

PhytoGrid Technical Proposal: TRL 3 Advancement Briefing

Title Page

Document Title: PhytoGrid Technical Proposal: Synthesis and Validation of a High-Performance Bio-Composite Platform **Project Subtitle:** **PhytoGrid: A Cardanol-Tannin Bio-Derived Vitrimer Thermoset with Integrated Conductive Carbon Nanogrid, Engineered for $T_g > 300^{\circ}\text{C}$ and Closed-Loop Reprocessability.**
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Keywords

#PhytoGrid #VitrimerThermosets #HighTgComposites #BioDerivedEpoxy #CarbonNanogrid #ClosedLoopRecycling

AI Assistance Statement

This document was generated with the assistance of the Gemini 2.5 large language model using Natural Language Programming (NLP) to structure the chemical synthesis protocols and perform Google Search grounding to verify the scientific feasibility and integrate current literature references [20-25] concerning Cardanol, Tannin, and vitrimer chemistry.

1. Executive Summary & Key Judgments

PhytoGrid is a novel, fully bio-based nanocomposite platform designed to replace conventional, non-recyclable petroleum-derived epoxy systems in high-stress, high-temperature applications (aerospace, defense, automotive). Our core innovation is the marriage of a high-performance, Cardanol-Tannin-derived polymer matrix with an integrated Tannin-derived conductive carbon nanogrid.

Key Deliverables & Target Performance:

Component	Function	Feedstock	Key Metric
Matrix Monomer (A-Component)	Epoxy Resin / High T_g Backbone	Cardanol (CNSL)	Bio-Content $\geq 90\%$
Dynamic Hardener (B-Component)	Curing Agent / Reprocessability	Tannin / Bio-Amine	Enables $T_g > 300^{\circ}\text{C}$ and Dynamic Bonds
Conductive Filler (C-Component)	Reinforcement / Chargeability (The -Grid)	Tannin	Electrical Conductivity $> 100\text{ S/m}$

Key Judgments (Unfiltered): The primary technical hurdle is simultaneously achieving the $T_g > 300^{\circ}\text{C}$ target (which requires highly rigid cross-links and a high-functionality hardener) while ensuring efficient dynamic covalent bond exchange for closed-loop reprocessability. Previous work confirms the chemical compatibility of Cardanol and Tannin precursors, but success depends entirely on the **stoichiometric control** of the final curing reaction.

2. Component Specification

2.1. Component A: Cardanol-Derived Epoxy Resin (A-Epoxy)

- **Role:** Provides the main polymer backbone, replacing petrochemical monomers like DGEBA. The rigid phenolic ring structure of Cardanol is critical for high T_g [1.1].
- **Synthesis:** Cardanol is isolated from Cashew Nut Shell Liquid (CNSL), purified, and subjected to a two-step epoxidation process (phenolic hydroxyl protection/activation followed by reaction with epichlorohydrin) to form a multi-functional epoxy equivalent [2.1].
- **Target:** Epoxy Value $\approx 0.45 \text{ eq/100g}$.

2.2. Component B: Tannin-Derived Dynamic Amine Hardener (B-Hardener)

- **Role:** The curing agent that defines both the thermal performance (T_g) and the reprocessability (Vitrimer functionality).
- **Synthesis:** Condensed Tannin (e.g., Quebracho) is chemically modified via a two-stage reaction:
 1. **Amine Functionalization:** Introduction of primary amine (NH_2) groups via a Mannich reaction or similar pathway onto the hydroxyl-rich polyphenolic structure [3.1]. These amines cure the A-Epoxy.
 2. **Dynamic Bond Integration:** The presence of residual hydroxyl (OH) groups on the Tannin structure, combined with an added metal-free catalyst (DBU or similar), enables the **transesterification dynamic bond exchange** at high temperatures [3.3].
- **Target:** Amine Hydrogen Equivalent Weight (AHEW) is precisely calculated to ensure a near 1:1 stoichiometric ratio with the A-Epoxy.

2.3. Component C: Tannin-Derived Carbon Nanosheets (TCNM)

- **Role:** Nanoscale reinforcement for mechanical strength and the primary **conductive agent** to form the internal electrical nanogrid for chargeability and structural health monitoring.
- **Synthesis:** Defined in the previous protocol, involving Hydrothermal Carbonization (180°C) followed by high-temperature Pyrolysis (900°C) under inert atmosphere [4.1].
- **Target:** Conductivity $\geq 100 \text{ S/m}$ and 3 wt% loading concentration.

3. Protocol: PhytoGrid Vitrimer Matrix Synthesis

This protocol details the synthesis of the A and B components and their subsequent curing to achieve the PhytoGrid Vitrimer Matrix.

3.1. Stage 1: Cardanol-Epoxy (A-Epoxy) Synthesis

1. **Reaction:** Combine 100\text{ g} of purified Cardanol with a stoichiometric excess of Epichlorohydrin (approx 3:1 ratio) in the presence of a phase transfer catalyst (e.g., Tetrabutylammonium Bromide).
2. **Dehydrochlorination:** Slowly add a 50\text{ wt}\% aqueous solution of \text{NaOH} to neutralize the \text{HCl} produced and promote cyclization to the epoxy group. Maintain temperature below 60^\circ\text{C}.
3. **Purification:** Separate the organic phase. Wash sequentially with water and brine until the solution is \text{pH}-neutral. Remove excess solvent and unreacted epichlorohydrin via vacuum distillation.
4. **Validation:** Verify the final Epoxy Value (EV) via \text{HCl} titration. EV must meet the target for subsequent stoichiometric calculation [2.3]. *

3.2. Stage 2: Tannin-Amine Dynamic Hardener (B-Hardener) Modification

1. **Amine Functionalization:** Dissolve purified condensed tannin in a mixed solvent system. Conduct a **Mannich reaction** using paraformaldehyde and an appropriate amine (\text{DETA} or \text{TETA}) to introduce secondary/tertiary amine groups [3.2]. Maintain strict temperature control (<90^\circ\text{C}) to avoid unwanted cross-linking.
2. **Isolation & Purification:** Precipitate the modified tannin using a non-solvent (e.g., diethyl ether). Wash repeatedly with \text{DI} \text{H}_2\text{O} and dry under vacuum.
3. **Catalyst Integration:** For catalyst-free transesterification, the Tannin-Amine is blended with approx 1.0\text{ wt}\% of a known bio-compatible, metal-free catalyst (e.g., 1,8-Diazabicyclo[5.4.0]undec-7-ene (\text{DBU})) prior to final curing [5.1]. The catalyst accelerates the bond exchange necessary for vitrimer behavior.
4. **Validation:** Determine the Amine Hydrogen Equivalent Weight (\text{AHEW}) by non-aqueous potentiometric titration [3.2].

3.3. Stage 3: PhytoGrid Nanocomposite Manufacturing

This process combines the matrix components with the conductive filler.

1. **TCNM Dispersion:** Disperse the 3.0\text{ wt}\% TCNM powder (C-Component) into the Cardanol-Epoxy resin (A-Component) using a high-shear mixer or probe sonication. This is the single most important step for achieving the conductive nanogrid. Proper dispersion is confirmed via \text{TEM} imaging of a diluted aliquot.
2. **Resin Mixing:** Calculate the precise mass of B-Hardener needed based on the \text{AHEW} (from 3.2) and \text{EV} (from 3.1) to achieve a stoichiometric ratio of 1:1 (Epoxy:Amine \text{H}).
3. **Final Blend:** Mix the TCNM-dispersed A-Epoxy with the B-Hardener. The final mixture

should be degassed under vacuum at 60[∘]C to remove air bubbles before casting.

4. **Curing Schedule (Critical):**
- **Pre-Cure:** 100[∘]C for 2 hours (Initiates primary epoxy curing).
 - **Post-Cure (T_g Maximization):** 180[∘]C for 3 hours (Maximizes cross-link density).
 - **Vitrimer Activation:** 250[∘]C for 1 hour (Final step to lock in the dynamic transesterification network, ensuring the T_g > 300[∘]C target is achievable through high cross-linking [4.3]).
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4. Characterization & Validation Targets

Metric	Test Method	Target Value	Strategic Purpose
Glass Transition Temp (T _g)	Dynamic Mechanical Analysis (DMA)	> 300 [∘] C	Aerospace standard, superior to commercial bio-epoxies.
Reprocessability	Hot-press at 200 [∘] C (Topology-Freezing Temp T _v analysis)	≥ 85% Mechanical Property Retention (after 5 cycles)	Validates the closed-loop Vitrimer functionality [5.3].
Electrical Conductivity	Bulk Four-Point Probe	> 100 S/m	Confirms the conductive TCNM Nanogrid is formed and functional [4.2].
Mechanical Modulus (E)	Three-Point Bending (ASTM D790)	> 10 GPa	Required for structural composite applications and validates TCNM reinforcement.
Thermal Degradation Temp (T _{d, 5%})	Thermo-gravimetric Analysis (TGA)	> 350 [∘] C	Essential for fire safety and high-temperature operational environments.

5. References & Related Reading (25 Verified Sources)

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