

Technical Synthesis Protocol: Structural Bio-Vitrimer Matrix

Cloned Formulation Framework for Advanced Compounding & Nanocomposite Research

Intellectual Property & Academic Attribution:

This formulation protocol is derived from public patent disclosures, state-of-the-art green chemistry frameworks, and open academic literature pioneered by **Dr. Jinwen Zhang's Laboratory at Washington State University (WSU)**. The structural stabilization techniques and commercial translation methodologies of this specific hempseed oil-derived dynamic network architecture are commercialized under license by **Zila Bioworks**.

Purpose: This document acts as a standardized baseline matrix recipe for secondary compounding research ("Hempoxies" micro/nano-filler integration projects).

1. Executive Summary & Technical Intent

Traditional epoxidized vegetable oils (EVOs) face engineering limits due to the high flexibility of their aliphatic triglyceride backbones, which reduces their crosslinking density and results in low glass transition temperatures (T_g). This protocol outlines the synthesis of a high-performance, bio-based **Covalent Adaptable Network (CAN)**, or vitrimer, utilizing industrial hempseed oil feedstock. By converting raw unsaturated fatty acids into a rigid polyacid hardener and pairing it with epoxidized hempseed oil, the platform achieves mechanical properties suitable for structural composites while retaining full closed-loop recyclability via transesterification bond-shuffling.

2. Component A: Synthesis of HO-Polyacid (The Hardener)

The objective of this phase is to isolate free Hempseed Oil Fatty Acids (HOFA) and convert their isolated double bonds into a rigid, highly reactive poly(carboxylic acid) crosslinker through conjugation and Diels-Alder maleation.

Step 1: Alkaline Hydrolysis (Saponification)

- Reagents:** 100g Crude Industrial Hempseed Oil, 16g NaOH , 140 mL of an ethanol- H_2O blend (1:1 v/v).
- Reaction Profile:** Heat the ethanol- H_2O -alkali system to 70°C under vigorous magnetic stirring. Add the crude hempseed oil dropwise over 30 minutes. Maintain temperature for 3 hours to ensure complete hydrolysis.
- Acid Isolation:** Cool the mixture and adjust the system to $\text{pH } 2\text{--}3$ using 1 M HCl to precipitate the free HOFAs. Reflux the acidified slurry at 70°C for 60 minutes. Isolate the upper organic layer via a separating funnel, wash three times with distilled water, and dry under vacuum.

Step 2: Conjugation & Diels-Alder Maleation

- **Isomerization/Conjugation:** Charge a multi-neck flask with 50g of isolated HOFA, 50g *KOH*, and 200 mL of ethylene glycol acting as a high-boiling-point solvent. Reflux at 200°C for 10 hours under a continuous nitrogen (N_2) blanket. This shifts the natural non-conjugated skipped dienes into highly reactive conjugated configurations.
- **Maleation Action:** Cool the vessel to 90°C . Introduce 38.6g of Maleic Anhydride, 138 mL of glacial acetic acid, and 843.6 mg of Hydroquinone (acting as a free-radical inhibitor to prevent premature polymerization). Raise the temperature and reflux at 120°C for 9 hours.
- **Hydrolysis to Free Triacid:** Directly inject 20 mL of deionized water into the refluxing mixture and maintain at 120°C for an additional 30 minutes. This converts remaining anhydride rings into active carboxylic acid structures, yielding a highly functionalized **Hempseed Oil Polyacid (HO-polyacid)**. Wash the product with ether and water, then dry over anhydrous magnesium sulfate (*MgSO₄*).

3. Component B: Synthesis of Epoxidized Hempseed Oil (EHO Monomer)

To establish the oxirane ring architecture that pairs with the synthesized polyacid hardener, the aliphatic double bonds of crude hempseed oil must undergo controlled epoxidation.

- **The Prilezhaev Reaction Setup:** React untreated crude hempseed oil with an *in situ* generated peroxy acid. Typically, formic acid or acetic acid is combined with 30% to 50% H_2O_2 .
- **Catalytic Control:** Run the reaction using an Acidic Ion-Exchange Resin (AIER) catalyst, specifically **Amberlite IR120 H⁺**. Maintain processing parameters strictly at 55°C to 60°C for 5 to 7 hours to avoid unintended oxirane ring-opening side reactions.
- **Target Parameters:** The resulting Epoxidized Hempseed Oil (EHO) must yield an Epoxide Equivalent Weight (EEW) tracking between **180 to 220 g/mol**, corresponding to an active oxirane oxygen content of approximately 8.4% to 8.6%.

4. Phase C: Vitrimer Crosslinking & Compounding Formula

To establish a functional Covalent Adaptable Network (CAN) capable of thermal reprocessing, the stoichiometric ratio between the oxirane rings (Component B) and the carboxyl groups (Component A) must maintain a precise balance, ensuring a controlled environment for associative transesterification.

Component / Role	Mass Fraction / Ratio	Engineering Mechanics / Function
Component B (EHO Monomer) Base Resin Matrix	Calculated to meet Stoichiometric Equivalence	Provides the highly functionalized aliphatic oxirane network backbone.
Component A (HO-Polyacid) Bio-Derived Flexible Hardener	50% to 70% of total hardener equivalents	Acts as the primary crosslinking engine; imparts tough, impact-resistant properties.
Rosin-Derived Anhydride Rigid Cyclo-Aliphatic Co-Hardener	30% to 50% of total hardener equivalents	Introduces rigid phenanthrene rings to elevate the glass transition temperature (T_g) past 80°C .
Triethanolamine (TEOA) Organic Amine Co-Catalyst	2.0 wt% to 5.0 wt% relative to total resin mass	Drives base curing while providing the dangling hydroxyl (-OH) groups required for transesterification shuffling.
Micro / Nano Fillers (e.g., Graphene, Hurd, HNTs)	Variable (0.5 wt% to 15 wt% application dependent)	Added to create targeted "Hempoxies" variants (Structural, Smart, or PureBio).

Mixing, Curing, and Reprocessing Checklist

- Filler Incorporation:** Micro- or nano-fillers must be thoroughly dispersed into Component B (EHO) *prior* to hardener introduction using high-shear mechanical or planetary centrifugal mixing to prevent agglomeration.
- Stoichiometry Rule:** Maintain an absolute Epoxide-to-Carboxyl (EP/COOH) ratio of **1.0 : 1.0**.
- Thermal Cure Profile:** Gel the compound at 100°C for 2 hours, follow with a network consolidation phase at 140°C for 2 hours, and post-cure at 160°C for 1 hour.
- Vitrimer Reprocessing Window (T_v):** Solid-state mechanical recycling or hot-press reshaping of composite scrap is achieved by applying a constant pressure of **2 to 5 MPa** at **170°C to 190°C** for 15 to 30 minutes.
- Formulation Caution:** Ensure fillers do not bind to or chemically block the active ester linkages, as an external aqueous zinc salt solution (zinc acetate) is required to trigger the depolymerization loop for fiber/filler reclamation.