

Hempoxies v.13A "Deca-Hemp": A Sovereign 10-Component 100% Bio-Derived Structural Vitrimer System

Marie-Soleil Seshat Landry

CEO, Spymaster, and Owner

Landry Industries | ORCID iD: 0009-0008-5027-3337

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Abstract

The **Hempoxies™ Omega Platform (v.13A)** establishes the "Deca-Hemp" baseline: a 100% hemp-derived structural vitrimer system. This system utilizes exactly 10 hemp-derived components to create a high-performance Covalent Adaptable Network (CAN): (1) **EHSO** matrix monomer (Futura 75), (2) **QF-MHL** catalyst/cross-linker (Santhica 27), (3) **FGE** reactive diluent for viscosity control, (4) **HDA** phenolic amine hardener, (5) **Bio-Silica Sol** coupling agent (Tiborszallasi), (6) **Mitlinite HDCNS** 2D nano-reinforcement for conductivity, (7) **HDB** micro-filler for rigidity, (8) **HDCF** graphitized macro-reinforcement, (9) **D-Limonene** processing solvent, and (10) **Vitrimer Adducts** for self-healing at 120°C. This document details the 11 Standard Operating Procedures (SOPs) required to synthesize and integrate these components—including the optimized "One-Pot, Two-Stage" Green Chemistry protocol for lignin modification—into a structural skeleton capable of self-repair, achieving flexural modulus values exceeding 25 GPa and enabling thermal recycling through transesterification exchange at 180°C. The resulting material system represents a paradigm shift toward petroleum-independent structural composites with embedded circularity.

1 Introduction

1.1 The Petroleum Dependency Crisis

The global reliance on petroleum-based thermosets presents a significant barrier to the Organic Revolution 2030. Conventional epoxy resins, polyurethanes, and unsaturated polyesters account for approximately 18 million metric tons of annual production, with minimal end-of-life recycling infrastructure [1]. These materials, once cured, form permanent three-dimensional networks that resist reprocessing, contributing to composite waste accumulation in landfills and marine environments. While vitrimers offer recyclability through dynamic bond exchange at elevated temperatures [2], current bio-based iterations lack the mechanical "skeleton" required for heavy-duty applications such as automotive panels, wind turbine blades, and civil infrastructure.

1.2 The Vitrimer Advantage

Vitrimers represent a third class of polymers that exhibit properties intermediate between thermoplastics and thermosets. Unlike traditional thermosets with permanent covalent cross-links, vitrimers contain exchangeable bonds that rearrange under thermal or catalytic stimulus while maintaining network integrity [3]. This associative exchange mechanism enables:

- Thermal reprocessability without depolymerization
- Stress relaxation and self-healing capabilities

- Welding and reshaping at moderate temperatures (120–180°C)
- Solvent resistance comparable to conventional thermosets
- Tunable glass transition temperatures through network design

However, bio-derived vitrimers have historically suffered from low modulus (1–5 GPa), poor impact resistance, and limited electrical conductivity, restricting their application to non-structural roles such as coatings and adhesives.

1.3 Formula 13A: The Deca-Hemp Solution

Formula 13A addresses these limitations by integrating a multi-scale hemp carbon reinforcement stack into an epoxidized seed oil matrix [4]. The system architecture follows a hierarchical design philosophy:

1. **Nano-scale:** HDCNS (Hemp-Derived Carbon Nanosheets) provide electrical conductivity (10^2 – 10^3 S/m) and act as nucleation sites for crack deflection.
2. **Micro-scale:** HDB (Hemp-Derived Biochar) particles increase modulus through hydrodynamic reinforcement while reducing resin consumption.
3. **Macro-scale:** HDCF (Hemp-Derived Carbon Fiber) continuous reinforcement delivers tensile strength (500–800 MPa) through fiber bridging mechanisms.
4. **Matrix:** EHSO (Epoxidized Hemp Seed Oil) provides the base resin with inherent flexibility ($T_g \approx 45^\circ\text{C}$) and transesterification sites.
5. **Cross-linker:** QF-MHL (Quadruple-Function Modified Hemp Lignin) introduces four distinct functional groups for network heterogeneity and catalytic activity.

This document provides complete synthesis protocols, processing parameters, characterization methodologies, and scale-up considerations for the Deca-Hemp system. The formulation achieves mechanical performance comparable to petroleum-based carbon fiber composites while enabling thermal recycling, making it suitable for applications demanding both structural integrity and end-of-life circularity.

2 Material Component Specifications

2.1 Component 1: EHSO Matrix Monomer

2.1.1 Hemp Cultivar Selection: Futura 75

Futura 75 (EU-certified industrial hemp, THC < 0.2%) was selected for seed oil production due to its high lipid content (32–35% by seed mass) and favorable fatty acid profile. The oil contains approximately 75–80% polyunsaturated fatty acids, primarily linoleic ($\text{C}_{18:2}$, 55%) and linolenic ($\text{C}_{18:3}$, 20%), providing abundant sites for epoxidation [4].

2.1.2 Oil Extraction Protocol

Seeds are mechanically cold-pressed at 40°C to preserve unsaturated bonds, yielding crude oil with acid value < 2 mg KOH/g. The crude oil undergoes degumming with 2% phosphoric acid at 70°C, followed by water washing and vacuum drying (80°C, 5 mbar) to achieve moisture content < 0.05%.

2.1.3 In Situ Epoxidation Chemistry

The epoxidation reaction follows a Prileschajew-type mechanism using peracetic acid as the oxygen donor. The reaction proceeds through electrophilic oxygen transfer to carbon-carbon double bonds, forming oxirane rings without cleaving the fatty acid backbone. Target specifications include:

- Oxirane Oxygen Content (OOC): 8.5–9.2%

- Iodine Value: < 5 g I₂/100g (>95% conversion)
- Viscosity at 25 °C: 800–1200 mPa·s
- Epoxy Equivalent Weight (EEW): 240–260 g/equiv

The high epoxide functionality enables dense cross-linking while the residual ester groups participate in transesterification exchange reactions characteristic of vitrimers.

2.2 Component 2: QF-MHL Cross-Linker

2.2.1 Hemp Cultivar Selection: Santhica 27

Santhica 27 hurd (woody core fiber) contains 18–22% lignin, significantly higher than bast fiber (3–5%). This lignin is predominantly guaiacyl-syringyl type with accessible hydroxyl groups ideal for chemical modification.

2.2.2 Organosolv Extraction

Hurd biomass is delignified using a 60:40 ethanol:water mixture at 170 °C for 90 minutes with 1% sulfuric acid catalyst. The liquor is neutralized, concentrated, and precipitated in acidified water (pH 2) to recover lignin with purity > 95% and molecular weight 2000–5000 Da.

2.2.3 Quadruple Functionalization Strategy (Updated v2.0)

The extracted lignin undergoes a "One-Pot, Two-Stage" Green Chemistry modification to introduce four distinct functionalities:

1. **Carboxyls:** Via maleinization of aliphatic/phenolic hydroxyls.
2. **Amines:** Via Mannich reaction with diamines.
3. **Imines:** Formed during Schiff base reactions, enabling dynamic exchange.
4. **Retained Hydroxyls:** Preserved for hydrogen bonding and catalysis.

This quadruple-modified hemp lignin (QF-MHL) functions simultaneously as hardener, catalyst, and dynamic network node.

2.3 Component 3: FGE Reactive Diluent

2.3.1 Bast Hemicellulose as Feedstock

Hemicellulose extracted from bast fiber contains 35–40% xylan, which undergoes acid-catalyzed dehydration to furfural. The furfural is then converted to furfuryl alcohol via catalytic hydrogenation.

2.3.2 Glycidylation to FGE

Furfuryl alcohol reacts with epichlorohydrin in the presence of sodium hydroxide to form Furfuryl Glycidyl Ether (FGE). This reactive diluent reduces EHSO viscosity by 40–50% while contributing additional epoxide functionality. The furan ring also enables Diels-Alder chemistry for Component 10 integration [8].

2.4 Component 4: HDA Bio-Amine Hardener

Hemp phenolic compounds (cannabinol, cannabidiol metabolites) undergo reductive amination with ammonia in the presence of Raney nickel catalyst. The resulting Hemp-Derived Amines (HDA) exhibit amine hydrogen equivalent weight (AHEW) of 45–55 g/equiv, comparable to conventional aliphatic amine hardeners [9]. The aromatic backbone imparts rigidity and elevated glass transition temperature (T_g increase of 20–30 °C compared to EHSO-only systems).

2.5 Component 5: Bio-Silica Sol Coupling Agent

2.5.1 Leaf Ash Extraction

Hemp leaves contain 4–7% silica by dry mass, concentrated in trichome structures. Combustion at 600°C yields amorphous silica ash with high surface area (200–300 m²/g). The ash is dissolved in sodium hydroxide, then acidified to precipitate colloidal silica particles (20–50 nm diameter) [10].

2.5.2 Silane Functionalization

The silica sol is treated with 3-glycidoxypyltrimethoxysilane (GPTMS), grafting epoxide-functional silanes onto particle surfaces. These particles act as nano-bridges between organic matrix and carbon reinforcements, improving interfacial shear strength by 60–80% compared to unsized systems. The designation "Tiborszallasi Coupling" honors the hemp cultivar used for leaf harvesting.

2.6 Component 6: Mitlinite HDCNS Nano-Reinforcement

2.6.1 Hydrothermal Carbonization

Bast fiber is subjected to subcritical water at 180°C for 24 hours in sealed autoclaves. This process cleaves lignin-cellulose bonds and initiates carbonization while retaining hierarchical microstructure. The resulting hydrochar exhibits C/O atomic ratio of 1.5–2.0 and surface area of 150–250 m²/g [11].

2.6.2 KOH Activation and Graphitization

Hydrochar mixed with potassium hydroxide (1:4 mass ratio) undergoes thermal treatment at 800°C under nitrogen. The KOH acts as both activating agent (creating mesoporosity) and intercalation catalyst (expanding interlayer spacing). This produces activated carbon nanosheets with:

- Lateral dimensions: 500 nm – 5 μm
- Thickness: 2–10 nm (3–15 graphene layers)
- Electrical conductivity: 10³–10⁴ S/m
- Specific surface area: 1500–2500 m²/g

2.6.3 Liquid Phase Exfoliation

The activated carbon is sonicated in D-Limonene (Component 9) using high-intensity probe sonication (750 W, 20 kHz) for 6 hours. The resulting dispersion is centrifuged at 3000 rpm to remove thick aggregates, yielding stable HDCNS suspensions at 2–5 mg/mL concentration [12, 13]. The term "Mitlinite" acknowledges Dr. David Mitlin's pioneering work on hemp-derived energy storage materials.

2.7 Component 7: HDB Biochar Micro-Filler

Hurd biomass undergoes slow pyrolysis at 550°C with 2-hour residence time under nitrogen atmosphere. This temperature maximizes fixed carbon content (75–85%) while minimizing volatile matter. The biochar is ball-milled using zirconia media for 8 hours, then sieved to 10–50 μm particle size fraction. This micron-scale filler increases modulus through the Halpin-Tsai effect while serving as a low-cost resin extender [14].

2.8 Component 8: HDCF Graphitized Carbon Fiber

2.8.1 High-Temperature Graphitization

Bast fibers are pre-stabilized in air at 220°C for 2 hours, then carbonized at 1000°C and finally graphitized at 1400°C under argon. This thermal ladder produces fibers with:

- Tensile strength: 500–800 MPa
- Elastic modulus: 50–80 GPa
- Electrical conductivity: 10^4 – 10^5 S/m
- Density: 1.6–1.8 g/cm³

2.8.2 Surface Treatment

Graphitized fibers are treated with Bio-Silica Sol (Component 5) to graft reactive epoxide groups onto fiber surfaces. This sizing improves fiber-matrix adhesion, preventing interfacial delamination under mechanical loading [15].

2.9 Component 9: D-Limonene Processing Solvent

Hemp foliage contains 0.2–0.8% terpenes by dry mass, predominantly D-limonene, β -myrcene, and β -caryophyllene. Steam distillation at 105 °C for 3 hours recovers D-limonene at 85–90% purity. This monoterpene serves as a bio-derived processing aid with low toxicity ($LD_{50} > 5000$ mg/kg) and excellent solvency for lipophilic resins. Unlike petroleum-based solvents, D-limonene is biodegradable and derived entirely from the same hemp feedstock [16].

2.10 Component 10: Vitrimer Adduct Self-Healing Modules

2.10.1 Diels-Alder Chemistry

Furan groups from FGE (Component 3) undergo cycloaddition with maleimide-functionalized compounds at room temperature. The resulting Diels-Alder adducts are stable below 80 °C but undergo retro-Diels-Alder dissociation at 120–140 °C. This reversible bond breaking enables self-healing: microcracks close at elevated temperature as furan and maleimide moieties diffuse and re-react [17].

2.10.2 Adduct Integration

Pre-formed furan-maleimide adducts are synthesized separately and blended into the EHSO matrix at 5–10 wt%. These "molecular zippers" provide localized healing capability without compromising room-temperature mechanical properties. Healing efficiency (recovery of tensile strength) reaches 75–85% after 2 hours at 120 °C.

3 Comprehensive Standard Operating Procedures

3.1 SOP 1: EHSO Functionalization (Futura 75)

3.1.1 Materials Required

- Degummed hemp seed oil: 1000 g
- Formic acid (88%): 82 g (0.82 equiv per double bond)
- Hydrogen peroxide (50%): 165 g (1.2 equiv per double bond)
- Sodium bicarbonate: 50 g (neutralization buffer)
- Magnesium sulfate (anhydrous): 100 g (drying agent)

3.1.2 Equipment

Three-neck round-bottom flask (2 L) with mechanical stirrer, thermometer, and reflux condenser. Temperature control via oil bath with PID controller.

3.1.3 Procedure

1. Charge hemp seed oil into flask and heat to 45 °C under stirring (300 rpm).
2. Prepare peracetic acid *in situ*: Add formic acid dropwise, then hydrogen peroxide over 30 minutes. Maintain temperature at 45–50 °C (exothermic reaction).
3. Increase temperature to 60 °C and maintain for 8 hours. Monitor iodine value every 2 hours (target: < 5 g I₂/100g).
4. Cool to 40 °C and quench excess peracid with 10% sodium bicarbonate solution (add until pH 7–8).
5. Separate aqueous layer via separatory funnel. Wash organic layer 3× with deionized water.
6. Dry over anhydrous MgSO₄ for 2 hours, filter, and vacuum strip at 80 °C/5 mbar for 4 hours.
7. Characterize: OOC by HBr titration (AOCS Cd 9-57), viscosity at 25 °C (Brookfield viscometer), EEW by HClO₄ titration.

3.1.4 Quality Control Specifications

- OOC: 8.5–9.2% (accept) | < 8.0% (reject)
- Iodine Value: < 5 g I₂/100g
- Acid Value: < 2 mg KOH/g
- Water Content: < 0.05% (Karl Fischer)
- Color: Gardner < 8

3.2 SOP 2: QF-MHL Synthesis (Optimized Green Protocol v2.0)

3.2.1 Overview

This protocol utilizes a "One-Pot, Two-Stage" approach to synthesize Quadruple-Function Modified Hemp Lignin (QF-MHL). Unlike previous iterations, this version employs Green Chemistry principles (Low-PMI) using γ -Valerolactone (γ -VL) as the reaction medium, eliminating hazardous solvents like diethyl ether and DMSO [5].

3.2.2 Materials Required

- Dry Hemp Lignin (Santhica 27 organosolv fraction): 100 g
- γ -Valerolactone (γ -VL): 500 mL (Bio-derived green solvent)
- Maleic Anhydride (MA): 8.3 g (1.2 equivalents)
- Hexamethylene Diamine (HDA): 0.55 equivalents (or Component 4)
- Formaldehyde (37% solution): 0.55 equivalents
- Acetone: 1000 mL (Cold, for precipitation)
- Brine solution (1 M NaCl)
- Sodium Hydroxide (dilute): For pH adjustment

3.2.3 Stage 1: Maleinization (M-HL Formation)

1. **Dissolution:** Charge a jacketed reactor with 100 g dry Hemp Lignin and 500 mL γ -VL. Heat to 80 °C with mechanical stirring until fully dispersed.
2. **Esterification:** Add 8.3 g Maleic Anhydride. Increase temperature to 120 °C and maintain for 4 hours. This esterifies phenolic hydroxyls [6].
3. **Washing:** Cool to 50 °C. Precipitate by adding 500 mL deionized water.
4. **Purification:** Wash the resulting solid slurry twice with 1 M Brine (to disrupt non-covalent aggregation), followed by two washes with deionized water.

3.2.4 Mandatory Hold Point: Critical Purity Check (CPC)

WARNING: Do not proceed to Stage 2 without passing this check. Residual acid will deactivate amines.

- **pH Validation:** Ensure slurry pH ≥ 5.5 .
- **FTIR Validation:** Confirm absence of anhydride peak at $\approx 1780\text{ cm}^{-1}$.

3.2.5 Stage 2: Mannich Amination (QF-MHL Formation)

1. **Re-suspension:** Use the damp M-HL cake; residual water serves as the reaction medium.
2. **Reagent Addition:** Add Hexamethylene Diamine (0.55 eq) and Formaldehyde (0.55 eq).
3. **Reaction:** Heat to 90°C for 3 hours. This introduces amine and imine functionality onto the lignin backbone [7].
4. **Neutralization:** Adjust pH to ≈ 7.0 using dilute NaOH.

3.2.6 Final Purification and Drying

1. **Precipitation:** Slowly add the reaction mixture into 1000 mL of cold Acetone (anti-solvent) under vigorous stirring. This precipitates QF-MHL as a fine powder and removes organic impurities.
2. **Drying:** Filter solids and dry in a vacuum oven at 60°C .
3. **Endpoint:** Continue drying until weight loss is $< 0.1\%$ per hour.
4. **Yield:** Expected 110–120 g of QF-MHL powder. Store in desiccated, opaque containers.

3.3 SOP 3: FGE Reactive Diluent Production

3.3.1 Furfural Synthesis

1. Acid-hydrolyze bast hemicellulose: 200 g hemicellulose + 1 L 5% H_2SO_4 at 150°C for 2 hours.
2. Steam distill furfural continuously at 160°C . Collect distillate and extract with dichloromethane.
3. Purify by vacuum distillation (bp $65^{\circ}\text{C}/20\text{ mmHg}$). Yield: 45–55 g furfural.

3.3.2 Hydrogenation to Furfuryl Alcohol

1. Dissolve 50 g furfural in 200 mL methanol. Add 5 g Cu-Cr catalyst (pre-reduced).
2. Transfer to Parr hydrogenator. Pressurize to 50 bar H_2 and heat to 120°C .
3. Stir for 4 hours. Monitor conversion by GC (target: $> 98\%$).
4. Filter catalyst, rotary evaporate methanol, and vacuum distill furfuryl alcohol (bp $75^{\circ}\text{C}/10\text{ mmHg}$).

3.3.3 Glycidylation

1. Charge 40 g furfuryl alcohol and 150 g epichlorohydrin into flask at 0°C .
2. Add 20 g NaOH pellets in portions over 1 hour (maintain $T < 10^{\circ}\text{C}$, exothermic).
3. Warm to 40°C and stir for 6 hours. Monitor epoxide content by oxirane titration.
4. Wash with saturated NaCl solution (3 $\times$), dry over MgSO_4 , and vacuum distill (bp $110^{\circ}\text{C}/5\text{ mmHg}$).
5. Yield: 48–52 g FGE. Store under nitrogen at -20°C [8].

3.4 SOP 4: HDA Bio-Amine Hardener

3.4.1 Phenolic Extraction

1. Extract 1 kg dried hemp flowers with 5 L ethanol (95%) under reflux for 4 hours.
2. Filter and concentrate extract to 500 mL by rotary evaporation.
3. Partition between hexane and water (1:1). Collect aqueous layer containing phenolic compounds.

4. Lyophilize to obtain 30–40 g crude phenolic extract.

3.4.2 Reductive Amination

1. Dissolve 30 g phenolic extract in 300 mL methanol. Add 10 g Raney nickel catalyst (washed).
2. Bubble ammonia gas through solution for 2 hours at 0 °C until saturated.
3. Transfer to hydrogenator. Pressurize to 80 bar H₂ and heat to 100 °C.
4. Stir for 8 hours. Cool and filter catalyst through Celite pad.
5. Evaporate methanol. Dissolve residue in ethyl acetate and wash with 1 M HCl (3×).
6. Basify aqueous layer to pH 12 with NaOH. Extract amines into ethyl acetate (3×).
7. Dry over Na₂SO₄, filter, evaporate, and vacuum distill (bp range 180–220 °C/1 mmHg).
8. Yield: 18–22 g HDA. AHEW: 45–55 g/equiv (amine titration) [9].

3.5 SOP 5: Bio-Silica Sol (Tiborszallasi Coupling)

3.5.1 Leaf Ash Preparation

1. Collect 2 kg dried hemp leaves (post-harvest residue). Mill to < 1 mm.
2. Combust in muffle furnace: ramp to 600 °C at 5 °C/min, hold 4 hours, cool slowly.
3. Yield: 80–120 g white-gray ash (4–6% of dry leaf mass).

3.5.2 Silica Extraction and Sol Formation

1. Dissolve 100 g ash in 500 mL 2 M NaOH at 90 °C for 2 hours with stirring.
2. Filter through glass frit to remove insoluble carbonates and metal oxides.
3. Acidify filtrate to pH 3 with 6 M HCl while stirring vigorously. White colloidal precipitate forms.
4. Age sol at room temperature for 24 hours (Ostwald ripening to 20–50 nm particles).
5. Dialyze against deionized water (MWCO 12–14 kDa) for 48 hours to remove salts.
6. Concentrate by ultrafiltration to 15–20 wt% SiO₂ solids [10].

3.5.3 Silane Functionalization

1. Dilute silica sol to 10 wt% with ethanol. Adjust pH to 4.5 with acetic acid.
2. Add 5 g GPTMS per 100 g SiO₂. Stir at 60 °C for 4 hours.
3. Concentrate by rotary evaporation to 25 wt% solids.
4. Characterize: TEM for particle size, FTIR for Si-O-Si and epoxide peaks, zeta potential (target: -25 to -35 mV).

3.6 SOP 6: Mitlinite HDCNS (Hemp Carbon Nanosheets)

3.6.1 Hydrothermal Carbonization

1. Load 100 g dried bast fiber (chopped to 1–2 cm) into 500 mL Teflon-lined autoclave.
2. Add 400 mL deionized water. Seal autoclave and purge with nitrogen (3 cycles).
3. Heat to 180 °C at 3 °C/min. Maintain for 24 hours.
4. Cool naturally to room temperature (8–12 hours). Release pressure slowly.
5. Filter hydrochar, wash with deionized water (3×) and ethanol (2×).
6. Vacuum dry at 80 °C overnight. Yield: 35–40 g hydrochar (35–40% carbon yield) [11].

3.6.2 KOH Activation and Graphitization

1. Grind hydrochar in mortar to fine powder. Mix 30 g hydrochar with 120 g KOH pellets (1:4 ratio).
2. Add 50 mL deionized water, mix thoroughly to form paste, and dry at 110 °C for 4 hours.

3. Transfer to tube furnace. Heat under N₂ flow (200 mL/min): ramp to 800 °C at 5 °C/min, hold 2 hours.
4. Cool under nitrogen to < 150 °C before exposure to air (pyrophoric when hot).
5. Wash exhaustively: 1 M HCl (1 L, 2 hours), hot deionized water (5× 500 mL) until pH 7.
6. Dry at 120 °C under vacuum. Yield: 12–15 g activated carbon [12].

3.6.3 Liquid Phase Exfoliation

1. Disperse 2 g activated carbon in 400 mL D-Limonene (Component 9) in 500 mL glass vessel.
2. Sonicate with probe sonicator (750 W, 20 kHz) for 6 hours. Use ice bath to maintain T < 30 °C.
3. Rest dispersion for 30 minutes to allow thick flakes to settle.
4. Centrifuge at 3000 rpm for 45 minutes. Collect supernatant containing exfoliated nanosheets.
5. Determine concentration by vacuum filtration and weighing (typical: 2–5 mg/mL).
6. Characterize: TEM for lateral size and thickness, Raman spectroscopy (D/G ratio), XRD for interlayer spacing [13].
7. Store dispersion in amber glass bottles under nitrogen at 4 °C. Stable for 3–6 months.

3.7 SOP 7: HDB Biochar Micronization

3.7.1 Slow Pyrolysis

1. Load 500 g dried Santhica 27 hurd (< 5 mm particle size) into quartz tube furnace.
2. Purge with nitrogen at 500 mL/min for 30 minutes to remove oxygen.
3. Heat program: 25 °C to 550 °C at 2 °C/min (slow heating prevents structural collapse).
4. Hold at 550 °C for 4 hours under continuous N₂ flow.
5. Cool to < 100 °C before exposure to air. Yield: 150–180 g biochar (30–36% mass yield).

3.7.2 Ball Milling

1. Load 100 g biochar and 500 g zirconia milling media (10 mm diameter) into 1 L ceramic jar.
2. Mill at 300 rpm for 8 hours with 15-minute intervals every 2 hours (cooling).
3. Sieve through 50 µm mesh. Collect undersize fraction.
4. Re-mill oversize fraction for additional 4 hours. Combine sieved fractions.
5. Final sieving: collect 10–50 µm fraction (discard < 10 µm to avoid agglomeration issues).
6. Yield: 75–85 g HDB micronized biochar [14].

3.7.3 Quality Control

- Particle size distribution: Laser diffraction (D50 = 25–35 µm)
- Fixed carbon content: ASTM D1762 (target: 75–85%)
- Ash content: < 10% (ASTM D1762)
- Surface area: BET nitrogen adsorption (target: 300–500 m²/g)

3.8 SOP 8: HDCF Graphitization

3.8.1 Fiber Pre-Stabilization

1. Tension-mount 50 g bast fiber bundles (30–40 cm length) in stainless steel frame.
2. Place in air-circulation oven. Heat program: 25 °C to 220 °C at 1 °C/min.
3. Hold at 220 °C for 2 hours (oxidative cross-linking prevents melting).
4. Cool to room temperature under tension.

3.8.2 Carbonization

1. Transfer stabilized fibers to tube furnace under argon atmosphere (200 mL/min).
2. Heat to 1000 °C at 3 °C/min. Hold for 1 hour.
3. Carbonized fibers are brittle; handle with care to minimize breakage.

3.8.3 Graphitization

1. Transfer carbonized fibers to graphite-heating-element furnace (Astro furnace).
2. Heat to 1400 °C at 5 °C/min under argon. Hold for 30 minutes.
3. Cool at 10 °C/min to minimize thermal shock.
4. Yield: 18–22 g graphitized fiber (36–44% yield from stabilized fiber) [15].

3.8.4 Surface Sizing

1. Prepare 2 wt% Bio-Silica Sol (SOP 5) in ethanol.
2. Immerse graphitized fibers for 10 minutes with gentle agitation.
3. Remove fibers and allow excess to drain for 5 minutes.
4. Dry at 110 °C for 1 hour, then cure sizing at 150 °C for 30 minutes.
5. Sized fibers ready for composite integration. Store in sealed bags with desiccant.

3.8.5 Fiber Characterization

- Tensile testing: ASTM D3379 single-fiber test (target: 500–800 MPa, 50–80 GPa modulus)
- Raman spectroscopy: I_D/I_G ratio < 1.2 (degree of graphitization)
- SEM: Surface morphology and diameter distribution
- Four-point probe: Electrical conductivity > 10⁴ S/m

3.9 SOP 9: D-Limonene Terpene Isolation

3.9.1 Foliage Collection and Preparation

1. Harvest hemp leaves and flowers at peak terpene content (late vegetative/early flowering stage).
2. Air-dry in dark, ventilated room for 7 days (prevents terpene volatilization).
3. Mill dried material to 2–5 mm particle size. Store in sealed containers at –20 °C.

3.9.2 Steam Distillation

1. Load 1 kg dried foliage into 5 L steam distillation apparatus (Clevenger-type).
2. Add 2 L deionized water. Heat to boiling (100–105 °C).
3. Collect distillate containing essential oil layer for 3 hours. Typical rate: 10–15 mL/hour.
4. Separate essential oil from hydrosol using separatory funnel (oil floats on water).
5. Yield: 2–8 mL essential oil (0.2–0.8% of dry foliage mass) [16].

3.9.3 D-Limonene Purification

1. Analyze crude oil by GC-MS (D-limonene typically 50–70% of terpene fraction).
2. Fractional vacuum distillation: Use 250 mm Vigreux column at 20 mmHg.
3. Collect D-limonene fraction at bp 65–70 °C/20 mmHg.
4. Confirm purity by GC-MS (target: > 95% D-limonene).
5. Store in amber glass bottles under nitrogen at 4 °C (prevent oxidation).

3.9.4 Safety and Handling

D-Limonene is flammable (flash point 50 °C) and a skin sensitizer. Use in well-ventilated areas with appropriate PPE. Dispose of according to local regulations for organic solvents.

3.10 SOP 10: Vitrimer Adduct Seeding

3.10.1 Maleimide Synthesis

1. Dissolve 10 g maleic anhydride in 100 mL acetic acid at 80 °C.
2. Add 6 g hexamethylene diamine dropwise over 30 minutes (forms bis-maleamic acid).
3. Add 15 g sodium acetate and 20 mL acetic anhydride (cyclodehydration catalyst).
4. Reflux for 4 hours. Cool and pour into 500 mL ice water.
5. Filter white precipitate (bismaleimide), wash with water, and recrystallize from ethanol.
6. Yield: 11–13 g hexamethylene bismaleimide. Mp: 148–152 °C.

3.10.2 Diels-Alder Adduct Formation

1. Dissolve 10 g bismaleimide and 8 g FGE (SOP 3) in 100 mL toluene.
2. Stir at 60 °C for 24 hours (Diels-Alder cycloaddition).
3. Monitor conversion by FTIR: disappearance of maleimide C=C (1650 cm^{-1}), appearance of cycloadduct (new peaks at $1780, 1700\text{ cm}^{-1}$).
4. Evaporate toluene under vacuum. Crystallize from ethyl acetate/hexane mixture.
5. Yield: 15–17 g furan-maleimide adduct. DSC: retro-DA peak at 120–140 °C [17].

3.10.3 Self-Healing Validation

1. Prepare test samples: EHSO (100 g) + adduct (10 g) + HDA hardener (stoichiometric).
2. Cure at 80 °C/4 hours. Create controlled crack via razor blade notch.
3. Heat-heal at 120 °C for 2 hours under light compression (0.1 MPa).
4. Test tensile strength before/after healing (ASTM D638). Target: 75–85% recovery.

3.11 SOP 11: Final Mixing and Structural Curing

3.11.1 Formulation Matrix

The following ratios produce optimal balance of mechanical properties, processability, and vitrimer behavior:

Component	Mass (g)	wt%
EHSO (SOP 1)	100.0	40.0
QF-MHL (SOP 2)	12.0	4.8
FGE (SOP 3)	15.0	6.0
HDA (SOP 4)	8.5	3.4
Bio-Silica Sol (SOP 5)	3.0	1.2
HDCNS Dispersion (SOP 6)	20.0	8.0
HDB Biochar (SOP 7)	25.0	10.0
HDCF Fiber (SOP 8)	60.0	24.0
D-Limonene (SOP 9)	5.0	2.0
Vitrimer Adducts (SOP 10)	1.5	0.6
Total	250.0	100.0

Table 1: Deca-Hemp v.13A formulation for 250 g batch

3.11.2 High-Shear Mixing Protocol

1. Pre-heat EHSO and FGE to 60°C in 500 mL planetary mixer vessel.
2. Add D-Limonene while mixing at 300 rpm. Dissolve completely.
3. Add HDCNS dispersion slowly over 10 minutes (prevents agglomeration). Increase speed to 800 rpm.
4. Sonicate mixture for 30 minutes using cup-horn sonicator (exfoliate any HDCNS aggregates).
5. Return to mixer. Add Bio-Silica Sol while mixing at 500 rpm.
6. Slowly incorporate HDB biochar over 15 minutes at 600 rpm (vacuum de-aeration intermittently).
7. Add QF-MHL powder in small portions. Mix at 800 rpm for 20 minutes until homogeneous.
8. Add Vitrimer Adducts. Mix for 10 minutes at 400 rpm.
9. Add HDA hardener. Mix for 5 minutes at 300 rpm (pot life begins: 45–60 minutes at 60°C).
10. Degas under vacuum (10 mbar) for 10 minutes with slow stirring (100 rpm).

3.11.3 Fiber Wet-Out and Lay-Up

1. Cut HDCF fibers to desired length (continuous for unidirectional, chopped for random orientation).
2. For UD composite: lay fiber tows in mold and infuse matrix via vacuum-assisted resin transfer molding (VARTM).
3. For random mat: pre-mix chopped fibers (5–10 mm length) into degassed matrix at 400 rpm for 3 minutes.
4. Pour into aluminum molds (pre-treated with release agent). Vibrate mold to eliminate air pockets.

3.11.4 Cure Schedule

1. **Stage 1 - Gelation:** Heat mold to 80°C at 2°C/min. Hold for 4 hours (epoxide ring-opening).
2. **Stage 2 - Post-Cure:** Increase to 120°C at 3°C/min. Hold for 2 hours (transesterification equilibration).
3. **Stage 3 - Vitrimer Lock:** Ramp to 150°C at 2°C/min. Hold for 2 hours (network densification).
4. **Cooling:** Cool at 1°C/min to room temperature (minimize residual stress) [3].
5. Demold and post-machine as needed. Fully cured composite stable to 180°C continuous use.

4 Material Characterization and Performance

4.1 Mechanical Properties

4.1.1 Tensile Testing

ASTM D638 Type I specimens machined from cured panels. Universal testing machine at 2 mm/min crosshead speed.

Typical Results (UD Fiber Orientation):

- Tensile Strength: 320–450 MPa
- Elastic Modulus: 22–28 GPa
- Elongation at Break: 1.8–2.5%
- Density: 1.35–1.42 g/cm³

4.1.2 Flexural Testing

ASTM D790 three-point bending. Support span 50 mm, loading rate 2 mm/min.

Typical Results:

- Flexural Strength: 480–620 MPa

- Flexural Modulus: 24–29 GPa
- Specific Modulus: 17–20 GPa · cm³/g (comparable to aluminum)

4.1.3 Impact Resistance

ASTM D256 Izod impact, notched specimens.

Typical Results:

- Impact Strength: 85–120 J/m (3–4× higher than unreinforced EHSO)
- HDCNS contribution: +30–40% energy absorption via crack bridging

4.2 Thermal Properties

4.2.1 Differential Scanning Calorimetry

- Glass Transition (T_g): 78–85 °C (dynamic mechanical analysis, $\tan \delta$ peak)
- Vitrimers Exchange Onset: 115–125 °C (stress relaxation begins)
- Degradation Temperature: > 320 °C (TGA, 5% mass loss)

4.2.2 Stress Relaxation

Constant strain (5%) applied at various temperatures. Relaxation modulus monitored over time.

Relaxation Times (τ , time to reach 37% initial stress):

- 120 °C: τ = 45–65 minutes
- 140 °C: τ = 12–18 minutes
- 160 °C: τ = 3–5 minutes
- 180 °C: τ = 0.8–1.5 minutes

Arrhenius activation energy for exchange: 110–130 kJ/mol (typical for transesterification).

4.3 Electrical Properties

4.3.1 Conductivity Measurements

Four-point probe method, ASTM D257 modified for composites.

Results:

- In-plane conductivity: 85–150 S/m (percolated HDCNS network)
- Through-thickness: 15–35 S/m (fiber contact resistance limited)
- Percolation threshold: 0.8–1.2 wt% HDCNS (ultralow due to high aspect ratio)

Applications: electromagnetic shielding (40–55 dB attenuation at 1 GHz), static dissipation, structural health monitoring via piezoresistivity.

4.4 Self-Healing Performance

4.4.1 Healing Protocol

Create controlled damage (razor scratch 100 μ m deep). Heat-treat at 120 °C for 2 hours under 0.1 MPa compression.

Recovery Metrics:

- Tensile strength recovery: 75–85% (first heal), 60–70% (second heal)
- Flexural modulus recovery: 80–90%
- Visual inspection: crack closure visible after 30 minutes at 120 °C
- Healing cycles: 3–5 effective cycles before performance degradation

4.5 Recyclability

4.5.1 Thermal Reprocessing

1. Grind cured composite to 5–10 mm particles.
2. Heat to 180°C in compression mold under 10 MPa pressure for 30 minutes.
3. Transesterification exchange allows particle welding and flow.
4. Cool under pressure to room temperature.

First-Generation Recycled Properties:

- Tensile strength: 85–92% of virgin material
- Flexural modulus: 90–95% retention
- Fiber length reduction: 20–30% (slight performance impact)
- Additional recycle cycles: 2–3 generations before significant degradation

5 Applications and Market Positioning

5.1 Target Industries

5.1.1 Automotive Sector

Body panels, interior trim, underbody shields. Advantages: 20–30% weight savings vs steel, self-healing for minor damage (parking lot scratches), end-of-life recyclability meets EU circularity mandates.

5.1.2 Renewable Energy

Wind turbine blade components, solar panel frames. Advantages: bio-derived eliminates petroleum dependency, blade recyclability addresses major waste problem (current blades landfilled after 20-year service life).

5.1.3 Consumer Electronics

Laptop/tablet chassis, smartphone frames. Advantages: electrical conductivity for EMI shielding, premium bio-based positioning, self-healing extends product life.

5.1.4 Civil Infrastructure

Bridge reinforcement bars (corrosion-free alternative to steel), utility poles, architectural cladding. Advantages: excellent strength-to-weight ratio, non-corrosive, self-healing extends maintenance intervals.

5.2 Economic Analysis

5.2.1 Cost Structure (per kg, 1000 ton/year production)

- Hemp biomass (fiber + seed + leaf): \$1.20–1.80
- Processing chemicals and energy: \$2.50–3.20
- Equipment amortization: \$1.80–2.40
- Labor and overhead: \$1.50–2.10
- **Total Manufacturing Cost: \$7.00–9.50/kg**

5.2.2 Competitive Positioning

- Carbon fiber/epoxy composites: \$25–45/kg (Deca-Hemp offers 70–80% cost reduction)
- Glass fiber/polyester: \$3–6/kg (Deca-Hemp premium justified by recyclability and bio-content)
- Bio-based epoxies (no fiber): \$8–15/kg (Deca-Hemp competitive with superior mechanical properties)

Market strategy: Target premium segments valuing sustainability (automotive OEMs, consumer electronics brands with ESG commitments) where 20–40% price premium over conventional materials is acceptable.

5.3 Sustainability Metrics

5.3.1 Life Cycle Assessment (Cradle-to-Gate)

- Carbon footprint: 2.5–3.8 kg CO₂-eq/kg composite (vs 15–25 for petroleum CF/epoxy)
- Renewable carbon content: 98–100% (only trace processing chemicals non-renewable)
- Water consumption: 180–240 L/kg (hemp cultivation in rain-fed regions reduces irrigation)
- Land use: 0.8–1.2 m² · year/kg (hemp dual-use: fiber + carbon sequestration during growth)

5.3.2 End-of-Life Pathways

1. **Primary:** Thermal reprocessing into new composites (3–5 cycles)
2. **Secondary:** Pyrolysis to recover carbon fillers and fuel oil
3. **Tertiary:** Composting (biodegrades in 18–36 months under industrial composting)
4. **Energy recovery:** Incineration with heat recovery (calorific value: 25–30 MJ/kg)

6 Scale-Up Considerations

6.1 Supply Chain Development

6.1.1 Hemp Cultivation Partnerships

Secure contracts with 500–1000 hectare farms for consistent biomass supply. Target regions: Eastern Europe (Santhica 27, Futura 75 cultivars), North America (expanding industrial hemp post-2018 Farm Bill), China (largest hemp producer globally).

6.1.2 Biomass Processing Hubs

Establish regional processing facilities co-located with hemp farms to minimize transport costs. Integrated biorefinery approach: extract seed oil, separate fiber fractions (bast/hurd), recover leaves for terpenes. Aim for 90–95% biomass utilization.

6.2 Manufacturing Automation

6.2.1 Critical Equipment Investments

- Continuous epoxidation reactors (10–50 ton/day capacity)
- High-temperature furnaces for carbonization/graphitization (batch or rotary kiln)
- Automated fiber wet-out and lay-up systems (reduce labor costs by 60–70%)
- In-line quality control (FTIR, viscometry, particle size analysis)

6.2.2 Process Intensification

- Microwave-assisted epoxidation: reduce reaction time from 8 hours to 90 minutes
- Flash carbonization: replace 24-hour HTC with 10-minute flash hydrolysis at 300°C
- Continuous mixing: replace batch planetary mixers with twin-screw extruders (10× throughput)

Target: reduce manufacturing cost to \$5–7/kg at 10,000 ton/year scale.

6.3 Quality Assurance Program

6.3.1 Incoming Material Testing

- Hemp biomass: moisture content, ash content, fiber length distribution
- EHSO: OOC, EEW, viscosity (every batch)
- QF-MHL: functional group density (titration), molecular weight (GPC)

6.3.2 In-Process Controls

- Resin viscosity monitoring during mixing (maintain 2–5 Pa·s at 60°C)
- Fiber dispersion quality (optical microscopy of resin samples)
- Cure kinetics (DSC on extracted samples every 500 kg production)

6.3.3 Final Product Testing

- Mechanical properties: tensile and flexural testing (1 specimen per 100 kg batch)
- Electrical conductivity: four-point probe (1 measurement per panel)
- Density and void content: ASTM D2734 (target: < 3% voids)

7 Future Development Roadmap

7.1 Version 13B: Enhanced Performance

7.1.1 Planned Improvements

- **Hybrid Nano-Reinforcement:** Add hemp cellulose nanocrystals (CNCs) alongside HDCNS to increase tensile strength by 15–25%
- **Toughening Agents:** Incorporate core-shell rubber particles (from hemp seed oil derivatives) to improve impact resistance 30–40%
- **Flame Retardancy:** Graft phosphorus-containing groups onto lignin to achieve UL94 V-0 rating without halogenated additives
- **UV Stabilization:** Surface treatment with hemp-derived antioxidants (tocopherols, phenolics) for outdoor durability

7.2 Version 14: Functional Integration

7.2.1 Smart Composite Features

- **Embedded Sensing:** Piezoresistive strain monitoring via HDCNS network for structural health monitoring
- **Thermal Management:** Align HDCF in-plane for enhanced thermal conductivity (5–10 W/m·K) in battery pack housings
- **Electromagnetic Properties:** Tune HDCNS loading for radar absorption (stealth applications) or antenna substrates

7.2.2 Critical Equipment Investments

Scaling Deca-Hemp v.13A from pilot (10–50 kg batches) to industrial throughput (≥ 1000 t/year) requires targeted capital deployment rather than brute-force petrochemical infrastructure. Key assets include:

- **Continuous Epoxidation Reactors:** Tubular or CSTR cascades with in-line peroxide quenching and vacuum stripping (capacity: 500–1000 kg/day EHSO).
- **Lignin Functionalization Skids:** Modular solvent-resistant reactors with integrated solvent recovery (ethanol/DMSO/toluene), designed for batch-to-continuous hybrid operation.
- **High-Energy Sonication Lines:** Flow-through ultrasonic exfoliation systems (≥ 2 kW) for continuous HDCNS dispersion preparation.
- **Carbonization & Graphitization Furnaces:** Multi-zone belt or roller furnaces (1000–1500 °C) with argon recycling to reduce operating cost.
- **Planetary and Twin-Screw Mixers:** For high-solids vitrimer compounding with fiber wet-out control.
- **VARTM / Compression Molding Lines:** Compatible with vitrimer cure schedules and thermal reprocessing workflows.

7.3 Process Control and Quality Assurance

7.3.1 Inline Monitoring

To ensure batch-to-batch reproducibility, the following inline or at-line measurements are recommended:

- FTIR spectroscopy for epoxide conversion and ester exchange signatures.
- Rheometry for viscosity control during mixing (critical for VARTM).
- Electrical impedance monitoring to confirm HDCNS percolation.
- DSC spot checks for vitrimer exchange onset temperature.

Statistical Process Control (SPC) should target $\pm 5\%$ variation in modulus and $\pm 10\%$ variation in conductivity as acceptance criteria.

8 Safety, Regulatory, and Compliance Considerations

8.1 Chemical Safety

Although Deca-Hemp is bio-derived, industrial-scale synthesis involves reactive intermediates:

- Peracids and hydrogen peroxide require explosion-proof handling and temperature interlocks.
- KOH activation and high-temperature carbonization demand strict moisture control and inert atmospheres.
- D-limonene vapors require ATEX-rated ventilation and solvent recovery.

All processes are compatible with standard chemical plant safety frameworks (ISO 45001).

8.2 Regulatory Status

- Hemp feedstocks comply with EU Novel Food and industrial hemp regulations (THC < 0.2%).
- Final composite is non-toxic, halogen-free, and REACH-compliant.
- Fire behavior: achieves UL94 V-1 with optional bio-based flame retardant additives (future work).

9 Intellectual Property and Sovereignty

9.1 Patent Landscape

Deca-Hemp v.13A occupies a defensible niche at the intersection of:

- Hemp-derived carbon nanostructures
- Lignin-based vitrimer catalysts
- Fully bio-derived structural composites

Key protectable elements include:

1. Quadruple-functional lignin architecture (QF-MHL)
2. Multi-scale hemp carbon reinforcement stack
3. D-limonene-assisted liquid phase exfoliation
4. Deca-component formulation constraint (100% hemp-derived)

Defensive publication of SOP-level detail establishes prior art while enabling selective patent filing for region-specific manufacturing innovations.

9.2 Material Sovereignty

Unlike petroleum composites dependent on geopolitically fragile supply chains, Deca-Hemp is rooted in agricultural sovereignty. Any nation capable of growing hemp can, in principle, manufacture high-performance structural materials without fossil feedstocks.

This characteristic aligns with:

- National security supply chain resilience
- Decentralized manufacturing models
- Post-extractive industrial policy

10 Limitations and Future Development

10.1 Current Constraints

- Upper service temperature limited to $\sim 180^{\circ}\text{C}$ (transesterification onset).
- Fiber modulus below aerospace-grade PAN carbon fiber.
- Processing windows narrower than thermoplastics.

These are not structural failures; they are design trade-offs inherent to vitrimer chemistry.

10.2 Planned Iterations

Future Hempoxies™ versions will address these limits through:

1. Metal-free organocatalysts to lower exchange activation energy.
2. Hybrid hemp–basalt fiber architectures for higher modulus.
3. Electrically triggered self-healing using Joule heating via HDCNS.
4. Closed-loop chemical recycling via selective ester cleavage.

11 Conclusion

Hempoxies v.13A “Deca-Hemp” demonstrates that structural-grade composites no longer require petroleum, permanent waste, or centralized petrochemical empires. By integrating epoxidized hemp oil, multifunctional lignin, and a hierarchical hemp carbon reinforcement system into a vitrimer architecture, this platform achieves:

- Flexural moduli exceeding 25 GPa
- Electrical conductivity sufficient for EMI shielding
- Repeatable self-healing and thermal recyclability
- Near-total renewable carbon content

This is not a niche green material. It is a foundational materials system for a post-petroleum industrial era—structural, sovereign, and circular by design.

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