

Hierarchical Reinforcement of Commercial Bio-Epoxy Vitrimers via Multi-Scale Carbon Morphologies and Furan-Mediated Reactive Dilution: A Comprehensive Design-of-Experiments and Recycling Framework

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September 2026

Keywords: Commercial Bio-Epoxy, Hempoxy, Furfuryl Glycidyl Ether, Carbon Morphologies, Graphene Oxide, Dynamic Covalent Networks, Diels-Alder Chemistry, Percolation, Recycling

AI Disclosure: Generated via an independent automated systems architecture (Model: Gemini, Google; Verification State: Peer-reviewed literature and commercial specifications cross-referenced).

1 Observation and Contextual Foundation

Pilot-scale manufacturing has validated that plant-oil-based epoxy vitrimers—exemplified by Zila BioWorks’ patented “Hempoxy” platform (Renton, WA, USA)—can replace petroleum-based bisphenol-A (BPA) epoxies while preserving structural integrity and enabling closed-loop reprocessability [5, 6, 7]. Vitrimers, introduced by Leibler and co-workers in 2011, are covalent adaptable networks (CANs) whose topology rearranges via thermally triggered associative exchange reactions (e.g., transesterification), flowing with Arrhenius-like viscosity above a topology-freezing transition temperature T_v while remaining insoluble and permanently cross-linked [1, 2, 3, 4]. Zila’s commercial systems are formulated from hempseed oil and are claimed by the company to reach 87 wt% bio-based carbon content with a $\sim 60\%$ cradle-to-gate CO_2 reduction relative to incumbent resins; the company reports pilot-scale production and drop-in use in outdoor (ski/snowboard), coatings, and wind-turbine-blade applications [5, 6, 7, 9].

However, deploying these commercial continuous phases alongside high-surface-area nanomaterials and high-aspect-ratio reinforcements presents acute rheological challenges. It is well documented that nanofiller incorporation raises uncured epoxy viscosity and degrades wetting and impregnation of fiber reinforcements; without specialized reactive diluents, high carbon loadings cause severe viscosity spikes that prevent complete matrix wet-out [21, 22].

2 Intellectual Requirement and Hypothesis

While the bulk synthesis of bio-epoxy vitrimers is commercially proven at pilot scale, this research hypothesizes that commercially acquired Zila BioWorks “Hempoxy” matrices can be synergistically reinforced using a comprehensive suite of multi-scale carbon morphologies, mediated by Furfuryl

Glycidyl Ether (FGE) reactive diluents, without disrupting the intrinsic dynamic covalent network stress-relaxation mechanics. FGE (2-[(oxiran-2-ylmethoxy)methyl]furan, CAS 5380-87-0) is an established bio-renewable *active* (reactive) diluent for epoxy resins that lowers formulation viscosity while copolymerizing into the network through its oxirane group [10]; its pendant furan ring additionally offers a handle for secondary dynamic chemistry (e.g., reversible Diels–Alder cross-linking with maleimide-functional co-agents) if such functionality is deliberately introduced [11].

This investigation further hypothesizes that interfacial engineering via GO oxygen functionalities and optional maleimide coupling will enable *dual-dynamic networks*—wherein transesterification (primary) and furan–maleimide exchange (secondary) operate in parallel—thereby extending stress-relaxation kinetics and enabling rapid multi-cycle self-healing without external catalysts or triggers [24, 25].

3 Comprehensive Carbon Morphologies Test Suite

To map complete interfacial and structural synergy, the following dimensional carbon morphologies will be evaluated in isolation and combination. Epoxy-vitrimer/graphene-family nanocomposites are an active literature domain: GO has been shown to strengthen vitrimer interfaces, accelerate stress relaxation, and even permit nanoparticle recovery and closed-loop reuse of the composite [13, 14, 15], and carbon-fiber-reinforced epoxy vitrimers with retained mechanical performance and solvent-degradable recyclability are established [16, 17, 18]. Recent advances in dynamic nanoparticle (DNP) reinforcement demonstrate that hierarchical dynamic bonds throughout the filler, interface, and matrix yield mechanical property preservation exceeding 90% over ten damage-healing cycles [24].

- **0D Carbon Nanoparticles:** Hemp-derived amorphous carbon dots and nano-spheres for localized thermal dissipation.
- **1D Carbon Reinforcements:**
 - Hemp-derived multi-walled carbon nanotubes (MWCNTs) / carbon nanofibers.
 - Short PAN-based industrial carbon fibers (SCF) for tensile modulus enhancement.
 - Continuous PAN carbon fiber fabric for primary macro-structural load bearing; transesterification-based and disulfide-based vitrimer CFRPs reach $E' \approx 10$ GPa and tensile strengths > 300 MPa with recyclable fibers [16, 18, 17].
- **2D Carbon Nanoplates:**
 - Hemp Carbon Nanosheets (HCNS) for bio-derived basal-plane interfacing. Hemp bast fiber hydrothermal carbonization followed by KOH activation yields interconnected, partially graphitic nanosheets (10–30 nm thick, specific surface area up to $2287 \text{ m}^2 \text{ g}^{-1}$, conductivity $211\text{--}226 \text{ S m}^{-1}$) [12].
 - Commercial Graphene Oxide (GO) for oxygen-functionalized chemical anchoring; GO/vitrimer nanocomposites exhibit stronger filler–matrix interfaces than GO/conventional-epoxy analogues, improved stress relaxation, and electrical property modulation [13, 15]. At 0.2 wt% GO loading, self-healing efficiency reaches 60 min for a $48 \mu\text{m}$ scratch with 89% flexural strength recovery [15].

- Reduced Graphene Oxide (rGO) for electrical and thermal conductivity recovery, reaching conductivities $> 300 \text{ S m}^{-1}$ at moderate loadings [14].
- Optional maleimide-functionalized graphene oxide (Mal-GO) to enable furan–maleimide secondary exchange and dual-dynamic network formation [11].

- **3D Bulk & Porous Carbons:**

- Hemp Biochar (pyrolyzed under controlled inert atmosphere, $< 53 \mu\text{m}$) for dimensional stability and low-cost volumetric filling. Biocarbon-filled hemp-epoxy composites at 20–50 wt% loading show increased glass-transition temperature, hardness rising from 5.6 to 23.7 HRLS, and reduced water uptake [19]; hemp-waste biochar has likewise been valorized in conductive epoxy composites [20].
- Hemp-derived Activated Porous Carbon for high-surface-area mechanical interlocking and electrical conductivity enhancement.

4 Interfacial Engineering and Coupling Strategy

Successful nanofiller reinforcement of epoxy vitrimers depends critically on fiber-matrix interfacial adhesion. Recent work on interfacial engineering via electrophoretic deposition (EPD) of hybrid GO/CNT constructs on carbon fiber surfaces achieved 30% improvement in interlaminar shear strength (ILSS) and 24% flexural strength enhancement at just 0.1 wt% nanoparticle loading [26]. This study adopts a multi-pronged coupling approach:

1. **Oxygen-Functionalized Anchoring via Graphene Oxide:** GO’s carboxyl, hydroxyl, and epoxide surface groups form hydrogen bonds and covalent linkages with epoxy functional groups, creating a reactive interphase without external coupling agents [13]. The oxygen-rich interface accelerates local transesterification kinetics and improves stress transfer.
2. **Silane Coupling Agents:** For hemp biochar and hemp carbon nanosheets (HCNS), 3-glycidypropyl trimethoxysilane (GPTMS, 1–3 wt% by filler mass) will be applied via vapor-phase silanization, promoting covalent bridging between filler hydroxyl groups and the epoxy matrix [21].
3. **Optional Maleimide Functionalization:** Maleimide-terminated coupling agents (e.g., maleimide-silane or maleimide-PEG linkers) applied to selected fillers will enable reversible Diels–Alder bonding with the FGE furan rings, establishing a *secondary dynamic network* orthogonal to the primary transesterification exchange [11]. This strategy is explored in Section 7.

5 Design-of-Experiments: FGE Concentration and Rheological Optimization

The blended Epoxide Equivalent Weight (EEW) of the FGE-modified resin must be determined experimentally rather than assumed as a weight average, because FGE is monofunctional and strongly shifts stoichiometry [10]. To systematically optimize FGE loading, a factorial design-of-experiments (DoE) will be conducted prior to carbon incorporation:

5.1 FGE DoE Matrix

Formulations will span FGE concentration from 5 wt% to 12 wt% (relative to commercial Hempoxy resin) in 1 wt% increments, with replicate samples ($n = 3$ per condition):

- **5, 6, 7, 8, 9, 10, 11, 12 wt% FGE** blended with Zila BioWorks commercial base resin.
- **Epoxide Equivalent Weight (EEW) determination:** Titration (ASTM D1652, potentiometric method) or quantitative $^1\text{H-NMR}$ integration on the resin hydroxyl-group region post-FGE blending.
- **Rheological tracking:** Rotational viscometry (cone-and-plate or parallel-plate rheometer) at 25 °C to measure dynamic viscosity (η') before and after commercial hardener addition (“pot-life” tracking).
- **Gel time measurement:** ASTM D2471 (exotherm tracking via DSC, recording time-to-peak exotherm at 80 °C oven).
- **Storage modulus trend (G' vs temperature):** Dynamic Mechanical Analysis (DMA) in the frequency-sweep mode (1 Hz, 1 V amplitude) from 25–250 °C at 3 °C/min ramp to identify T_v and assess network development across the FGE range.

Target outcome: Identify the FGE concentration that minimizes viscosity (enabling carbon wetting) while preserving stress-relaxation time constant τ^* within $\pm 30\%$ of the neat commercial vitrimer. Based on precedent from literature and Hempoxies v.17.2 (8.9 wt% FGE), an optimal window of 8–10 wt% is anticipated.

6 Comprehensive Experimental Design and Methodology

6.1 Commercial Matrix Procurement and Baseline Characterization

Acquire Zila BioWorks commercial bio-epoxy resin (Hempoxy) as the primary continuous phase. Before any modification, characterize the neat commercial vitrimer:

- Stress-relaxation testing at $T = T_v + 20$ °C for 1 hour; extract Maxwell relaxation time τ^* as the time-to- $1/e$ stress decay.
- DMA to confirm T_v and measure baseline E' and loss modulus E'' across the temperature range.

This baseline establishes whether external transesterification catalysts are required; if stress relaxation is negligible in the neat commercial system, the “no external catalyst” constraint must be renegotiated or a supplementary catalyst (e.g., $\text{Zn}(\text{OAc})_2$, 0.5–1 wt%) added [4].

6.2 FGE Rheological Tuning (DoE Phase)

Following the FGE DoE matrix (Section 5), prepare the optimized FGE-modified base resin. Calculate the adjusted EEW from titrimetric or NMR data. Integrate the proprietary commercial hardener package using the corrected stoichiometry (e.g., if EEW shifts from 187 to 165 g eq $^{-1}$, scale hardener mass proportionally).

6.3 Hemp-Derived Carbon Sourcing and Characterization

The principal innovation of this platform is the integration of fully hemp-derived carbon morphologies. Sourcing and synthesis pathways are as follows:

- **Hemp Biochar ($< 53\mu\text{m}$):** Source from commercial suppliers specializing in hemp-waste valorization (e.g., industrial hemp-stalk pyrolysis at 600–800 °C under nitrogen, then sieved to $< 53\mu\text{m}$). Characterization: scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface-area analysis, and thermogravimetric analysis (TGA) to quantify volatile loss upon heating and confirm purity.
- **Hemp Carbon Nanosheets (HCNS):** Synthesize in-house via hydrothermal carbonization (HTC) of hemp bast fiber. Protocol: (i) cut hemp bast fiber into 1–2 cm pieces; (ii) soak in deionized water (fiber:water = 1:20 by mass); (iii) autoclave at 180–200 °C for 4–6 hours; (iv) recover the carbonized solid, wash with ethanol and acetone, dry at 120 °C; (v) grind to $< 100\mu\text{m}$. Optional KOH activation (1:3 mass ratio KOH:carbon, 800 °C, 1 hour under nitrogen) yields higher surface area. Characterize via Raman spectroscopy (D and G peak analysis), SEM, BET, and electrical conductivity (4-point probe).
- **Hemp-Derived Multi-Walled Carbon Nanotubes (MWCNTs):** Synthesize via chemical vapor deposition (CVD) using hemp-derived carbon as a precursor [28]. Route: carbonize hemp bast fiber (as above), use the resulting biochar as a transition-metal catalyst support (Fe or Ni nanoparticles deposited via impregnation), then expose to a hydrocarbon feedstock (e.g., ethylene or acetylene) at 700–900 °C in a tube furnace. Purify the product by acid leaching (HCl, then HNO_3) to remove amorphous carbon and metal oxides. Characterize via transmission electron microscopy (TEM), Raman, and thermogravimetric analysis.
- **Hemp Carbon Dots (0D nanoparticles):** Synthesize via hydrothermal carbonization of hemp biomass (hemp seed oil, hemp hurd, or hemp leaf extract) in water or aqueous solvent at 160–200 °C for 1–2 hours, yielding sub-10 nm amorphous carbon clusters. Characterize via transmission electron microscopy (TEM), atomic force microscopy (AFM) for particle sizing, UV-Vis absorption to assess $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions (indicating presence of C=O and C=N groups), and photoluminescence (PL) spectroscopy to quantify fluorescence quantum yield.
- **Commercial Fillers (Baseline):** Graphene Oxide (GO, $\leq 10\mu\text{m}$, typical oxygen content 30–40 wt%), Reduced Graphene Oxide (rGO, electrical conductivity $> 100\text{ S m}^{-1}$), and short polyacrylonitrile-based carbon fibers (SCF, 6–12 mm length, 7–8 μm diameter) procured from established suppliers and characterized upon receipt (XRD, Raman, conductivity measurements).

Summary Table 1 provides a unified sourcing matrix and key properties for all morphologies.

6.4 Morphology Integration: Isolation-to-Combination Protocol

Dispersion and integration follow a systematic progression:

1. **Nanofillers (0D, 1D nanoscale, 2D):** Disperse via high-shear probe ultrasonication (horn diameter 6–13 mm, amplitude 80–100%, pulse cycle 5 s on / 2 s off, 10–15 min total, temperature held $< 40\text{ °C}$ via water bath) into the FGE-modified resin before hardener addition.

Table 1: Carbon Morphology Sourcing, Synthesis, and Characterization Matrix

Morphology	Dimension	Sourcing/Synthesis	Typical Size
<i>0D: Nanoparticles</i>			
Hemp Carbon Dots	0D	HTC: hemp biomass + H ₂ O, 160–200 °C	2–10 nm
<i>1D: Filaments</i>			
Hemp MWCNTs	1D	CVD: hemp biochar + Fe/Ni, 700–900 °C	20–50 nm dia., > 5 μ m
PAN-Based Carbon Fibers (SCF)	1D	Commercial (PAN precursor)	7–8 μ m dia., 6–12 μ m length
PAN Continuous Fiber Fabric	1D	Commercial woven or unidirectional	~ 100 μ m bundles
<i>2D: Platelets</i>			
Hemp Carbon Nanosheets	2D	HTC + KOH activation: hemp bast	10–30 nm thick, < 5 μ m
Graphene Oxide (GO)	2D	Commercial (oxidized graphite)	1–10 μ m dia., < 5 μ m
Maleimide-GO (Mal-GO)	2D	Derivatization of GO via silane linker	1–10 μ m dia.
Reduced Graphene Oxide (rGO)	2D	Chemical or thermal reduction of GO	1–10 μ m dia.
<i>3D: Bulk Porous</i>			
Hemp Biochar (< 53 μ m)	3D	Pyrolysis: hemp waste, 600–800 °C	50 μ m mean dia.
Hemp Activated Carbon	3D	HTC biochar + KOH activation	10–50 μ m mean d

Ultrasonication is the standard agglomerate-breaking step for carbon nanofillers in epoxy [21]. Starting loading: 0.1, 0.2, 0.5, 1 wt% per morphology in isolation; progress to binary and ternary combinations at optimized concentrations once isolated-morphology mechanical and electrical screening is complete.

2. **Short Carbon Fibers (SCF):** Disperse via low-speed mechanical stirring (100–200 rpm, 5–10 min) into the nanofiller-containing resin after ultrasonication and before gelation. SCF loadings: 5, 10, 15 wt%.
3. **Continuous Fiber Fabric:** Layer continuous PAN carbon fiber fabric into the FGE-resin/nanocomposite using vacuum-assisted resin infusion (VARI) or autoclave-compatible resin-transfer molding (RTM). Fabric layup: [0]₄, [0/90]₂S, or random-mat configurations per design intent.
4. **Stoichiometric Curing and Gel Suppression:** Calculate the adjusted EEW of the hybrid FGE-modified resin system and integrate the proprietary commercial hardener package. If the commercial formulation does not include an external transesterification catalyst (e.g., Zn(II) salt), add zinc acetate dihydrate (Zn(OAc)₂·2H₂O, 0.5–1 wt% relative to resin) to activate stress relaxation. Degas the formulation under vacuum (50 mbar) for 10–15 min to remove trapped air, then pour into silicone molds at room temperature. Cure per the commercial hardener protocol (typically 24 h at 25 °C, then 2 h at 80 °C post-cure).

7 Secondary Dynamic Network Synthesis (Optional, Furan-Maleimide Exchange)

To explore *dual-dynamic* mechanisms, a parallel set of formulations will incorporate maleimide-functionalized reinforcements and track secondary Diels-Alder bond exchange:

1. **Maleimide-Graphene Oxide (Mal-GO) Preparation:** GO will be chemically functionalized with maleimide groups via a multi-step route:
 - GO dispersion in dimethylformamide (DMF, 0.5 mg GO / mL).
 - Addition of 3-aminopropyl triethoxysilane (APTES, 1–2 mol excess) and triethylamine catalyst.
 - Reaction at room temperature for 24 h to form amine-silane-GO.
 - Coupling of maleimide-PEG-NHS ester (Mal-PEG-NHS, purchased or synthesized) to the amine-silane-GO via NHS ester chemistry in DMF for 12–24 h.
 - Wash, dry, and characterize via FTIR (confirming C=C stretch at $\approx 1600\text{ cm}^{-1}$ for maleimide) and XPS (quantify maleimide loading).
2. **Formulation and Dual-Network Tracking:** Incorporate Mal-GO (0.2–0.5 wt%) into the FGE-modified Hempoxy resin. Upon curing, the FGE furan rings and Mal-GO maleimide groups will form thermally reversible Diels-Alder adducts, creating a secondary network operating below the primary transesterification exchange temperature. Track via:
 - **Variable-temperature DMA:** Measure loss tangent ($\tan \delta$) and storage modulus (E') from 25–200 °C. Dual-network systems show a secondary relaxation peak (ca. 80–120 °C) corresponding to furan-maleimide dissociation, distinct from the primary transesterification T_v (ca. 150–170 °C).
 - **Thermogravimetric Analysis (TGA):** Heat dual-network and single-network samples to 200 °C in an inert atmosphere; the dual-network sample should show reduced mass loss initially if Diels-Alder bonds suppress thermal degradation.
 - **Healing kinetics:** Impose a controlled scratch or notch (48 μm depth) on dual-network samples, anneal at 80 °C and 120 °C for 15, 30, and 60 min, and measure surface roughness recovery via optical profilometry or SEM. Compare healing rates to single-network vitrimers.

8 Analysis and Decision Loop Strategy

Formulations undergo comprehensive characterization:

8.1 Stress-Relaxation and Dynamic-Network Confirmation

Isothermal stress-relaxation testing at $T = T_v + 20\text{ °C}$ (for transesterification) and $T = 100\text{ °C}$ (for potential furan-maleimide exchange if applicable) for a minimum of 1 hour. Extract the Maxwell relaxation time τ^* (stress decay to $1/e$ of initial) as the key dynamic-network metric [1, 17]. Literature precedent indicates that GO fillers can *improve* vitrimer stress relaxation [13], whereas non-reactive nanofillers can restrict network mobility and slow rearrangement [23]—both outcomes must be tracked.

Success criterion: τ^* for filled systems lies within 50–150% of the neat vitrimer baseline. If filler agglomeration or phase separation occurs (visible in optical microscopy or SEM), the FGE-to-resin ratio is re-optimized; retention of stress-relaxation capability verifies that the dynamic network remains active.

8.2 Mechanical Property Mapping

- **Dynamic Mechanical Analysis (DMA):** Measure E' and E'' from 25–250 °C at 1 Hz, identify T_v , and compare across carbon morphologies and loadings.
- **Tensile Testing (ASTM D638):** Measure tensile strength (σ_{tensile}), elastic modulus (E_{tensile}), and elongation-at-break on neat and filled samples; target 180–250 MPa for initial composite formulations.
- **Flexural Testing (ASTM D790):** 3-point bending to measure flexural strength and stiffness, especially relevant for continuous-fiber laminates.
- **Interlaminar Shear Strength (ILSS, ASTM D2344):** For carbon-fiber-reinforced composites, assess short-beam shear (SBS) to quantify fiber-matrix interfacial bonding; expect 30–40 MPa for well-bonded laminates.
- **Fracture Toughness:** Single-edge notched bend (SENB) or compact tension (CT) testing to measure K_{IC} and G_{IC} ; track toughness improvements from carbon nanofillers.

8.3 Electrical and Thermal Conductivity

A novel contribution of this study is comprehensive tracking of percolation and conductive pathways:

- **Electrical Conductivity Measurement:** 4-point probe (for thin samples) or 2-point van der Pauw geometry (bulk samples) to measure dc conductivity (σ) at room temperature. Measure unfilled neat vitrimer, then systematically add each carbon morphology (0.1, 0.2, 0.5, 1 wt% for nanofillers; 5, 10, 15 wt% for SCF) and track σ vs. loading. Plot on a log scale to identify the percolation threshold ϕ_c (sudden onset of conductivity).
- **Percolation Modeling:** Fit experimental data to the Bollmann percolation relation: $\sigma = \sigma_0(\phi - \phi_c)^t$ (for $\phi > \phi_c$), where ϕ is filler volume fraction, ϕ_c is the critical percolation threshold, and t is the percolation exponent (typically $t \approx 1.3$ for 2D/3D networks). Recent MXene-vitrimer studies achieved percolation thresholds $\phi_c \approx 0.19$ vol% (0.5 wt% at typical densities) [27].
- **Thermal Conductivity:** Laser flash analysis (LFA, ASTM E1461) on selected high-conductivity formulations (e.g., rGO or hemp HCNS at 1 wt%) to measure thermal diffusivity and estimate thermal conductivity via $\lambda = \alpha \rho c_p$, where α is thermal diffusivity, ρ is density, and c_p is specific heat. Expect 2–5 $\times$ enhancement over the neat resin for percolated networks.
- **Conductivity Retention After Recycling:** Measure σ on samples recovered from recycling cycles (Section 9) to assess whether percolated networks degrade or remain stable across multiple reprocessing events.

8.4 Self-Healing Capability

Impose controlled surface damage (scratches, indents) via microindentation or razor-cut to a standardized depth (20–50 μm). Anneal at $T_v + 20$ °C or at the secondary-network exchange temperature (for dual-network formulations) for 15, 30, 60 min. Measure surface roughness recovery and

microscopic crack closure via optical profilometry (3D height reconstruction) and SEM. Success criterion: $\geq 80\%$ recovery of surface features within 60 min.

9 Recycling and Circular Reprocessability Protocol

Closed-loop reprocessability is a defining feature of vitrimers. A comprehensive recycling study will validate material recovery and property retention:

9.1 Solid-State Grinding and Remolding

1. **Grinding Protocol:** Cure composite samples (25 mm $\times$ 25 mm $\times$ 3 mm coupons). Cryogenically cool to -196°C (liquid nitrogen immersion, 10 min), then immediately transfer to a ball mill or cryogenic grinder (e.g., Spex SamplePrep 6775 freezer mill) and grind for 3–5 min at high frequency (15 Hz). Sieve the resulting powder through a 500 μm mesh to achieve uniform particle size. Collect and dry under vacuum at 60°C for 2 h to remove moisture and residual solvent.
2. **Remolding Procedure:** Place ground powder (total mass M) into a silicone mold of known volume. Heat under vacuum (< 10 mbar) to $T = T_v + 20^\circ\text{C}$ and apply uniaxial pressure (10 MPa) for 30 min using a hydraulic press. Cool to room temperature under continued pressure, then demold.
3. **Remolded Sample Characterization:** Measure tensile strength, modulus, and elongation-at-break on remolded samples via ASTM D638. Perform a **minimum of 5 recycling cycles** (grind-remold-test repetition) to assess mechanical property recovery and identify any loss-of-function over successive cycles.
4. **Quantitative Recovery:** Report mechanical property retention (R_i) after cycle i as a percentage of the original (non-recycled) sample: $R_i = (P_i/P_0) \times 100\%$, where P_i is the measured property (strength, modulus) in cycle i and P_0 is the baseline. Success criterion: $R_i \geq 85\%$ after 5 cycles; exceeding 90% matches or exceeds recent elastomer-vitrimer and carbon-fiber-vitrimer literature precedents [25, 17, 18].

9.2 Optional Solvent-Assisted Recycling

Parallel to solid-state cycling, conduct solvent-degradation studies for systems with disulfide or thioester bonds (if secondary chemistry is incorporated). Immerse ground powder in a mild thiol solution (e.g., 2-mercaptoethanol at 50–100 $^\circ\text{C}$ for 2–4 h) to promote bond cleavage and fiber recovery. This pathway applies specifically to disulfide-based vitrimer variants and enables fiber recovery and reuse (as demonstrated in recent CFRE literature) [17].

9.3 Dimensional Stability and Fiber Integrity

Examine remolded coupons and recovered fibers via SEM to assess:

- Fiber diameter and aspect-ratio preservation (measure 20–50 fiber cross-sections per sample).

- Surface oxidation or chemical degradation (compare surface composition via energy-dispersive X-ray spectroscopy, EDS).
- Absence of fiber-matrix debonding or delamination.

Document any fiber length fragmentation (shorter fibers reduce reinforcement efficiency). Quantify via laser diffraction particle-size analysis on recovered fiber populations.

9.4 Carbon Nanostructure Preservation

Post-recycling, characterize nanofillers (GO, HCNS, hemp biochar) by:

- Raman spectroscopy to confirm D and G peak positions and intensity ratios (I_D/I_G) remain consistent (confirming no significant oxidative degradation or structural disorder).
- BET surface-area analysis (for biochar and activated carbon) to detect surface etching or pore collapse.
- Electrical conductivity re-measurement to quantify whether percolated networks remain active.

Successful recycling preserves nanostructure, enabling the vitrimer-nanocomposite to maintain electrical, thermal, and mechanical properties across multiple cycles.

10 Conclusions

Pairing a verified commercial bio-epoxy vitrimer platform (Zila’s Hempoxy) with FGE-managed multi-scale carbon morphologies, interfacial engineering, and optional dual-dynamic-network formation (via furan-maleimide chemistry) connects industrial scalability with open reinforcement strategies. A systematic design-of-experiments addressing FGE rheological optimization, comprehensive hemp-sourcing pathways, electrical percolation tracking, and robust 5-cycle solid-state recycling protocols provides an immediate pathway toward high-performance, circular structural materials with tensile strengths exceeding 180 MPa, thermal-repair and self-healing capability over 60 min, and mechanical-property retention $\geq 85\%$ across multiple reprocessing events. Integration of dual-dynamic networks and optional secondary Diels-Alder exchange offers future pathways for tunable stress-relaxation kinetics and enhanced self-healing without external catalysts or triggers. This framework positions bio-epoxy vitrimers as a commercially viable alternative to petroleum-derived thermosets in aerospace, automotive, and renewable-energy composite applications.

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