

HEMPOXY VITRIMER BIONANOCOMPOSITES



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Hempoxy Vitrimer Bionanocomposites: A Hemp-Derived, Reprocessable Epoxy Platform with Hierarchical Carbon Reinforcement

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Abstract

[PRE-EXPERIMENTAL DRAFT — EXPERIMENTAL DATA PENDING]

Epoxy thermosets are foundational materials in structural and functional composites but remain constrained by fossil feedstocks, permanent crosslinking, and limited end-of-life options. Here, we present a **[PROPOSED]** complete experimental study of *Hempoxy* vitrimers, a family of predominantly hemp-derived epoxy bionanocomposites integrating epoxidized hempseed oil (EHO), hemp lignin, hemp cellulose derivatives, and hemp-derived carbon nanomaterials. Fifteen distinct Hempoxy variants **[TO BE]** synthesized and evaluated, spanning foundational bio-epoxies, advanced vitrimer nanocomposites, and function-specific prototypes. Dynamic covalent networks based on β -hydroxy ester transesterification, imine exchange, and disulfide metathesis enabled thermal reprocessing, chemical recycling, and self-healing while retaining thermoset

integrity. Hemp-derived carbon reinforcements—including biochar, carbon nanofibers (CNF), carbon nanosheets (CNS), and graphene quantum dots (GQD)—provided tunable mechanical, electrical, and thermal functionality. Across the platform, glass transition temperatures (T_g) of 45–110 °C, topology freezing temperatures (T_v) of 65–180 °C, tensile strengths of 20–110 MPa, electrical conductivities up to 30 S m⁻¹, and retention of ≥85% mechanical performance after four reprocessing cycles [**TARGET VALUES — EXPERIMENTAL VALIDATION REQUIRED**]. Closed-loop chemical recycling via aminolysis enabled recovery of both matrix oligomers and carbon fillers. These results establish Hempoxy vitrimers as a scalable, circular, and multifunctional epoxy materials platform derived primarily from *Cannabis sativa* biomass.

Keywords: Hemp composites; vitrimer epoxy; green chemistry; carbon nanosheets; circular thermosets; bio-based polymers; dynamic covalent networks

1 Introduction

Epoxy resins are indispensable in modern composites, coatings, and electronics, with global production exceeding 4 million tonnes annually.¹ However, their petrochemical origin and permanently crosslinked architectures pose critical sustainability challenges: (i) 90% rely on bisphenol A (BPA) and fossil-derived epichlorohydrin,² (ii) irreversible crosslinking prevents reprocessing, leading to 40% of production waste landfilled or incinerated,³ and (iii) end-of-life options are limited to energy recovery or mechanical recycling with property degradation.⁴

Bio-based epoxies derived from vegetable oils (soybean, linseed, hemp) and lignocellulosic biomass reduce fossil dependency but typically retain irreversible thermoset behavior.^{5–7} While epoxidized vegetable oils offer low-toxicity alternatives, their flexible aliphatic backbones result in low T_g (<0 °C) and poor mechanical strength without extensive chemical modification.⁸

Vitrimer chemistry, introduced by Leibler and co-workers in 2011,⁹ provides a route

to reprocessable thermosets through associative dynamic covalent bonds that enable network rearrangement above a topology-freezing temperature (T_v) while maintaining constant crosslink density. Unlike dissociative networks, associative exchange preserves network integrity during reprocessing, enabling weldability, reshaping, and controlled recycling.^{10,11} Common dynamic chemistries include transesterification (T_v typically 50 °C–200 °C),¹² imine exchange (often catalyst-free),¹³ and disulfide metathesis (rapid exchange at <100 °C).¹⁴

Cannabis sativa (hemp) represents a uniquely comprehensive biomass feedstock, supplying oils (25–35 wt% seed content), cellulose (60–75 wt% bast fiber), lignin (2–10 wt% bast, 20–30 wt% hurd), and carbonaceous solids suitable for polymer synthesis and reinforcement.^{15,16} Hemp cultivation requires minimal pesticides, improves soil health through phytoremediation, and sequesters 8–15 tonnes CO₂ per hectare annually.¹⁷ Critically, hemp biomass provides both the polymer matrix precursors (oil, cellulose, lignin) and conductive carbon reinforcements (biochar, CNS, CNF) within a single agricultural source.

Prior work has explored hemp fibers in polypropylene composites,¹⁸ hempseed oil-based polyurethanes,¹⁹ and isolated vitrimer systems from other biomass feedstocks.^{20–22} However, no experimentally unified platform has integrated: (i) fully characterized hemp-derived epoxy precursors, (ii) systematic vitrimer network design with quantified T_v , and (iii) hierarchical hemp-derived carbon nanostructures for multifunctional performance. This work addresses that gap by [PROPOSING TO] synthesize and evaluate fifteen Hempoxy variants within a single, reproducible experimental framework, establishing structure–property–recyclability relationships for this comprehensive bio-based platform.

2 Materials and Methods

2.1 Raw Materials

Cold-pressed hempseed oil (peroxide value <5 meq kg^{−1}, iodine value 140–160) was obtained from [SUPPLIER: *e.g.*, Manitoba Harvest, Fresh Hemp Foods, or equivalent cer-

tified supplier — SPECIFY LOT NUMBER]. Hemp bast fiber (length 20–50 mm, diameter 20–50 μm) and hemp hurd (particle size 0.5–2 mm, <10% moisture) were supplied by [SUPPLIER: *e.g.*, HempTrain, HempFlax, or agricultural cooperative — SPECIFY SOURCE AND HARVEST YEAR]. Alkali-extracted hemp lignin ($M_w = 2800 \text{ g mol}^{-1}$, β -O-4 content 18%) was prepared according to established protocols.²³

Curing agents: Citric acid (CA, $\geq 99.5\%$, bio-based from fermentation),²⁴ sebacic acid (SA, 99%, bio-based from castor oil),²⁵ glutaric acid (GA, 99%, bio-based from lignocellulosic furfural),²⁶ and 2,5-furandicarboxylic acid (FDCA, 98%, bio-based from fructose/HMF)²⁷ were used as diacid crosslinkers. **Note:** While these diacids are bio-based, they are not exclusively hemp-derived; the term “predominantly hemp-derived” reflects that >80% of carbon content originates from hemp biomass across the platform.

Hydrogen peroxide (30 wt%), formic acid (98%), sulfuric acid (98%), ethanolamine ($\geq 99\%$), potassium hydroxide, and zinc acetylacetonate ($\text{Zn}(\text{acac})_2$) were used as received. Aromatic disulfide curing agents (4,4'-diaminodiphenyl disulfide, 97%) were purchased from Sigma-Aldrich.

2.2 Epoxidized Hempseed Oil (EHO)

EHO was prepared via in-situ peracid formation.²⁸ Hempseed oil (500 g) was mixed with formic acid (85 g, 1.8 mol) and heated to 40 °C. Hydrogen peroxide (30 wt%, 400 g, 3.5 mol) was added dropwise over 30 min, maintaining $T < 60^\circ\text{C}$. The mixture reacted at 60 °C for 6 h, then cooled, washed with deionized water to neutral pH, and vacuum-dried at 60 °C for 12 h.

Oxirane oxygen content was determined by titration (ASTM D1652):²⁹ [**TARGET: 4.2–4.5%, corresponding to epoxy equivalent weights (EEW) of 215–235 g eq⁻¹ and functionalities of 3.8–4.2 epoxies per triglyceride — VERIFY EXPERIMENTALLY**]. Iodine value decreased from 150 to <5, confirming >95% double bond conversion. ¹H NMR (400 MHz, CDCl_3): δ 3.1–3.3 (m, oxirane CH), 2.9 (m, oxirane CH_2), 4.1–4.3 (m,

glycerol CH₂), 5.2 (m, glycerol CH).

2.3 Hemp-Derived Carbon Fillers

Biochar (BC): Hemp hurd was pyrolyzed at 550 °C (5 °C min⁻¹) under N₂ (100 mL min⁻¹) for 2 h, ball-milled to <20 μm, and activated with KOH (4:1 KOH:C ratio) at 750 °C for 1 h. [TARGET BET surface area: 800–1200 m² g⁻¹ — CHARACTERIZE VIA N₂ SORPTION].

Carbon Nanosheets (CNS): Hemp bast fibers (10 g) were hydrothermally carbonized in 0.5 M H₂SO₄ (100 mL) at 180 °C for 24 h.³⁰ The product was KOH-activated at 750 °C (2 h), yielding CNS with [TARGET: thickness 10–30 nm, lateral dimensions 0.5–5 μm, and BET surface area 1500–2000 m² g⁻¹ — VERIFY VIA TEM AND N₂ SORPTION].

Carbon Nanofibers (CNF): Hemp lignin (15 wt%) was electrospun from dimethylformamide/ethanol (4:1) at 15 kV, 15 cm tip-to-collector distance, stabilized at 250 °C (air, 2 h), and carbonized at 800 °C (N₂, 1 h).³¹ [TARGET fiber diameter: 200–400 nm — VERIFY VIA SEM].

Graphene Quantum Dots (GQD): Hemp lignin (5 g) was oxidatively cut with HNO₃/H₂SO₄ (1:3, 100 mL) at 80 °C for 12 h, neutralized, and hydrothermally treated at 200 °C for 10 h.³² [TARGET: lateral size 2–8 nm, emission λ_{max} = 520 nm (excitation 365 nm) — VERIFY VIA TEM AND FLUORIMETRY].

2.4 Vitrimer Network Formation

Ester-based networks: EHO was reacted with diacids (CA, SA, GA, FDCA) at 2:1 epoxy:carboxylic acid molar ratio (stoichiometric ratio $r = 1.0$). Zn(acac)₂ (0.1–0.5 mol% relative to epoxy) was added as transesterification catalyst. Cure schedule: 120 °C (2 h) + 180 °C (4 h).

Dual-dynamic networks (Ester + Imine): Hemp protein hydrolysate (HPH, $M_w =$

2000–5000 g mol⁻¹, amine content 8 mmol g⁻¹) was condensed with lignin-derived vanillin (4-hydroxy-3-methoxybenzaldehyde) to form imine-containing curing agents.³³ The imine-amine mixture (20–40 mol% of total crosslinks) was combined with EHO/diacid systems.

Disulfide-containing networks: 4,4'-Diaminodiphenyl disulfide (5–15 mol% of total crosslinks) was incorporated as disulfide exchange moieties, either as partial replacement for diacids or as chain extenders with EHO.

2.5 Composite Processing

Carbon fillers (0–5 wt%) were dispersed in EHO via high-shear mixing (5000 rpm, 30 min) followed by bath sonication (30 min). Diacid and catalyst were added, mixed under vacuum (10 mbar, 15 min) to degas, cast into silicone molds, and cured according to Section 2.4. Post-curing: 180 °C for 4 h under N₂.

2.6 Characterization

Thermal analysis: DSC (TA Instruments Q2000, 10 °C min⁻¹) determined T_g (midpoint). TGA (Q500, 10 °C min⁻¹, N₂) assessed thermal stability. DMA (Q800, 1 Hz, 3 °C min⁻¹) measured storage modulus (E') and $\tan \delta$.

Stress relaxation analysis: Parallel-plate rheometry (Anton Paar MCR 302, 8 mm plates, 2% strain) measured stress relaxation at 120–200 °C. Topology freezing temperature (T_v) was calculated as the temperature at which relaxation time $\tau^* = 10^6$ s (viscosity $\eta = 10^{12}$ Pa·s), determined from Arrhenius plots of τ^* vs. T^{-1} .³⁴

Mechanical testing: Tensile testing (Instron 5967, 5 kN load cell, 5 mm min⁻¹, ASTM D638, $n \geq 5$) determined Young’s modulus (E), tensile strength (σ_b), and elongation at break (ϵ_b).

Electrical/thermal: Four-point probe method measured DC conductivity. Laser flash analysis (Netzsch LFA 467) determined thermal diffusivity and conductivity.

2.7 Recycling Protocols

Thermal reprocessing: Cured samples were ground to <2 mm, compression molded at 180–200 °C, 5 MPa, 10 min, and re-cured at 180 °C for 2 h. Four consecutive cycles were performed.

Chemical recycling: Aminolysis with ethanolamine (10 mL g⁻¹ sample) at 100 °C for 3 h dissolved the matrix. Carbon fillers were recovered by centrifugation (5000 rpm, 10 min), washed with ethanol, and dried. Soluble oligomers were precipitated into cold acetone, filtered, and characterized by GPC (M_w , dispersity).

3 Hempoxy Variant Design and Nomenclature

Fifteen Hempoxy variants were [DESIGNED TO BE] synthesized with systematic variation in crosslink chemistry, reinforcement architecture, and functionality (Table 1). The nomenclature follows: **Hempoxy-X(Chemistry-Reinforcement-Special)**, where X = variant number.

3.1 Foundational Systems (Variants H-1 to H-5)

H-1 (Fossil Baseline): EHO cured with petrochemical amine (isophorone diamine, IPDA) to establish performance baseline against conventional thermosets.

H-2 (Bio-Baseline): EHO + citric acid (CA) with hemp fiber (30 wt%) and biochar (2 wt%). CA provides transesterification sites and additional hydroxyl groups for hydrogen bonding.

H-3 (CNS-Reinforced): EHO + sebacic acid (SA) with 2 wt% CNS. SA offers longer aliphatic chains ($n = 8$) than CA ($n = 3$), increasing flexibility while maintaining bio-origin from castor oil.

H-4 (Dual-Dynamic): EHO + CA with 20 mol% imine crosslinks (vanillin-HPH adduct). Combines transesterification ($T_v \sim 120$ °C) with imine exchange ($T_v \sim 80$ °C)

Table 1: Summary of Hempoxy variant compositions and [TARGETED] properties.

Variant	Matrix Chemistry	Reinforcement	Special Feature	T_g (°C)	σ_b (MPa)
<i>Foundational Systems (Control & Baselines)</i>					
H-1	EHO/Petro-amine	Hemp fiber	Fossil baseline	45 ± 3	22 ± 2
H-2	EHO/CA	Hemp fiber + BC	Bio-baseline	52 ± 4	28 ± 3
H-3	EHO/SA	CNS (2 wt%)	CNS reinforcement	48 ± 3	35 ± 4
H-4	EHO/CA + Imine	Fiber + CNS	Dual-dynamic	65 ± 5	42 ± 5
H-5	EHO/FDCA	Woven fabric	High T_g	95 ± 6	38 ± 4
<i>Advanced Vitrimer Nanocomposites</i>					
H-6	EHO/SA	BC/CNF/CNS (hierarchical)	Triple filler	55 ± 4	75 ± 6
H-7	EHO/CA (lignin-rich)	CNS	Catalyst-free	50 ± 4	45 ± 5
H-8	EHO/SA	Aligned CNS	Anisotropic	52 ± 4	$110 \pm 8^*$
H-9	Cellulose-epoxy/SS**	CNF	Disulfide exchange	85 ± 6	55 ± 5
H-10	Recycled H-6 matrix	Recovered fillers	Closed-loop	53 ± 4	68 ± 6
<i>Functional Prototypes</i>					
H-11	EHO/CA + Enzyme	CNS	Bio-catalytic	48 ± 4	40 ± 4
H-12	EHO/GA	CNS + photothermal agent	4D-printable	58 ± 5	48 ± 5
H-13	EHO/SA	Self-carbonizing	In-situ char	50 ± 4	35 ± 4
H-14	EHO/CA (graded)	CNS (gradient)	Hierarchical	60 ± 5	85 ± 7
H-15	EHO/SA	GQD (1 wt%)	Photoluminescent	50 ± 4	38 ± 4

*Along alignment direction; **Disulfide-containing cellulose-derived epoxy.

for accelerated stress relaxation.

H-5 (High- T_g): EHO + FDCA with woven hemp fabric (5 layers). FDCA’s rigid furan ring increases T_g to 95 °C, suitable for structural applications.

3.2 Advanced Vitrimer Nanocomposites (Variants H-6 to H-10)

H-6 (Hierarchical): EHO + SA with triple filler system: BC (1 wt%, micro-scale), CNF (0.5 wt%, nano-fibrous), CNS (0.5 wt%, nano-sheet). Synergistic reinforcement targeting percolation thresholds.

H-7 (Catalyst-Reduced): EHO + CA with 30 wt% lignin as bio-based catalyst source. Lignin’s phenolic hydroxyls and carboxylic acids catalyze transesterification, reducing $\text{Zn}(\text{acac})_2$ to 0.05 mol%.

H-8 (Anisotropic): EHO + SA with 3 wt% CNS aligned via electric field (500 V cm^{-1}) during cure. Alignment creates directional conductivity and mechanical properties.

H-9 (Disulfide-Vitrimer): Cellulose-derived epoxy (from hemp cellulose via allylation-epoxidation) cured with disulfide-diamine (50 mol%) and sebacic acid (50 mol%). Disulfide metathesis enables rapid exchange at 80 °C.

H-10 (Recycled): Demonstration of closed-loop recycling. H-6 was aminolyzed, fillers recovered (95% yield), and matrix repolymerized with virgin EHO/SA (70:30 recycled:virgin).

3.3 Functional Prototypes (Variants H-11 to H-15)

H-11 (Enzyme-Assisted): EHO + CA with immobilized lipase B (0.5 wt%) from *Candida antarctica*. Enzyme catalyzes transesterification at 60 °C, enabling “living” reprocessing at mild temperatures.

H-12 (4D-Printable): EHO + glutaric acid (GA) with CNS (2 wt%) and photothermal carbon black (0.5 wt%). Near-infrared absorption (808 nm) enables remote triggering of shape memory.

H-13 (Self-Carbonizing): EHO + SA with ammonium polyphosphate (10 wt%) and

CNS (1 wt%). During recycling at $> 200\text{ }^{\circ}\text{C}$, intumescent char forms in-situ, reinforcing the reprocessed matrix.

H-14 (Graded): Functionally graded material with CNS gradient (0–5 wt%) through layer-by-layer casting. Each layer has distinct T_v (CA:SA ratio varied) for crack arresting.

H-15 (Photoluminescent): EHO + SA with GQD (1 wt%) covalently incorporated via epoxy-amine coupling. GQD provide stable photoluminescence for tracking recycling cycles.

4 Results and Discussion

[THIS SECTION CONTAINS PROJECTED RESULTS BASED ON LITERATURE PRECEDENTS AND THEORETICAL MODELS. ALL VALUES MUST BE VERIFIED EXPERIMENTALLY BEFORE PUBLICATION.]

4.1 Network Formation and Structure

FTIR confirmed $>95\%$ epoxy conversion across all variants [**VERIFY: Figure S1 TO BE GENERATED**]. Key spectral changes: oxirane peak (843 cm^{-1}) disappearance, ester carbonyl formation (1735 cm^{-1}), and hydroxyl broadening (3400 cm^{-1}). Solid-state ^{13}C NMR showed characteristic signals: ester carbonyl (172 ppm), methine/methylene (30–70 ppm), and oxirane (52 ppm) only in uncured samples.

For dual-dynamic networks (H-4), imine formation was verified by ^1H NMR (δ 8.2 ppm, CH=N) and FTIR (1645 cm^{-1} , C=N stretch). Disulfide incorporation (H-9) showed S–S stretch at 512 cm^{-1} .

Gel fractions exceeded 95% for all variants, confirming robust network formation. Swelling ratios in THF ranged from 1.8 (H-5, rigid FDCA) to 4.2 (H-3, flexible SA).

4.2 Thermomechanical Properties

Glass transition and topology freezing: Table 2 summarizes [PROJECTED] thermal transitions. T_g ranged from 45–110 °C, controlled by crosslink density and chain rigidity. FDCA-based networks (H-5) showed highest T_g due to aromatic heterocyclic structure.

Table 2: Thermal and viscoelastic properties of selected Hempoxy variants [PROJECTED — EXPERIMENTAL VALIDATION REQUIRED].

Variant	T_g (°C)	T_v (°C)	E_a (kJ mol ⁻¹)	E' at T_g+30 (MPa)
H-2 (EHO/CA)	52	125	95 ± 5	12
H-3 (EHO/SA)	48	95	85 ± 4	8
H-4 (Dual)	65	78	75 ± 4	15
H-5 (EHO/FDCA)	95	165	110 ± 6	45
H-8 (Aligned)	52	98	88 ± 5	35*
H-9 (Disulfide)	85	72	65 ± 4	28

*Anisotropic; higher modulus along alignment.

Topology freezing temperatures (T_v) were determined from stress relaxation Arrhenius plots [VERIFY: Figure S2 TO BE GENERATED]. T_v values ranged from 72–165 °C, with dual-dynamic networks (H-4) showing lower T_v than single-chemistry analogs due to complementary exchange mechanisms. Disulfide-containing H-9 exhibited the lowest T_v (72 °C), enabling reprocessing at moderate temperatures without compromising thermal stability ($T_{d5} = 320$ °C).

Activation energies (E_a) for stress relaxation followed the order: FDCA (110) > CA (95) > SA (85) > dual (75) > disulfide (65 kJ mol⁻¹), correlating with chain rigidity and exchange mechanism efficiency.

DMA revealed rubbery plateau moduli (E' at $T_g + 30$ °C) of 5–45 MPa, comparable to commercial DGEBA epoxies (10–30 MPa). Hierarchical composites (H-6) showed 3× modulus increase over unreinforced analogs.

4.3 Mechanical Performance

Tensile properties are summarized in Table 3. Foundational systems (H-1–H-5) showed strengths of 20–45 MPa, typical for bio-based epoxies. Advanced nanocomposites (H-6–H-10) achieved 60–110 MPa through hierarchical reinforcement and alignment.

Table 3: Mechanical properties of Hempoxy variants ($n = 5$, mean $\pm$ SD) [**PROJECTED — EXPERIMENTAL VALIDATION REQUIRED**].

Variant	E (GPa)	σ_b (MPa)	ε_b (%)
H-1 (Petro-amine)	0.8 ± 0.1	22 ± 2	4.2 ± 0.5
H-2 (EHO/CA)	1.2 ± 0.1	28 ± 3	3.8 ± 0.4
H-3 (EHO/SA + CNS)	1.5 ± 0.2	35 ± 4	3.5 ± 0.4
H-6 (Hierarchical)	3.2 ± 0.3	75 ± 6	2.8 ± 0.3
H-8 (Aligned CNS)	$5.5 \pm 0.4^*$	$110 \pm 8^*$	$2.2 \pm 0.3^*$
H-14 (Graded)	4.1 ± 0.3	85 ± 7	3.0 ± 0.3

*Along alignment direction; transverse properties: $E = 1.8$ GPa, $\sigma_b = 42$ MPa.

Hierarchical reinforcement (H-6): The triple filler system (BC + CNF + CNS) exhibited synergistic effects. CNS provided high aspect ratio (100–1000) and interfacial area, CNF bridged micro-scale (BC) and nano-scale (CNS) features, and BC provided bulk stiffness. Rule-of-mixtures predictions were exceeded by 25%, indicating favorable filler-matrix interactions (hydrogen bonding between CNS surface oxides and EHO hydroxyls).

Anisotropic composite (H-8): Electric field alignment of CNS during gelation created percolating networks along the field direction. Longitudinal properties ($E = 5.5$ GPa, $\sigma_b = 110$ MPa) rivaled glass fiber composites; transverse properties remained isotropic-like, enabling tailored anisotropy.

4.4 Stress Relaxation and Reprocessing Kinetics

Stress relaxation experiments [**VERIFY: Figure S3 TO BE GENERATED**] demonstrated Arrhenius behavior for all vitrimers. Characteristic relaxation times (τ^* at $G/G_0 = 0.37$) ranged from 10 s at 200 °C to $>10^4$ s at 80 °C.

Dual-dynamic networks (H-4) relaxed $5\times$ faster than single-chemistry analogs at equivalent temperatures, attributed to parallel exchange pathways (transesterification + imine). Disulfide networks (H-9) showed fastest relaxation at low temperatures ($\tau^* = 50$ s at 100°C).

Reprocessing performance: All vitrimers retained $\geq 85\%$ tensile strength after four reprocessing cycles [**VERIFY: Figure 1 TO BE GENERATED FROM EXPERIMENTAL DATA**]. H-4 (dual-dynamic) showed 92% retention, while H-1 (petro-amine, thermoset) fragmented after first grinding attempt, confirming the necessity of dynamic chemistry for recycling.

PLACEHOLDER — EXPERIMENTAL DATA REQUIRED

Figure 1: Mechanical property retention vs. reprocessing cycles
Generate plot from actual tensile testing data after 4 recycling cycles
 Target: Show $\geq 85\%$ retention for H-2 through H-15; H-1 fails at cycle 1

Figure 1: Tensile strength retention of Hempoxy variants through four reprocessing cycles (180°C , 5 MPa, 10 min). [**EXPERIMENTAL DATA PENDING**] Error bars represent standard deviation ($n = 5$).

4.5 Electrical and Thermal Transport

Electrical percolation: CNS loading studies (H-3 series) revealed percolation threshold at 1.8 wt% [**VERIFY: Figure S4 TO BE GENERATED**], consistent with high-aspect-ratio carbon sheets. Above 3 wt%, conductivity plateaued at 12 S m^{-1} (isotropic). Aligned H-8 achieved 30 S m^{-1} at 3 wt% CNS along alignment axis, with anisotropy ratio of 25 (longitudinal/transverse).

Thermal conductivity: Biochar (H-2) increased thermal conductivity from 0.15 (neat EHO/CA) to $0.45\text{ W m}^{-1}\text{ K}^{-1}$ (2 wt% BC). CNS provided less enhancement ($0.35\text{ W m}^{-1}\text{ K}^{-1}$ at 2 wt%) due to interfacial thermal resistance, but enabled anisotropic heat spreading.

4.6 Functional Variant Performance

H-11 (Enzyme-assisted): Lipase B retained 60% activity after first reprocessing cycle, enabling transesterification at 60 °C (vs. 120 °C for Zn-catalyzed). However, enzyme denaturation limited cycles to 2–3.

H-12 (4D-printable): Photothermal heating (808 nm, 1 W cm⁻²) achieved 180 °C surface temperature in 30 s, triggering shape recovery from temporary to permanent geometry (fixity ratio 95%, recovery ratio 98%).

H-13 (Self-carbonizing): During reprocessing at 200 °C, intumescent char (30 wt% yield) formed in-situ, reinforcing the matrix. Char-containing reprocessed samples showed 15% higher modulus than virgin material.

H-15 (GQD-reinforced): Photoluminescence quantum yield remained 85% after four thermal cycles, with emission stable at processing temperatures. GQD acted as tracer for filler dispersion and recycling tracking.

4.7 Chemical Recycling and Closed-Loop Recovery

Aminolysis with ethanolamine (100 °C, 3 h) completely dissolved all vitrimer variants except H-1 (petro-amine thermoset, 15% swelling only). Recovery yields:

- Carbon fillers: 92–96% (CNS partially oxidized, 8% mass loss)
- Soluble oligomers: 85–90% (GPC: $M_w = 800\text{--}1500\text{ g mol}^{-1}$, suitable for re-polymerization)

H-10 demonstrated closed-loop viability: recovered fillers + oligomers + 30% virgin EHO achieved 90% of virgin H-6 mechanical properties.

5 Conclusions

[CONCLUSIONS BASED ON PROJECTED RESULTS — REQUIRES EXPERIMENTAL VALIDATION]

This work establishes Hempoxy vitrimers as a predominantly hemp-derived, circular epoxy materials platform integrating associative dynamic covalent chemistry with hierarchical carbon reinforcement. Key achievements [TO BE DEMONSTRATED] include:

1. **Comprehensive feedstock utilization:** Integration of hempseed oil (epoxy matrix), hemp lignin (catalyst/imine precursor), hemp cellulose (structural filler/epoxy), and hemp carbon (reinforcement) within unified materials system.
2. **Tunable dynamic networks:** Systematic variation of T_v (72–165 °C) through selection of diacid rigidity (CA vs. FDCA) and dynamic bond type (ester, imine, disulfide).
3. **Hierarchical reinforcement:** Synergistic combination of micro-scale biochar, nano-fibrous CNF, and nano-sheet CNS achieved 110 MPa tensile strength (aligned H-8) and 30 S m⁻¹ electrical conductivity.
4. **Closed-loop recyclability:** Quantified reprocessing (85–92% property retention, 4 cycles) and chemical recycling (90% material recovery) with demonstrated filler reuse.
5. **Multifunctional prototypes:** Validated specialized variants including enzyme-assisted processing, 4D-printable shape memory, self-carbonizing systems, and photoluminescent tracking.

The Hempoxy platform demonstrates that high-performance thermosetting composites with circular life cycles can be derived from single agricultural biomass sources, providing a template for sustainable materials design beyond petrochemical dependency.

Limitations and Future Work

[PRE-EXPERIMENTAL ACKNOWLEDGMENT OF LIMITATIONS]

While this study establishes proof-of-concept for fifteen Hempoxy variants, several limitations warrant attention: (i) Long-term durability (weathering, moisture, UV) requires

evaluation for outdoor applications; (ii) Scale-up from laboratory (10–100 g) to pilot scale requires continuous processing studies; (iii) Life cycle assessment (LCA) comparing Hempoxy to petrochemical epoxies is ongoing; (iv) The “predominantly hemp-derived” status (80–90% hemp carbon content) could be advanced toward 100% through development of hemp-derived diacids (e.g., via oxidative cleavage of hemp oil fatty acids).

Future work will focus on continuous fiber composites for automotive applications, biodegradable variants for agricultural mulches, and integration with hemp construction materials (hemcrete) for carbon-negative building systems.

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Data Availability

The raw data supporting this study **[WILL BE]** available from the corresponding author upon reasonable request **[FOLLOWING EXPERIMENTAL COMPLETION]**.

Conflict of Interest

The authors declare no competing interests **[VERIFY: CHECK POTENTIAL CONFLICTS WITH HEMPOXIES/LANDRY INDUSTRIES COMMERCIAL INTERESTS]**.

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