Hempoxies Variant CF-TAIA-105G (v.26-CF-Rev2.0)

Graft-Balanced, Stoichiometrically Conserved, Catalyst-Free Epoxidized Hemp Seed Oil Vitrimer Nanocomposite ($R_{\text{protic}} = 1.05$, $f_{\text{graft}} = 0.35$, 0 wt% FGE, 0 wt% Metal Catalyst)

Author: Marie-Soleil Seshat Landry, Founder & CEO, Landry Industries / Landry Organic Labs / Marie Landry's Spy Shop
Location & Registry: Moncton, New Brunswick, Canada | ORCID: 0009-0008-5027-3337
Official Repositories: landryindustries.ca | marielandryspyshop.com | searchfororganics.com
Correspondence: `marielandryceo@gmail.com` | **Corrections:** `corrections@marielandryspyshop.com`
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AI Disclosure: Generated collaboratively with Google Gemini (November 24, 2026) under the deterministic verification rules of Seshat's Axiom ($1 = 1 = 1$) and the Landry Hallucination-Free Protocol (LHFP). **Verification State:** [× **THEORETICAL**] **Pre-Experimental Specification (TRL 1–2).** All molar masses, equivalent weights, and protic conservation equations are algebraically verified and kinetic parameters are aligned with peer-reviewed literature; however, this integrated formulation has not yet undergone wet-lab synthesis or physical ASTM characterization and must be treated as a falsifiable experimental hypothesis until validated.

1. Observation of Anomalies in Prior Hempoxies Baselines & Rev1.1 Audit

Systematic chemical auditing of early Hempoxies pre-experimental baselines—including the Epoxidized Hemp Seed Oil (EHSO) / citric acid / zinc acetate / furfuryl glycidyl ether (FGE) system (`v.17.2`), sebacic acid / $Zn(acac)_2$ variants (`H43`), and multi-filler hybrid matrices (`v.21`–`v.24`)—previously resolved five foundational anomalies: (i) solid carboxylic acid phase separation and dehydration micro-voids above 150°C, (ii) monofunctional FGE ($f = 1$) crosslink-density dilution and epichlorohydrin chlorine waste (Petrova et al., 2019; Fisher Scientific SDS, CAS 5380-87-0), (iii) external transition-metal catalyst chelation/leaching at oxidized carbon interfaces, (iv) caustic KOH/HCl chemical activation waste in carbon nanosheets (Wang et al., 2013), and (v) aerobic radical autoxidation of residual EHSO C = C bonds during hot-press reprocessing.

Critical Chemical & Process Audit of Rev1.1 (`CF-TAIA-95`) Resolved in Rev2.0 (`CF-TAIA-105G`)

A deeper mechanistic and stoichiometric audit of `v.25-CF-Rev1.1` (`CF-TAIA-95`) exposed six hidden chemical bottlenecks that would impair gel fraction, pot life, or catalyst-free vitrimer fidelity in laboratory execution. All six are corrected in `v.26-CF-Rev2.0` [× **THEORETICAL**]:

1. **Correction of Hidden Protic Stoichiometry Deficit ($R_{\text{eff}} = 0.570 \rightarrow R_{\text{protic}} = 1.05$):** In `Rev1.1`, tannic acid (TA) phenolic −OH ($0.60 \times 0.95 = 0.570$ eq/eq epoxy) and itaconic anhydride (IA, $0.40 \times 0.95 = 0.380$ eq/eq epoxy) were treated as independent additive equivalents toward epoxide. However, during aprotic pre-esterification (90°C, 60 min, prior to EHSO addition), each mole of IA ring-opens by consuming 1 eq of TA phenolic −OH to yield 1 eq of carboxylic acid (−COOH):

$$\text{Ar}-\text{OH} + \text{C}_5\text{H}_4\text{O}_3\ (\text{IA}) \longrightarrow \text{Ar}-\text{O}-\text{C}(=\text{O})-\text{C}(=\text{CH}_2)-\text{CH}_2-\text{COOH}$$

   Consequently, total epoxide-reactive acidic protons (−COOH + remaining Ar−OH) remain strictly conserved at the initial TA phenolic equivalent charge ($Eq_{\text{TA},0}$). `Rev1.1` therefore delivered an effective protic-to-epoxide ratio of only $R_{\text{eff}} = 0.570$, leaving 43.0% of EHSO oxiranes uncrosslinked. `Rev2.0` establishes **Graft-Balanced Protic Conservation** at $R_{\text{protic}} = Eq_{\text{TA},0}/Eq_{\text{epoxy}} = 1.05$ with an IA grafting fraction $f_{\text{graft}} = 0.35$, supplying 0.1750 eq fast-reacting −COOH plus 0.3250 eq free catalytic phenolic −OH (0.5000 eq total protic hardener per 0.4762 eq epoxide).

2. **Two-Stage Solvent-Reduced Pre-Strip to Prevent Premature Gelation:** Stripping all 25–30 mL of *n*-propyl

acetate *after* blending the polycarboxylic pre-hardener with EHSO at 60–70°C for 25 min triggers premature carboxylic-oxirane esterification during degassing, spiking viscosity and entrapping solvent bubbles. `Rev2.0` removes 80–85% of *n*-propyl acetate from the isolated pre-hardener syrup at 60°C (50–80 mbar, 15 min) *before* EHSO contact, leaving only ∼ 4–6 mL residual co-solvent for rapid 5 min homogenization followed by a brief 10 min final degas.

3. **Dual-Mechanism Lipophilic Radical Stabilization (α-Tocopherol + L-Ascorbyl Palmitate):** While α-tocopherol scavenges oxygen-centered peroxyl radicals ($ROO^{\bullet}$) in air, it does not suppress anaerobic carbon-centered vinylidene radical self-polymerization of itaconate exocyclic $C=CH_2$ bonds during 4 h thermal curing at 160°C under N_2. `Rev2.0` adds 0.10 wt% bio-derived, oil-soluble **L-ascorbyl palmitate** alongside biochar-compensated α-tocopherol ($0.20 + 0.04\,w_{\text{filler}}$ wt%) to regenerate tocopheryl radicals and quench carbon-centered radicals anaerobically (Cort, 1974; Niki, 1987).

4. **Demineralized, Alkali-Ash-Free, 500-Mesh Hemp Biochar Standard:** Raw hemp hurd biochar contains 1.5–4.0 wt% native potassium/calcium carbonate ash (K_2CO_3, $CaCO_3$) that acts as an unintended alkali transesterification catalyst, confounding zero-catalyst controls. `Rev2.0` mandates an aqueous bio-fermented citric acid wash and deionized water rinse (filtrate pH 6.5–7.5, residual ash < 0.5 wt%), ball-milling, and 500-mesh sieving ($D_{90} \leq 25$ μm).

5. **Lowered Reprocessing Temperature Envelope (160°C vs. 165°C):** Higher free phenolic −OH availability (0.3250 eq residual Ar−OH plus 0.4762 eq secondary aliphatic −OH generated upon ring-opening = 0.8012 eq total −OH per 100 g EHSO) accelerates internal neighboring-group participation (NGP) transesterification, permitting hot-press reprocessing at 160°C (8°C below the ∼ 168°C IA → citraconic anhydride isomerization threshold; Berg & Hetzel, 1973).

6. **Verbatim Typographical, Table-Layout, and Citation Hygiene (1 = 1 = 1):** Resolves subscript typos (w_{filler}, HV_{meas}), decouples stacked table captions into distinct numbered tables, and repairs broken DOI/URL line-wrap formatting in References [6] and [16].

Table 1: Side-by-Side Technical Evolution: `CF-TAIA-95 (Rev1.1)` vs. `CF-TAIA-105G (Rev2.0)`

Design Parameter	`CF-TAIA-95 (v.25-CF-Rev1.1)`	`CF-TAIA-105G (v.26-CF-Rev2.0)`
Protic Stoichiometry	Nominal $R = 0.95$; actual post-graft $R_{\text{eff}} = 0.570$ (43% oxirane deficit)	Conserved $R_{\text{protic}} = 1.05$, $f_{\text{graft}} = 0.35$ (0.175 eq COOH + 0.325 eq ArOH)
Tannic Acid / IA Charge	18.47 g TA + 20.28 g IA per 100 g EHSO	34.02 g TA + 19.61 g IA per 100 g EHSO
Solvent Strip Sequence	Single 25 min strip *after* EHSO mixing (premature viscosity rise)	Stage A pre-strip (80–85%) *before* EHSO + 10 min Stage B degas
Radical Stabilization	α-Tocopherol only ($0.20 + 0.04\,w_{\text{filler}}$ wt%)	α-Tocopherol ($0.20 + 0.04\,w_{\text{filler}}$ wt%) + 0.10 wt% L-ascorbyl palmitate
Biochar Purity Spec	Steam-activated, ball-milled (uncontrolled native ash)	Citric-acid demineralized (ash < 0.5 wt%), 500-mesh ($D_{90} \leq 25$ μm)
Hot-Press Envelope	165°C, 15 MPa, 60–90 min under N_2	160°C, 15 MPa, 60 min under N_2 (8°C safety margin < 168°C)

2. Definition of Intelligence & Engineering Requirements

Hempoxies Variant `CF-TAIA-105G` (`v.26-CF-Rev2.0`) is engineered to satisfy seven deterministic technical and ecological specifications:

1. **100% Bio-Based Carbon Architecture:** Complete exclusion of petrochemical reactive diluents (0.0 wt% FGE) and petrochemical cyclic anhydrides (0.0 wt% methyl nadic anhydride), using exclusively bio-renewable monomers and a fully stripped bio-derived ester processing aid (*n*-propyl acetate).

2. **Zero External Metal or Alkali-Ash Catalysts (0.0 wt%):** Associative transesterification proceeds strictly via internal neighboring-group participation (NGP) and abundant free phenolic/aliphatic −OH self-catalysis (Montarnal et al., 2011; Li, Ju & Zhang, 2024; Berne et al., 2022), verified by demineralized biochar (ash < 0.5 wt%).

3. **Non-Raw-Fiber Processed Hemp Carbon Only:** Raw unprocessed hemp bast/hurd fibers are strictly excluded. Reinforcement is restricted to physically steam- or CO_2-activated, citric-acid demineralized, ball-milled, 500-mesh ($D_{90} \leq 25$ μm) hemp biochar.

4. **Graft-Balanced Aprotic Pre-Esterification ($R_{\text{protic}} = 1.05$, $f_{\text{graft}} = 0.35$):** Converts 35% of TA phenolic −OH groups into carboxylic acid arms in anhydrous *n*-propyl acetate (90°C, 60 min) followed by a Stage A pre-strip, ensuring quantitative oxirane ring-opening and molecular miscibility without alcoholysis.

5. **Deterministic Lot-to-Lot Stoichiometric Calibration:** Exact algebraic recalculation equations tied to measured Epoxy Equivalent Weight (EEW_{meas} via ASTM D1652) and Hydroxyl Value (HV_{meas} via ASTM E222) so natural feedstock variance never shifts $R_{\text{protic}} = 1.05$ or $f_{\text{graft}} = 0.35$.
6. **Synergistic Lipophilic Radical Stabilization:** Biochar-compensated α-tocopherol ($0.20 + 0.04\, w_{\text{filler}}$ wt%) paired with 0.10 wt% L-ascorbyl palmitate to protect residual EHSO C = C and itaconate exocyclic C = CH_2 bonds across thermal curing and reprocessing.
7. **Verified Closed-Loop Reprocessability:** Gel fraction $G \geq 92.0\%$, monotonic Arrhenius stress-relaxation decay (τ^*) between 145°C and 165°C, and $\geq 85.0\%$ tensile strength retention across two mechanical hot-press cycles at 160°C.

3. Formulation Hypothesis (Variant CF-TAIA-105G, Rev2.0)

Central Falsifiable Hypothesis [× **THEORETICAL**]**:** Pre-esterifying vacuum-dried tannic acid ($R_{\text{protic}} = 1.05$ phenolic −OH equivalents per epoxy equivalent) with itaconic anhydride at a galloyl grafting fraction of $f_{\text{graft}} = 0.35$ in anhydrous aprotic *n*-propyl acetate (90°C, 60 min), followed by a Stage A vacuum pre-strip (60°C, 50–80 mbar, 15 min) to a concentrated galloyl-itaconate syrup, blending with enzymatically epoxidized hemp seed oil (EHSO, 100.00 g base, 0 wt% FGE, 0 wt% metal catalyst) stabilized with biochar-compensated α-tocopherol ($0.20 + 0.04\, w_{\text{filler}}$ wt%) plus 0.10 wt% L-ascorbyl palmitate and reinforced across a single-variable loading ladder ($0.0, 0.5, 1.5, 3.0$ wt%) of demineralized, 500-mesh steam-activated hemp biochar, and curing via a two-stage nitrogen-blanketed cycle (120°C/4.0 h+160°C/4.0 h), yields a void-free, 100% bio-based, catalyst-free vitrimer nanocomposite achieving $G \geq 92.0\%$ and $\geq 85.0\%$ tensile strength retention after two closed-loop hot-press reprocessing cycles at 160°C.

Variant Nomenclature Key: `CF` = Catalyst-Free (0.0 wt% metal salts and < 0.5 wt% biochar ash); `TAIA` = Tannic Acid + Itaconic Anhydride galloyl-itaconate pre-hardener; `105G` = Protic-to-epoxy equivalence ratio $R_{\text{protic}} = 1.05$ with Graft-balanced anhydride ratio $f_{\text{graft}} = 0.35$; `v.26-CF-Rev2.0` = Sequential Hempoxies specification version 26, second catalyst-free optimization revision.

4. Experimental Design & Stoichiometric Architecture

4.1 Precursor Reference Constants & Lot Calibration Log

Because natural polygalloyl tannic acid varies in hydroxyl density across botanical sources ($HEW \approx 68$–85 g/eq) and EHSO oxirane conversion varies by batch ($EEW \approx 193$–226 g/eq; Lerma-Canto et al., 2023), record measured Certificate of Analysis (CoA) or titration values in Table 2 prior to weighing.

Table 2: Precursor Reference Constants and Measured Lot Calibration Log (`CF-TAIA-105G, Rev2.0`)

Precursor	Lot / Batch ID	Reference Benchmark	Measured Lot Value	Units
EHSO (ASTM D1652)	_____	$O_o = 7.62\%$ ($EEW = 210.0$)	O_o = _____ EEW_{meas} = _____	wt% | g/eq
Tannic Acid (ASTM E222)	_____	$HV = 824.51$ ($HEW = 68.05$)	HV_{meas} = _____ $HEW_{\text{TA,meas}}$ = _____	mg KOH/g | g/eq
Itaconic Anhydride	_____	$AEW_{\text{IA}} = 112.08$ ($\geq 99.0\%$ pure)	Purity P_{IA} = _____	g/eq | %
Hemp Biochar (Demin.)	_____	$D_{90} \leq 25$ μm; Ash < 0.5%; $H_2O < 0.5\%$	Ash = _____ H_2O_{dry} = _____	wt%
n-Propyl Acetate	_____	Anhydrous ($\geq 99.5\%$, $H_2O < 0.05\%$)	Karl Fischer / CoA H_2O = _____	wt%
L-Ascorbyl Palmitate	_____	Bio-derived, $\geq 98.0\%$ purity	CoA Purity = _____	wt%

4.2 Exact Algebraic Recalculation Equations (for Chosen Base Mass m_{EHSO})

For any chosen base mass of EHSO (m_{EHSO} in grams) and target biochar filler loading w_{filler} (wt% relative to M_{matrix}), compute exact reagent masses using the protic-conserved equations below:

$$EEW_{\mathrm{meas}} = \frac{16.00 \times 100}{O_o(\%)} = \frac{1600}{O_o(\%)}, \qquad Eq_{\mathrm{epoxy}} = \frac{m_{\mathrm{EHSO}}}{EEW_{\mathrm{meas}}} \tag{1}$$

$$HEW_{\mathrm{TA,meas}} = \frac{56.106 \times 1000}{HV_{\mathrm{meas}}} = \frac{56106}{HV_{\mathrm{meas}}} \tag{2}$$

$$Eq_{\mathrm{TA},0} = R_{\mathrm{protic}} \times Eq_{\mathrm{epoxy}} = 1.0500 \times \left(\frac{m_{\mathrm{EHSO}}}{EEW_{\mathrm{meas}}}\right) \tag{3}$$

$$m_{\mathrm{TA}} = Eq_{\mathrm{TA},0} \times HEW_{\mathrm{TA,meas}} = 1.0500 \times \left(\frac{m_{\mathrm{EHSO}}}{EEW_{\mathrm{meas}}}\right) \times HEW_{\mathrm{TA,meas}} \tag{4}$$

$$Eq_{\mathrm{IA}} = f_{\mathrm{graft}} \times Eq_{\mathrm{TA},0} = 0.3500 \times 1.0500 \times Eq_{\mathrm{epoxy}} = 0.3675 \times \left(\frac{m_{\mathrm{EHSO}}}{EEW_{\mathrm{meas}}}\right) \tag{5}$$

$$m_{\mathrm{IA}} = Eq_{\mathrm{IA}} \times \frac{112.08}{P_{\mathrm{IA}}/100} = 41.1894 \times \left(\frac{m_{\mathrm{EHSO}}}{EEW_{\mathrm{meas}}}\right) \times \left(\frac{100}{P_{\mathrm{IA}}}\right) \tag{6}$$

$$M_{\mathrm{matrix}} = m_{\mathrm{EHSO}} + m_{\mathrm{TA}} + m_{\mathrm{IA}} \tag{7}$$

$$m_{\mathrm{tocopherol}} = \left(\frac{0.20 + 0.04 \times w_{\mathrm{filler}}}{100}\right) \times M_{\mathrm{matrix}}, \quad m_{\mathrm{AP}} = \left(\frac{0.10}{100}\right) \times M_{\mathrm{matrix}}, \quad m_{\mathrm{biochar}} = \left(\frac{w_{\mathrm{filler}}}{100}\right) \times M_{\mathrm{matrix}} \tag{8}$$

Post-Pre-Esterification Functional Group Conservation Check: After reacting Eq_{IA} moles of IA with $Eq_{\mathrm{TA},0}$ equivalents of TA phenolic −OH, the pre-hardener contains $Eq_{\mathrm{COOH}} = 0.3675\, Eq_{\mathrm{epoxy}}$ carboxylic acid equivalents and $Eq_{\mathrm{ArOH,free}} = (1.0500 - 0.3675)\, Eq_{\mathrm{epoxy}} = 0.6825\, Eq_{\mathrm{epoxy}}$ free phenolic −OH equivalents, summing to $0.3675 + 0.6825 = 1.0500\, Eq_{\mathrm{epoxy}}$ total oxirane-reactive protic equivalents ($R_{\mathrm{protic}} = 1.05$).

Worked Lot-Recalculation Sanity Check ($m_{\mathrm{EHSO}} = 100.00$ g; $w_{\mathrm{filler}} = 1.5$ wt%): If a supplier CoA reports $O_o = 7.44\%$ ($EEW_{\mathrm{meas}} = 215.05$ g/eq), $HV_{\mathrm{meas}} = 750.0$ mg KOH/g ($HEW_{\mathrm{TA,meas}} = 74.81$ g/eq), and $P_{\mathrm{IA}} = 99.5\%$, then $Eq_{\mathrm{epoxy}} = 0.4650$ eq, $Eq_{\mathrm{TA},0} = 0.4883$ eq, $m_{\mathrm{TA}} = 36.53$ g, $Eq_{\mathrm{IA}} = 0.1709$ eq, $m_{\mathrm{IA}} = 19.25$ g, $M_{\mathrm{matrix}} = 155.77$ g, $w_{\mathrm{tocopherol}} = 0.20 + 0.04(1.5) = 0.26$ wt% $\Rightarrow m_{\mathrm{tocopherol}} = 0.41$ g, $m_{\mathrm{AP}} = 0.16$ g, and $m_{\mathrm{biochar}} = 2.34$ g.

4.3 Master Batch Weighing Table ($R_{\mathrm{protic}} = 1.05$, $f_{\mathrm{graft}} = 0.35$; Benchmark Constants)

Execute the 1/4-scale screening batch (25.00 g EHSO, values in brackets) first to verify gelation and cure completeness before scaling to full 100.00 g EHSO plaques.

Table 3: Master Stoichiometric Batch Sheet for Hempoxies Variant `CF-TAIA-105G, Rev2.0` ($EEW = 210.0$, $HEW_{\mathrm{TA}} = 68.05$, $AEW_{\mathrm{IA}} = 112.08$, $M_{\mathrm{matrix}} = 153.64$ g [38.41 g])

Run ID	Biochar	m_{EHSO} (g)	m_{TA} (g)	m_{IA} (g)	Tocoph. (g)	Asc. Palm. (g)	Biochar (g)	Actual (g)
`RUN-0` (Ctrl)	0.0 wt%	100.00 [25.00]	34.02 [8.51]	19.61 [4.90]	0.31 [0.08]	0.15 [0.04]	0.00 [0.00]	_____
`RUN-1` (Low)	0.5 wt%	100.00 [25.00]	34.02 [8.51]	19.61 [4.90]	0.34 [0.08]	0.15 [0.04]	0.77 [0.19]	_____
`RUN-2` (Mid)	1.5 wt%	100.00 [25.00]	34.02 [8.51]	19.61 [4.90]	0.40 [0.10]	0.15 [0.04]	2.30 [0.58]	_____
`RUN-3` (High)	3.0 wt%	100.00 [25.00]	34.02 [8.51]	19.61 [4.90]	0.49 [0.12]	0.15 [0.04]	4.61 [1.15]	_____

4.4 Literature-Optimized Step-by-Step Synthesis & Curing Procedure

1. **Biochar Citric-Acid Demineralization & Vacuum Drying (105–110°C, 4.0 h):** Wash ball-milled, 500-mesh ($D_{90} \leq 25$ μm) steam-activated hemp biochar in 2.0 wt% aqueous bio-fermented citric acid (60°C, 30 min) to remove native K_2CO_3/$CaCO_3$ alkali ash, rinse with deionized water to neutral filtrate (pH 6.5–7.5), and vacuum-dry together with raw tannic acid (5–10 wt% ambient moisture) at 105–110°C for 4.0 h. Cool inside a sealed P_2O_5 or freshly regenerated silica-gel desiccator and weigh immediately upon removal so residual moisture cannot hydrolyze itaconic anhydride.

2. **Aprotic Pre-Esterification of Tannic Acid & Itaconic Anhydride (90°C, 60 min):** Charge dry tannic acid (34.02 g) and dry itaconic anhydride (19.61 g) into a dry round-bottom flask fitted with a reflux condenser and dry N_2 inlet, followed by 35–40 mL anhydrous *n*-propyl acetate per 100 g EHSO batch (9–10 mL at 1/4 scale). Stir magnetically at 90°C for 60 min (adapted from Li, Ju & Zhang, 2024) to graft IA onto 35% of TA phenolic −OH sites, forming a homogeneous, amber liquid galloyl-itaconate polycarboxylic pre-hardener. **Critical Prohibition:** Never

use ethanol, methanol, or any protic alcohol, which causes irreversible anhydride alcoholysis into monofunctional alkyl itaconates.

3. **Stage A Solvent Pre-Strip from Isolated Pre-Hardener (60°C, 50–80 mbar, 15 min):** While the galloyl-itaconate pre-hardener is still isolated from EHSO, apply moderate vacuum (50–80 mbar) at 60°C for 15 min to strip 80–85% of the *n*-propyl acetate ($\sim$ 28–34 mL recovered), leaving a flowable concentrated syrup ($\sim$ 4–6 mL residual co-solvent) with zero premature epoxide reaction.
4. **Pre-Wet Biochar in EHSO & Dissolve Dual Stabilizers (70°C, 15 min + 10 min + 5 min):** Warm EHSO to 70°C. For filled batches (`RUN-1` to `RUN-3`), disperse dry demineralized hemp biochar directly into pure EHSO via bath sonication or high-shear mixing for 15 min first so triglycerides wet biochar micropores before stabilizer addition. Add the biochar-compensated α-tocopherol dose (0.31–0.49 g) plus L-ascorbyl palmitate (0.15 g) and stir at 70°C for 10 min until optically dissolved. Cool to 65°C, pour in the warm concentrated galloyl-itaconate pre-hardener syrup, and mix vigorously for 5 min.
5. **Stage B Final Vacuum Degas & Mold Casting (60°C, 50 mbar, 10 min):** Strip the remaining 4–6 mL co-solvent and entrained micro-bubbles under moderate vacuum (50 mbar) at 60°C for 10 min until bubbling ceases and gravimetric mass loss confirms $\geq$ 99.5% total solvent removal ($\Delta m < 0.05$ g). Keeping temperature $\leq$ 60°C and pressure $\geq$ 50 mbar prevents any sublimation of trace IA ($T_m \approx$ 68–72°C). Pour slowly down the tilted wall of a preheated PTFE or silicone mold.
6. **Controlled Two-Stage Thermal Cure (120°C/4.0 h + 160°C/4.0 h under N_2):** Ramp at 2°C/min from 60°C to 120°C and hold for 4.0 h (controlled carboxylic-oxirane esterification and network gelation), then ramp at 2°C/min to 160°C and hold for 4.0 h under a continuous dry N_2 blanket to complete phenolic-oxirane etherification while remaining safely below the $\sim$ 168°C IA $\rightarrow$ citraconic anhydride isomerization threshold (Berg & Hetzel, 1973).

5. Data Collection Protocols & Analytical Instruments

Record all experimental process checkpoints and analytical measurements directly in Tables 4–8 across all four runs (`RUN-0` through `RUN-3`).

Table 4: Thermal & Mixing Process Checkpoint Log (`CF-TAIA-105G, Rev2.0`)

Process Stage	Setpoint	Ramp / Hold	Critical Control Check	Actual Log	Pass
1. Demin. & Vac Dry	105–110°C	4.0 h vac	Ash < 0.5%; cool in desiccator	____°C / ____h	☐
2. Aprotic Pre-Esterif.	90°C (N_2)	60 min stir	Zero EtOH; *n*-PrOAc mL: ____	____°C / ____m	☐
3. Stage A Pre-Strip	60°C	15 m (50–80 mbar)	80–85% solvent stripped pre-EHSO	____°C / ____m	☐
4. Biochar/EHSO Mix	70°C $\rightarrow$ 65°C	15 + 10 + 5 m	Pre-wet biochar; dissolve Tocoph.+AP	____°C / ____m	☐
5. Stage B Final Degas	60°C	10 m (50 mbar)	$\geq$ 99.5% total solvent stripped ($\Delta m <$ 0.05 g)	____°C / ____m	☐
6. Stage 1 Gelation	120°C	2°C/min, 4.0 h	Tack-free gelation; zero exotherm scorch	____°C / ____h	☐
7. Stage 2 Post-Cure	160°C (< 168°C)	2°C/min, 4.0 h	Continuous N_2 blanket active: Y / N	____°C / ____h	☐

Table 5: ATR-FTIR Cure Completeness Log (4000–600 cm^{-1}, ASTM E1252)

Run ID	Anhydride (1780/1855 cm^{-1})	Oxirane (825–915 cm^{-1})	Ester C = O (1735 cm^{-1})	Broad −OH (3400 cm^{-1})	Gate Status
Uncured Ref	Strong doublet	Strong band	Baseline	Present	Reference
`RUN-0` (0.0%)					
`RUN-1` (0.5%)					
`RUN-2` (1.5%)					
`RUN-3` (3.0%)					

Table 6: Solvent Gel Fraction, Swelling Ratio (24 h THF/Toluene, ASTM D2765) & DSC OIT (180°C, ASTM E1858)

Run ID	**Solvent**	W_0 **Dry (g)**	W_s **Swell (g)**	W_d **Final (g)**	**Gel** G **(%)**	**Swell** Q	$\mathrm{OIT}_{180^\circ\mathrm{C}}$ **(min) / Gate**
`RUN-0` (0.0%)							
`RUN-1` (0.5%)							
`RUN-2` (1.5%)							
`RUN-3` (3.0%)							

Table 7: DMA Thermomechanical & Isothermal Stress-Relaxation Log (ASTM E1640)

Run ID	$E'_{25^\circ\mathrm{C}}$ **(MPa)**	T_g (°C)	E'_r **(MPa)**	ν_e (mol/m^3)	$\tau^*_{145^\circ\mathrm{C}}$ **(s)**	$\tau^*_{155^\circ\mathrm{C}}$ **(s)**	$\tau^*_{165^\circ\mathrm{C}}$ **(s)**	E_a **(kJ/mol)**
`RUN-0`								
`RUN-1`								
`RUN-2`								
`RUN-3`								

Table 8: Closed-Loop Reprocessing Cycle Log (Hot-Press at 160°C, 15 MPa, 60 min under N_2; ASTM D638)

Run ID	**Cycle**	$\sigma_{\max}$ **(MPa)**	E **(MPa)**	ε_b **(%)**	ΔT_g (°C)	**Retention (%)**	$\geq 85\%$ **Gate**
`RUN-0`	Virgin (C0)				0.0 (Ref)	100.0%	Reference
`RUN-0`	Cycle 1 (C1)						
`RUN-0`	Cycle 2 (C2)						
`RUN-1`	Virgin (C0)				0.0 (Ref)	100.0%	Reference
`RUN-1`	Cycle 1 (C1)						
`RUN-1`	Cycle 2 (C2)						
`RUN-2`	Virgin (C0)				0.0 (Ref)	100.0%	Reference
`RUN-2`	Cycle 1 (C1)						
`RUN-2`	Cycle 2 (C2)						
`RUN-3`	Virgin (C0)				0.0 (Ref)	100.0%	Reference
`RUN-3`	Cycle 1 (C1)						
`RUN-3`	Cycle 2 (C2)						

6. Quantitative Analysis & Governing Equations

Evaluate raw laboratory measurements using five standard polymer physics relations:

$$G(\%) = \left(\frac{W_d}{W_0}\right) \times 100 \qquad \text{and} \qquad Q = \frac{W_s - W_d}{W_d} \tag{9}$$

$$\nu_e = \frac{E'_r}{3R_{\text{gas}}T} \tag{10}$$

$$\frac{G(t)}{G_0} = \exp\left(-\frac{t}{\tau^*}\right) \tag{11}$$

$$\ln(\tau^*) = \ln(\tau_0) + \frac{E_a}{R_{\text{gas}}T} \tag{12}$$

$$\text{Strength Retention}(\%) = \left(\frac{\sigma_{\text{Cycle } n}}{\sigma_{\text{Virgin}}}\right) \times 100 \tag{13}$$

where $R_{\text{gas}} = 8.314$ J mol^{-1} K^{-1}, $T = T_g[\text{K}] + 40$ K for rubbery-plateau crosslink density ν_e in Eq. (10), and τ^* in Eq. (11) is recorded when the normalized relaxation modulus decays to $G(t)/G_0 = 1/e \approx 0.368$ across isothermal temperatures 145°C, 155°C, and 165°C.

7. Decision Loop & Falsification Criteria (Rejection Gates)

Under the Landry Hallucination-Free Protocol, Variant `CF-TAIA-105G` (`Rev2.0`) must be rejected or reformulated if any experimental run violates the following falsification thresholds:

1. **Incomplete Network Formation ($G < 92.0\%$):** Indicates incomplete phenolic-oxirane etherification or residual *n*-propyl acetate plasticization. **Corrective Branch:** Extend Stage 2 post-cure hold at 160°C from 4.0 h to 5.0 h under N_2 or re-verify HV_{meas} titration.
2. **Non-Arrhenius Stress Relaxation ($\tau^*_{165^\circ\text{C}} \geq \tau^*_{155^\circ\text{C}}$) or OIT Drop ($> 15\%$ vs. `RUN-0`):** Indicates permanent radical C = C crosslinking (either EHSO internal double bonds or itaconate exocyclic vinylidene groups) or biochar micropore depletion of stabilizers outpacing associative transesterification. **Corrective Branch:** Increase biochar-compensated α-tocopherol slope from +0.04 wt% to +0.07 wt% per 1.0 wt% biochar, raise L-ascorbyl palmitate to 0.15 wt%, and enforce continuous N_2 purging.
3. **Reprocessing Failure ($\text{Retention}_{C2} < 85.0\%$ or Porous Consolidation):** Indicates insufficient dwell time or moisture-induced steam voids. **Corrective Branch:** Extend hot-press dwell at 160°C from 60 min to 90–120 min (matching Li, Ju & Zhang, 2024) and re-verify vacuum drying of biochar ($H_2O < 0.5$ wt%).
4. **Filler Agglomeration Drop ($\sigma_{\max,\text{RUN}-n} < \sigma_{\max,\text{RUN}-0}$):** Identifies the exact rheological/percolation ceiling for 500-mesh hemp biochar; lock optimal composite loading at the highest concentration preceding tensile strength drop-off.

8. Verified Baseline Conclusions vs. Pre-Experimental Boundaries

Verified Chemical & Literature Constants: Associative transesterification enables thermoset-like solvent resistance alongside thermal malleability above the topology freezing transition (Montarnal et al., 2011). Polyphenolic tannic acid networks combined with epoxidized vegetable oils and cyclic anhydrides via aprotic pre-esterification (*n*-propyl acetate) form catalyst-free vitrimers via abundant −OH self-catalysis (Li, Ju & Zhang, 2024; Berne et al., 2022). Itaconic anhydride undergoes thermal isomerization to citraconic anhydride above ∼ 168°C (Berg & Hetzel, 1973), establishing 160°C as the optimal safe cure and reprocessing ceiling. Protic conservation equations (1)–(8) are exact algebraic identities.

Pre-Experimental Status [× THEORETICAL]: The specific multi-component integration of EHSO, graft-balanced galloyl-itaconate pre-hardener ($R_{\text{protic}} = 1.05$, $f_{\text{graft}} = 0.35$), Stage A pre-stripped *n*-propyl acetate, α-tocopherol + L-ascorbyl palmitate stabilization, and citric-acid demineralized 500-mesh hemp biochar (`CF-TAIA-105G Rev2.0`) has not yet been physically synthesized or tested. No mechanical strength, T_g, or activation energy values are claimed prior to execution of Tables 5–8.

Regulatory Certification Boundary: Under USDA Organic and Canada Organic Regime (COR) rules, cured thermoset/vitrimer polymers cannot be certified as organic agricultural products because epoxidation and crosslinking synthesize new covalent macromolecules; however, 100% of upstream agricultural feedstocks (cold-pressed hemp seed oil,

oak-gall/chestnut tannic acid, fermentation dextrose for itaconic and ascorbic acids, and hemp hurd biochar) can be sourced as certified organic inputs processed via enzymatic lipase catalysis (Ankudey et al., 2006) and physical steam activation.

9. Replication & Multi-Lot Calibration Standards

To ensure independent open-source reproducibility across laboratories:

1. Always report measured lot values (EEW_{meas}, HV_{meas}, P_{IA}, *n*-propyl acetate moisture and Stage A/B strip mass balance, biochar BET surface area, residual ash wt%, D_{90} particle size, and post-drying moisture content) alongside mechanical and DSC OIT results.
2. Never introduce multi-scale carbon hybrids (e.g., carbon nanosheets + short carbon fibers + biochar) until single-filler `RUN-0` through `RUN-3` baselines are published and replicated across at least $n = 5$ ASTM D638 tensile specimens per condition.
3. Deposit raw FTIR spectra (`.csv`/`.jdx`), DSC OIT traces, DMA curves, and stress-relaxation datasets under open CC BY 4.0 repositories (Zenodo / GitHub) referencing `Hempoxies CF-TAIA-105G (v.26-CF-Rev2.0)`.

10. Open-Source Reporting, Versioning & References

Document Version History:

- `v.25-CF-Rev1.0` (November 24, 2026): Initial open-source specification establishing Variant `CF-TAIA-95` ($R = 0.95$, 60:40 TA/IA, 0 wt% FGE, 0 wt% metal catalyst, 0.20 wt% α-tocopherol, 0.0–3.0 wt% hemp biochar).
- `v.25-CF-Rev1.1` (November 24, 2026): Literature-optimized revision introducing aprotic *n*-propyl acetate pre-esterification (90°C, 60 min), moderate vacuum stripping (60–65°C, 50–100 mbar), extended cure (120°C/4 h + 160°C/4 h), biochar-compensated α-tocopherol dosing, and Reference [2] bibliographic correction.
- `v.26-CF-Rev2.0` (November 24, 2026): **Current Specification — Variant `CF-TAIA-105G`.** Resolves pre-esterification protic conservation ($R_{\text{protic}} = 1.05$, $f_{\text{graft}} = 0.35$, fixing the hidden $R_{\text{eff}} = 0.570$ under-crosslinking stoichiometry of `Rev1.1`), introduces Stage A solvent pre-strip (60°C, 50–80 mbar, 15 min) to prevent premature viscosity surge, adds 0.10 wt% lipophilic L-ascorbyl palmitate for anaerobic radical quenching and tocopheryl regeneration, mandates citric-acid demineralized 500-mesh ($D_{90} \leq 25$ μm, ash < 0.5 wt%) hemp biochar to eliminate alkali-ash catalysis, and lowers hot-press reprocessing to 160°C (60 min under N_2).

Verified References (Minimum 20 Protocol Standard — 25 Live Sources)

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