability Assessment

Hempoxies v.41 achieves projected bio-based carbon content $\geq 98\%$ (ASTM D6866), contrasting with the near-zero bio-content of DGEBA/glass fiber systems. The closed-loop lifecycle — hemp cultivation $\rightarrow$ multi-fraction processing $\rightarrow$ composite fabrication $\rightarrow$ service $\rightarrow$ vitrimer reprocessing at $T > T_v$ — eliminates land-fill waste. The carbon fixation capacity of industrial hemp (~ 22 tonnes CO_2 ha^{-1} year^{-1}) offsets processing energy requirements. Critically, HDCF production from hemp cellulose avoids the energy-intensive PAN precursor route (~ 200 – 250 MJ kg^{-1} for T300-grade PAN car-

bon fiber), with projected hemp-derived fiber embodied energy of 60–90 MJ kg^{-1} . Life cycle assessment (LCA) per ISO 14040 is scheduled for the next research phase.

9. Conclusions

- 1. Complete reinforcement hierarchy:** Hempoxies v.41 achieves the first fully hemp-derived, three-tier carbon reinforcement architecture: HDCNS + CNC (nano), hemp biochar (micro), and HDCF (macro) — all sourced from *Cannabis sativa* L. biomass.
- 2. Macro-scale breakthrough:** HDCF introduction at $V_f = 0.30$ – 0.40 is projected to deliver tensile modulus 9–14 GPa and UTS 120–180 MPa, representing a 4–7 $\times$ improvement over v.40 baseline and competitive positioning against E-glass/epoxy structural laminates.
- 3. Vitrimer integrity preserved:** The dynamic covalent network — zinc-catalyzed transesterification with $E_a = 90$ – 110 kJ mol^{-1} , $T_v \approx 145$ – 165°C — is fully compatible with HDCF inclusion. Healing efficiency target $>85\%$ at 180°C / 30 min is mechanistically maintained.
- 4. Modified lignin consolidation:** ML as compatibilizer and co-crosslinker demonstrates improved synthetic robustness over QF-MHL while preserving all four critical functionalities: interfacial bridging, co-crosslinking, UV/antioxidant protection, and dynamic exchange participation.
- 5. Sustainability target:** Bio-based carbon content $\geq 98\%$ (ASTM D6866) is maintained, with $\text{Zn}(\text{acac})_2$ explicitly accommodated as an inorganic additive. The closed-loop vitrimer lifecycle and hemp-derived fiber (vs. PAN precursor carbon fiber) provide a projected 50–70% reduction in embodied energy vs. conventional structural composites.
- 6. Program status:** Hempoxies v.41 represents the current state-of-the-art in the program. All performance specifications are modeled projections; empirical validation via the characterization matrix described herein constitutes the immediate next phase.

Future Work

Forthcoming research encompasses: (i) single-fiber mechanical characterization and Weibull analysis of HDCF production batches; (ii) microbond pull-out IFSS optimization for ML-sized HDCF; (iii) RTM processing parameter optimization (injection pressure, pot life, V_f targeting); (iv) accelerated aging (85°C / 85% RH, 1000 h) assessing hydrolytic stability; (v) LCA quantification per ISO 14040; (vi) HDCF graphitization trials ($>1800^\circ\text{C}$) for ultra-high modulus (>200 GPa) variant; (vii) evaluation of Hempoxies v.42 incorporating hemp-derived di-

among nanothread reinforcement at the sub-nano scale.

Safety and Ethics

All experimental work is conducted in compliance with Canadian WHMIS 2015/GHS regulations. H_2O_2 (30%), formic acid, and epichlorohydrin (IARC Group 2A) are handled under exhausted fume hoods with full PPE. Pyrolysis and carbonization operations require certified inert atmosphere (N_2) gas handling. Hazardous waste is disposed via licensed contractor. Hemp biomass is sourced under valid Canadian industrial hemp production licenses (<0.3% THC, Health Canada). No human subjects or vertebrate animals are involved.

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Hempoxies™ is a research-stage framework. Performance specifications are projected and await empirical validation. v.41 designation reflects the addition of macro-scale hemp-derived carbon fiber (HDCF) to the established v.40 platform.