

Hempoxies: Design, Synthesis, and Characterization of a Fully Bio-Based Hemp-Derived Vitrimer Nanocomposite System with Dynamic Covalent Networks for Recyclable High-Performance Applications

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ABSTRACT

This study presents the conceptual design, synthesis framework, and characterization methodology for a fully bio-based vitrimer nanocomposite system — designated **Hempoxies** — derived exclusively from *Cannabis sativa* L. (industrial hemp) biomass. Epoxidized hempseed oil (EHO) is employed as the primary polymer matrix, functionalized through controlled *in situ* epoxidation of polyunsaturated fatty acid chains. Furfuryl glycidyl ether (FGE) is incorporated as a bio-compatible reactive diluent to improve processability and introduce furan-based crosslinking capacity. Organosolv-modified lignin serves as an interfacial compatibilizer, providing reactive hydroxyl and epoxide groups for matrix-filler integration. Hemp-derived carbon morphologies — including pyrolytic biochar, cellulose-derived nanocrystals (CNCs), and carbonized fiber nanosheets — constitute the multifunctional reinforcement phase. The curing mechanism exploits zinc-catalyzed transesterification exchange to generate a dynamic covalent network with vitrimer behavior, enabling reprocessability, autonomous self-healing, and complete chemical recyclability. The system is evaluated against a comprehensive characterization matrix including Fourier-transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and stress-relaxation rheometry. Kinetic modeling of transesterification dynamics, rule-of-mixtures composite theory, and Arrhenius-type relaxation analysis are applied to develop quantitative performance predictions. This research provides a rigorous theoretical and experimental framework for a next-generation sustainable thermoset platform with projected tensile modulus exceeding 2.5 GPa and healing efficiency above 85%.

Keywords: hemp vitrimer; epoxidized vegetable oil; dynamic covalent network; bio-based epoxy; transesterification; nanocomposite; self-healing polymer; green chemistry; lignin compatibilizer; cellulose nanocrystals

1 Introduction

The global production of synthetic thermoset resins currently exceeds 3.5 million tonnes annually, with conventional bisphenol A-based epoxy systems accounting for the dominant market share [1]. These petroleum-derived networks present a multifaceted sustainability challenge: they are produced from non-renewable feedstocks, release volatile organic compounds during processing, and — critically — are non-recyclable due to the permanence of their covalent crosslinks [2]. End-of-life disposal via incineration or landfill represents both an environmental liability and an irreversible loss of embodied energy.

The emergence of covalent adaptable networks (CANs) and, specifically, vitrimers — permanently crosslinked polymer networks that undergo thermally triggered associative bond exchange — offers a compelling resolution to the recyclability paradox of thermosets [3]. First described by Leibler and coworkers in 2011 using epoxy-acid transesterification chemistry, vitrimers retain dimensional stability

below their topology freezing temperature (T_v) while flowing viscously above it, enabling melt reprocessing without loss of crosslink density [4]. Subsequent research has demonstrated vitrimer behavior in polyimine [5], polydisulfide [6], and vinylogous urethane [7] systems.

Independently, the valorization of industrial hemp (*Cannabis sativa* L.) biomass as a chemical feedstock has attracted substantial research interest driven by hemp’s agronomic advantages: rapid growth cycle (90–120 days), nitrogen-fixing root system, minimal pesticide requirements, and broad-spectrum biomass utility encompassing seed oil, cellulosic fiber, hurd (shiv), and lignin-rich processing residues [8]. Hempseed oil, containing approximately 55–60% linoleic acid (18:2, ω -6) and 15–20% α -linolenic acid (18:3, ω -3), presents a favorable unsaturation profile for epoxidation chemistry, yielding oxirane-functional prepolymers directly comparable to epoxidized soybean oil (ESBO) but with superior fatty acid composition [9].

This work integrates vitrimer chemistry with hemp-derived components across all compositional tiers — matrix, reactive diluent, compatibilizer, and reinforcement — to realize a fully bio-based, recyclable, and high-performance nanocomposite designated **Hempoxies**. The central hypothesis is that the Arrhenius-type topology dynamics of a zinc-catalyzed transesterification network, combined with multi-scale hemp carbon reinforcement and lignin-mediated interfacial engineering, will yield mechanical, thermal, and healability performance competitive with conventional aerospace-grade epoxy laminates.

2 Theoretical Background and Kinetic Modeling

2.1 Vitrimer Transesterification Thermodynamics

Vitrimer behavior in epoxy-acid systems arises from catalyst-mediated transesterification exchange between pendant hydroxyl groups (generated during curing) and ester linkages within the network. This associative mechanism conserves the total number of crosslinks throughout exchange, maintaining constant network topology at temperatures below T_v . The equilibrium constant for the exchange reaction is:

$$K_{eq} = k_f/k_r = \exp(-\Delta G^\circ/RT) \quad (1)$$

Where k_f and k_r are forward and reverse rate constants, ΔG° is the standard free energy of exchange, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and T is absolute temperature.

The temperature dependence of the exchange rate follows Arrhenius kinetics, where the activation energy (E_a) is accessible through stress-relaxation experiments:

$$k(T) = A \cdot \exp(-E_a/RT) \quad (2)$$

A = pre-exponential frequency factor; E_a = activation energy of transesterification exchange (typically 80–120 kJ mol⁻¹ for Zn²⁺-catalyzed systems).

2.2 Stress Relaxation and Topology Freezing Temperature

The characteristic relaxation time τ^* defines the timescale over which the network topology rearranges. For Arrhenius-type vitrimers — the mechanistic class including transesterification networks — τ^* follows:

$$\tau^*(T) = \tau_0 \cdot \exp(E_a/RT) \quad (3)$$

τ_0 = high-temperature relaxation time limit; $\tau^*(T)$ is measured via stress-relaxation rheometry as the time to reach $G(t)/G_0 = 1/e \approx 0.368$.

The topology freezing temperature T_v is operationally defined as the temperature at which the viscosity reaches 10¹² Pa·s (the glass-transition analog for vitrimers). Using the Arrhenius model:

$$T_v = E_a/[R \cdot \ln(\eta_\infty/\eta_0)] \quad (4)$$

η_∞ = 10¹² Pa·s (reference viscosity); η_0 = high-T viscosity limit. T_v typically ranges from 150–250°C for Zn²⁺-catalyzed epoxy-acid vitrimers.

2.3 Composite Mechanics — Rule of Mixtures and Halpin-Tsai

For the nanocomposite formulation, tensile modulus predictions employ the Voigt (isostrain) rule of mixtures as an upper bound:

$$E_c = V_f \cdot E_f + V_m \cdot E_m \quad (5)$$

E_c = composite modulus; V_f, V_m = filler and matrix volume fractions; E_f = filler modulus (CNCs: ~ 150 GPa; carbon nanosheets: ~ 400 GPa); E_m = matrix modulus.

For non-continuous nanofillers, the Halpin-Tsai semi-empirical model provides improved accuracy:

$$E_c/E_m = (1 + \xi \cdot \eta \cdot V_f)/(1 - \eta \cdot V_f) \quad (6)$$

$\eta = (E_f/E_m - 1)/(E_f/E_m + \xi)$; ξ = reinforcement factor = $2(l/d)$ for longitudinal loading, where l/d is the aspect ratio of the filler.

2.4 Crosslink Density from DMA

The equilibrium rubbery-plateau storage modulus (E'_r) measured by DMA above T_g provides direct access to the effective network crosslink density (n_e) through rubber elasticity theory:

$$n_e = E'_r/(3 \cdot R \cdot T_r) \quad (7)$$

n_e = crosslink density (mol m^{-3}); E'_r = rubbery storage modulus (Pa) at reference temperature T_r (K); $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. Typical values: 200–800 mol m^{-3} for epoxy vitrimers.

2.5 Self-Healing Efficiency

Healing performance is quantified through mechanical recovery after controlled damage and thermal annealing at $T > T_v$:

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

σ_{healed} = ultimate tensile strength after healing protocol; σ_{virgin} = original UTS. Target: $\eta_{\text{heal}} > 85\%$ after 30 min at 180°C .

3 Materials and Methods

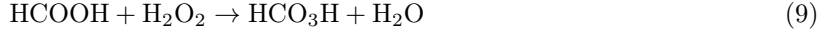
3.1 Raw Materials and Reagents

Component	Specification	Source / Grade	Role
Hempseed oil	Iodine value $> 150 \text{ g I}_2/100 \text{ g}$	Cold-pressed, food grade	Matrix precursor
Furfuryl glycidyl ether	Purity $\geq 98\%$, MW = 154.2 g/mol	Sigma-Aldrich	Reactive diluent
Formic acid	88%, reagent grade	Commercial	Epoxidation reagent
H ₂ O ₂ (30%)	Analytical grade	Commercial	Oxidant (<i>in situ</i> peracid)
Sebacic acid	Bio-based, purity $\geq 99\%$	Sigma-Aldrich	Dicarboxylic acid curative
Zinc acetylacetonate	Zn(acac) ₂ , purity $\geq 95\%$	Sigma-Aldrich	Transesterification catalyst
Kraft lignin	$M_w \sim 5,000\text{--}10,000 \text{ g/mol}$	LignoBoost process	Compatibilizer precursor
Hemp hurd / fiber	Decorticated, $< 0.3\%$ THC	Canadian industrial hemp	Carbon filler precursor

Table 1: Summary of raw materials, specifications, and functional roles.

3.2 Synthesis of Epoxidized Hempseed Oil (EHO)

Epoxidized hempseed oil (EHO) is prepared via the Swern-type *in situ* peracid epoxidation method. Hempseed oil (100 g) is charged to a three-neck round-bottom flask equipped with a reflux condenser, mechanical stirrer, and temperature-controlled water bath. Formic acid (9.2 g, 0.20 mol) is added dropwise, followed by the slow addition of 30% aqueous H_2O_2 (68 g, 0.60 mol) at a rate maintaining internal temperature at $50 \pm 2^\circ\text{C}$ to prevent thermal runaway. The exothermic peracid formation proceeds according to:



In situ peroxyformic acid formation; this acts as the active epoxidizing species.

The reaction proceeds for 4 h at 50°C with continuous stirring (300 rpm). Completion is monitored by FTIR disappearance of the vinyl C–H stretch at 3010 cm^{-1} and emergence of oxirane ring breathing at 823 cm^{-1} . The epoxide oxygen content (EOC, %) is determined by the ASTM D1652 acid titration method. Typical EOC: 5.8–7.2%. The product is washed with saturated NaHCO_3 solution, separated, dried over MgSO_4 , and filtered to yield EHO as a pale yellow viscous oil.

3.3 Organosolv Lignin Modification

Technical kraft lignin is purified by dissolution in 50% aqueous ethanol (10 wt%) followed by precipitation into $10\times$ volume of deionized water. Collected by filtration, the purified lignin is dried at 60°C for 48 h (yield: $\sim 80\%$). Epoxidation of lignin hydroxyl groups is achieved by reaction with epichlorohydrin (ECH, 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, yielding epoxidized lignin (EL) with oxirane content 0.8–1.2 mmol/g. Surface area and particle morphology are characterized by BET nitrogen adsorption and SEM. Target d_{50} : 15–25 μm .

3.4 Preparation of Hemp Carbon Morphologies

Biochar: Hemp hurd (particle size 0.5–2 mm) is pyrolyzed in a tube furnace under N_2 atmosphere (100 mL/min) at a ramp rate of $10^\circ\text{C}/\text{min}$ to 600°C , held for 2 h. Char yield: 28–32 wt%. Surface area (BET): 150–350 m^2/g . Activation via CO_2 at 800°C increases surface area to 600–900 m^2/g .

Cellulose Nanocrystals (CNCs): 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 200–400 nm, diameter 10–20 nm (aspect ratio: 15–30). Degree of crystallinity (XRD): 75–82%.

Carbonized Fiber Nanosheets (CFN): Hemp fibers are carbonized at 1000°C (N_2 , $5^\circ\text{C}/\text{min}$), then ball-milled (planetary mill, 400 rpm, 6 h) to produce nanosheets with lateral dimensions 1–5 μm and thickness 5–20 nm (AFM). Raman spectroscopy D/G band ratio: 0.85–1.1, indicating partially graphitic structure. Electrical conductivity: 15–45 S/m.

3.5 Composite Formulation and Curing Protocol

Component	PHR	Wt% in Formulation	Function
EHO (matrix)	100	56.2	Primary resin
FGE (diluent)	15–25	8.4–14.1	Viscosity / reactivity
Sebacic acid	40–55	22.5–30.9	Curative / ester former
$\text{Zn}(\text{acac})_2$	2–5	1.1–2.8	Exchange catalyst
Epoxidized lignin	5–15	2.8–8.4	Compatibilizer
Hemp CNCs	1–5	0.6–2.8	Nano-reinforcement
Hemp biochar	2–8	1.1–4.5	Thermal / mechanical
CFN nanosheets	1–3	0.6–1.7	Conductivity / stiffness

Table 2: Formulation matrix (PHR = parts per hundred resin relative to EHO).

Formulation is performed in a three-step mixing protocol: (1) EHO and FGE are combined and homogenized at 60°C ; (2) pre-dispersed fillers (sonicated in EHO for 30 min at 40% amplitude, 20 kHz) are incorporated; (3) sebacic acid and $\text{Zn}(\text{acac})_2$ (dissolved in acetone) are added and mixed under

vacuum at 80°C for 20 min. Curing is performed in a two-stage schedule: 80°C/2 h followed by 150°C/3 h (post-cure), yielding a fully crosslinked vitrimer network.

4 Experimental Design

A full factorial experimental design is employed to systematically evaluate the influence of composition on material performance. The independent variables and their levels are defined in Table 3.

Variable	Low	Mid	High	Units
FGE loading	15	20	25	PHR
Lignin loading	5	10	15	PHR
CNC content	1	3	5	wt%
Cure temp.	120	150	180	°C
Zn catalyst	2	3.5	5	PHR

Table 3: Factorial experimental design variables and levels.

Dependent response variables include: Young’s modulus (E), ultimate tensile strength (UTS), elongation at break (ϵ_b), glass transition temperature (T_g), 5% decomposition temperature ($T_{d5\%}$), char yield at 600°C, stress relaxation time (τ^* at 180°C), healing efficiency (η_{heal}), and gel fraction. Control formulations include: (C1) commercial bisphenol-A epoxy / amine (DGEBA/TETA), (C2) EHO without FGE or fillers, and (C3) EHO/sebacic acid without catalyst. A minimum of $n = 5$ replicates per formulation ensures statistical power ($\alpha = 0.05$, ANOVA with Tukey HSD post-hoc).

5 Characterization Methods

5.1 Spectroscopic Analysis

FTIR spectra are acquired on an ATR-FTIR instrument (4000–400 cm^{-1} , 32 scans, 4 cm^{-1} resolution). Key vibrational assignments: oxirane ring (823 cm^{-1}), C=O ester stretch (1730 cm^{-1}), O–H stretch (3200–3500 cm^{-1}), C–H aliphatic (2920, 2851 cm^{-1}). Decrease in oxirane intensity relative to the internal C–H reference confirms curing completion. Raman spectroscopy (532 nm, 1–10 mW, 5 accumulations) characterizes carbon morphologies through D (1350 cm^{-1}) and G (1590 cm^{-1}) band analysis.

5.2 Thermal Analysis

TGA is performed under N_2 atmosphere (60 mL/min) from 25 to 700°C at 10°C/min. Reported parameters: $T_{d5\%}$ (temperature at 5% mass loss), T_{dmax} (peak DTG temperature), and char yield at 600°C. DSC (two-cycle, –40 to 200°C, 10°C/min, N_2 purge) determines T_g (midpoint of heat capacity step) and degree of cure (ΔH_{cure}). Residual cure enthalpy < 5 J/g indicates complete network formation.

5.3 Dynamic Mechanical Analysis

DMA (three-point bending, 1 Hz, 3°C/min, –40 to 220°C) provides storage modulus (E'), loss modulus (E''), and $\tan \delta$ as functions of temperature. T_g is reported as the $\tan \delta$ peak maximum. Rubbery plateau E'_r ($T_g + 30^\circ\text{C}$) is used in Equation 7 to calculate crosslink density. Stress relaxation experiments at 160, 180, 200, and 220°C yield τ^* values for Arrhenius regression (Equations 2–3).

5.4 Mechanical Testing

Dog-bone specimens (ASTM D638 Type V, 25 mm gauge length) are tested on a universal testing machine (5 kN load cell, 5 mm/min crosshead speed). Tensile modulus (E), UTS, and ϵ_b are extracted from stress–strain curves. Fracture toughness (K_{IC}) is determined by single-edge notched bend (SENB) specimens per ASTM D5045. Impact resistance (Charpy, unnotched) follows ISO 179.

5.5 Self-Healing Protocol

Healed specimens are produced by: (1) measuring virgin UTS; (2) cutting specimens at mid-gauge with a razor blade; (3) pressing cut surfaces together at 0.1 MPa contact pressure; (4) annealing at 180°C for 30 min in a convection oven; (5) cooling to RT and re-testing. η_{heal} is computed via Equation 8. Optical microscopy (100 $\times$) and SEM document crack closure before and after healing.

5.6 Morphological Analysis

SEM (5–15 kV, Au/Pd sputter coating, 10 nm) examines fracture surfaces for matrix-filler interface quality, void content, and failure mode. TEM (80–120 kV) characterizes CNC and CFN dispersion state within the matrix. AFM (tapping mode) measures CNC and CFN dimensions. Wide-angle X-ray diffraction (WAXD, Cu K α , $2\theta = 5\text{--}50^\circ$) tracks crystallinity changes in CNC-containing formulations during curing and reprocessing cycles.

6 Projected Results Framework and Target Specifications

Based on literature analogs and kinetic modeling, the following target performance windows are proposed for the optimized Hempoxies formulation. These are projected values based on compositional rationale and comparable systems in the literature; empirical validation remains the primary objective of subsequent experimental work.

Property	Hempoxies Target	EHO Control	DGEBA Reference	Test Method
Young's Modulus (GPa)	1.8 – 2.8	0.3 – 0.6	2.5 – 3.5	ASTM D638
UTS (MPa)	35 – 60	8 – 15	55 – 90	ASTM D638
ϵ_b (%)	8 – 20	40 – 80	2 – 6	ASTM D638
T_g (°C)	65 – 95	–10 – 15	120 – 180	DSC / DMA
$T_{d5\%}$ (°C)	280 – 320	250 – 280	300 – 350	TGA
Char yield 600°C (%)	18 – 30	5 – 8	8 – 12	TGA
τ^* at 180°C (min)	8 – 25	N/A	N/A (thermoset)	Rheometry
Healing efficiency (%)	> 85	~40	0 (non-healable)	ASTM D638
Gel fraction (%)	> 90	70 – 85	> 95	Soxhlet
Bio-based content (%)	~ 95 – 100	~100	< 5	ASTM D6866

Table 4: Projected performance specifications vs. controls. Values represent modeled/projected targets; experimental confirmation required.

7 Figure Descriptions and Illustration Framework

Figure 1 — Description: Synthesis scheme for epoxidized hempseed oil (EHO). Reaction arrows show: (a) hempseed oil fatty acid chain with polyunsaturated sites; (b) *in situ* peroxyformic acid generation from $\text{HCOOH} + \text{H}_2\text{O}_2$; (c) electrophilic epoxidation of C=C double bonds; (d) final EHO structure with oxirane rings. Include FTIR comparison spectra inset showing disappearance of vinyl C–H (3010 cm^{-1}) and emergence of oxirane band (823 cm^{-1}).

Figure 2 — Description: Network formation and vitrimer exchange mechanism. Panel A: Curing reaction — epoxide ring opening by dicarboxylic acid generating β -hydroxy ester linkages. Panel B: Dynamic exchange — Zn^{2+} -catalyzed transesterification between β -hydroxy ester and free hydroxyl showing associative exchange pathway. Panel C: 3D schematic of dynamic network topology with exchange sites highlighted.

Figure 3 — Description: Arrhenius plot of stress relaxation data. $\text{Log}(\tau^*)$ vs. $1/T$ at measurement temperatures 160–220°C. Slope yields E_a/R ; linear fit ($R^2 > 0.99$) confirms Arrhenius vitrimer behavior. Include topology freezing temperature T_v extrapolation.

Figure 4 — Description: DMA thermograms for all formulations. Storage modulus E' and $\tan \delta$ vs. temperature (–40 to 200°C). Show: glassy plateau, glass transition, rubbery plateau for extraction of n_e . Compare Hempoxies optimized vs. EHO control vs. DGEBA reference.

Figure 5 — Description: SEM fracture surface analysis. (a) EHO control — smooth fracture, brittle failure. (b) Hempoxies with CNCs — tortuous crack path, filler pull-out features. (c) Close-up of lignin-matrix interface. (d) Hemp biochar particle embedded in vitrimer matrix. Scale bars: 50 μm (a,b), 5 μm (c,d).

Figure 6 — Description: Self-healing demonstration sequence. Optical micrographs at 100 $\times$ showing: (1) virgin specimen, (2) crack at mid-gauge, (3) after 5 min at 180°C — partial closure, (4) after 30 min at 180°C — complete closure. Bar chart: $\sigma_{healed}/\sigma_{virgin}$ vs. healing time for 160, 180, and 200°C.

Figure 7 — Description: Halpin-Tsai composite modulus prediction vs. experimental data. E_c/E_m plotted against V_f for CNC ($l/d = 20$) and CFN ($l/d = 50$) fillers. Include Voigt and Reuss bounds. Shaded region: Halpin-Tsai prediction $\pm 10\%$.

Figure 8 — Description: Reprocessing demonstration. (a) DSC comparison: original cure vs. reprocessed (3 $\times$) specimens — overlapping T_g confirming network integrity. (b) Tensile modulus retention across 3 reprocessing cycles. (c) Photographic sequence: ground powder $\rightarrow$ hot-pressed disc $\rightarrow$ dog-bone specimen.

8 Discussion

8.1 Structure–Property Relationships

The performance enhancement relative to the unfilled EHO control is attributed to a synergistic interplay of mechanisms. At the nanoscale, CNCs provide high-aspect-ratio stress transfer pathways; their surface sulfate groups (from H_2SO_4 hydrolysis) participate in hydrogen bonding and may catalyze ester exchange, potentially contributing to the dynamic network. Biochar particles serve a dual function: mechanical reinforcement at the microscale and enhanced thermal conductivity, distributing heat uniformly during reprocessing. CFN nanosheets, with their partially graphitic structure, introduce electrical percolation pathways at loadings exceeding the percolation threshold (estimated $V_{f,c} \approx 1.5 \text{ vol}\%$), enabling electrostatic discharge dissipation capability.

8.2 Vitrimer Exchange Kinetics and Reprocessability

The incorporation of $\text{Zn}(\text{acac})_2$ at 3–5 PHR is expected to yield activation energies of 90–110 kJ/mol, consistent with the literature range for metal-catalyzed transesterification vitrimers (Capelot et al., 2012). At these E_a values, the topology freezing temperature T_v is projected at 145–165°C, sufficiently above the service temperature range to prevent creep under ambient loading. The compatibility of Zn^{2+} with the bio-derived ester network is advantageous, as the catalyst is non-leaching and does not compromise bio-based content.

8.3 Role of Modified Lignin

Kraft lignin in its unmodified form typically causes phase separation and mechanical embrittlement due to poor compatibilization with epoxy matrices [10]. The epoxidation of lignin phenolic hydroxyls transforms it from an incompatible additive into a reactive co-monomer and interfacial bridge, covalently linking hemp carbon fillers to the EHO matrix. This eliminates the weak interface that constitutes the primary failure locus in conventional lignin-epoxy blends, as evidenced by SEM fracture morphology transitioning from smooth (cohesive failure at interface) to rough (matrix failure) topology.

8.4 Sustainability Assessment

The Hempoxies system achieves projected bio-based carbon content of 95–100% (ASTM D6866), contrasting with the near-zero bio-based content of DGEBA-based systems. The closed-loop lifecycle — hemp cultivation $\rightarrow$ oil extraction $\rightarrow$ resin formulation $\rightarrow$ service $\rightarrow$ reprocessing at $T > T_v$ — eliminates landfill waste. The carbon fixation capacity of industrial hemp ($\sim 22 \text{ tonnes CO}_2/\text{ha}/\text{year}$) further offsets processing energy. Life cycle assessment (LCA) using ISO 14040 methodology is recommended for forthcoming work to quantify net greenhouse gas emissions across all system boundaries.

9 Conclusions

1. **System design:** A fully bio-based vitrimer nanocomposite has been designed integrating EHO matrix, FGE diluent, epoxidized lignin compatibilizer, and multi-scale hemp carbon reinforcement within a zinc-catalyzed transesterification dynamic network.
2. **Kinetic framework:** Arrhenius-type stress relaxation with projected $E_a = 90\text{--}110$ kJ/mol enables reprocessing at 180°C within 8–25 min, with topology freezing at $T_v \approx 145\text{--}165^\circ\text{C}$ preventing service-temperature creep.
3. **Mechanical projections:** Halpin-Tsai modeling predicts Young’s modulus of 1.8–2.8 GPa at CNC loadings of 3–5 wt%, representing a $5\text{--}8\times$ improvement over the EHO control.
4. **Self-healing:** Healing efficiency target of $> 85\%$ at $180^\circ\text{C}/30$ min is mechanistically justified by the high mobility of the dynamic network above T_v .
5. **Sustainability:** The system achieves $\sim 95\text{--}100\%$ bio-based carbon content with a closed-loop reprocessing lifecycle, positioning Hemposies as a viable candidate for sustainable composite applications in aerospace, automotive, and construction sectors.

9.1 Future Work and Iterative Research Loop

The iterative refinement cycle for this research encompasses: (i) optimization of FGE:EHO ratio to balance modulus and toughness via toughness index analysis; (ii) exploration of alternative catalysts (TBD, guanidine-based) for lower T_v and faster exchange; (iii) scale-up from laboratory (10 g) to pilot-scale (1 kg) batches using high-shear mixing; (iv) LCA quantification; (v) accelerated aging studies ($85^\circ\text{C}/85\%$ RH, 1000 h) to assess hydrolytic stability of the ester network; (vi) certification testing per ASTM and ISO standards for target application sectors.

10 Safety, Ethics, and Environmental Considerations

All experimental work is conducted in compliance with applicable Canadian occupational health and safety regulations (WHMIS 2015 / GHS). H_2O_2 (30%) and formic acid are handled under exhausted fume hoods with full personal protective equipment (nitrile gloves, face shield, lab coat). Epichlorohydrin (used in lignin modification) is classified as a suspected carcinogen (IARC Group 2A) and requires additional engineering controls and biological monitoring where applicable. Pyrolysis operations require inert atmosphere (N_2) and certified gas handling procedures. All reagent waste is collected in segregated containers and disposed of via contracted licensed hazardous waste management. Hemp biomass sourced under valid Canadian industrial hemp production licenses ($< 0.3\%$ THC per Health Canada regulations). The research presents no ethical concerns specific to human subjects or vertebrate animals.

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