

# Comprehensive Catalog and Chemical Analysis of Hempseed Oil-Based Bioepoxy Vitrimer Chemistries

The transition from petrochemical thermosetting polymers to circular, bio-based alternatives represents a critical paradigm shift in macromolecular engineering<sup>1</sup>. Conventional thermoset epoxies, while offering exceptional mechanical strength, dimensional stability, and chemical resistance, are governed by permanently cross-linked networks that preclude post-cure reprocessing, recycling, or thermal reshaping<sup>1</sup>. Consequently, these materials contribute to escalating post-consumer waste and environmental degradation<sup>1</sup>.

Covalent adaptable networks (CANs), specifically vitrimers, offer a revolutionary solution to this challenge by integrating the high-temperature durability of traditional thermosets with the melt-reprocessability of thermoplastics<sup>5</sup>. Vitrimers operate via associative dynamic covalent bond exchange mechanisms<sup>5</sup>. Below the topological freezing transition temperature ( $T_v$ ), the network behaves as a solid-like, permanently cross-linked polymer<sup>5</sup>. Above  $T_v$ , thermally triggered dynamic bond exchange reactions allow the network topology to rearrange, facilitating stress relaxation, self-healing, thermal welding, and solid-state recycling without altering the net cross-link density<sup>5</sup>.

Hempseed oil (*Cannabis sativa* L.) has emerged as an exceptionally promising renewable platform for vitrimer synthesis<sup>9</sup>. Containing approximately 80% polyunsaturated fatty

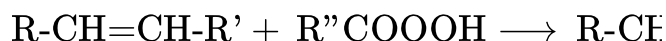
acids—principally linoleic acid (C18:2) and linolenic acid (C18:3)—hempseed oil offers a high density of carbon-carbon double bonds amenable to diverse functionalization pathways<sup>3</sup>. This technical report details the chemical architectures, synthesis conditions, curing profiles, viscoelastic mechanisms, and comparative performance properties of the emerging catalog of hempseed oil-based bioepoxy vitrimer chemistries.

## Precursor Functionalization and Chemical Intermediates

Utilizing raw hempseed oil in high-performance polymer networks requires strategic chemical modification to introduce reactive oxirane, glycidyl ester, or carboxylic acid functional groups<sup>11</sup>. The highly unsaturated triacylglycerol structure of hempseed oil is typically functionalized via two primary chemical pathways: direct epoxidation of the internal double bonds, or conversion of the fatty acids into glycidyl esters or polycarboxylic acids<sup>12</sup>.

### Direct Epoxidation to Epoxidized Hempseed Oil

The synthesis of epoxidized hempseed oil (EHSO, also designated under the standardized monomer registry as EVO 9) involves the conversion of internal alkenes along the fatty acid chains into reactive oxirane rings<sup>12</sup>. This is typically conducted via an *in situ* epoxidation method using hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and a carboxylic acid carrier (formic or acetic acid) in the presence of an acid catalyst, such as the cationic exchange resin Amberlite IR-120<sup>9</sup>.



The reaction is carried out at  $60^\circ\text{C}$  for a duration of 5.5 to 8 hours to maximize conversion while preventing premature acid-catalyzed ring-opening of the newly formed oxirane groups<sup>9</sup>. Under optimized parameters, this method yields EHSO with an oxirane oxygen content (OOC) ranging from 6.8% to 8.6%, a conversion of double bonds exceeding 99%, and a starting viscosity of approximately  $0.4$  to  $0.6 \text{ Pa} \cdot \text{s}$ <sup>9</sup>. The purified monomer exhibits an epoxy index (EI) of approximately  $5.6 \text{ meq} \cdot \text{g}^{-1}$  and an epoxide equivalent weight (EEW) of  $179 \text{ g} \cdot \text{eq}^{-1}$ <sup>16</sup>.

## Synthesis of Hempseed Oil-Derived Polyacid Curing Agents

To formulate a fully bio-based vitrimer, the fatty acids of hempseed oil can be modified into carboxylic acid-functionalized hardeners<sup>11</sup>. The cold-pressed hempseed oil is first hydrolyzed to yield free hempseed oil fatty acids (HOFA) with an acid value of approximately  $199 \text{ mg KOH} \cdot \text{g}^{-1}$ <sup>11</sup>. The unconjugated double bonds within the linoleic and linolenic fractions—which compose approximately 77% of the total fatty acid profile—are thermally conjugated at  $200^\circ\text{C}$  in the presence of ethylene glycol<sup>11</sup>. The conjugated intermediate is subsequently reacted with maleic anhydride via a Diels-Alder [4+2] cycloaddition<sup>11</sup>. Subsequent hydrolysis of the anhydride adducts yields a highly functionalized, flexible polycarboxylic acid curing agent, designated as HO-polyacid<sup>11</sup>.

The resulting HO-polyacid is a highly viscous liquid with a density of  $1.03 \text{ g} \cdot \text{cm}^{-3}$  at  $25^\circ\text{C}$  and a dynamic viscosity of  $14.83 \text{ Pa} \cdot \text{s}$ <sup>11</sup>. Purification via silica column chromatography yields a pure triacid intermediate, with mass spectrometry confirming key molecular ion peaks at  $m/z$  419  $[\text{M} + \text{Na}]^+$  and  $m/z$  435  $[\text{M} + \text{K}]^+$ <sup>11</sup>. The theoretical acid value of the triacid is  $423 \text{ mg KOH} \cdot \text{g}^{-1}$ , while experimental titration typically yields an acid value of  $362 \text{ mg KOH} \cdot \text{g}^{-1}$  due to steric hindrance or incomplete hydrolysis of the Diels-Alder adduct<sup>11</sup>.

## Synthesis of Terminally Glycidylated Hempseed Oil Epoxy

Although direct epoxidation of vegetable oils is chemically straightforward, the resulting EHSO contains internal oxirane groups along the aliphatic chain<sup>14</sup>. These internal epoxies are sterically hindered, reducing their reactivity toward standard amine or acid curing agents<sup>12</sup>. Furthermore, the long, dangling aliphatic chains act as plasticizers, which dramatically lowers the glass

transition temperature ( $T_g$ ) and mechanical modulus of the cured network<sup>3</sup>.

To overcome this limitation, a novel glycidyl ester-type epoxy monomer (HOEP) was developed<sup>3</sup>. The fatty acids from hempseed oil are first converted to the aforementioned HO-polyacid intermediates and subsequently glycidylated with epichlorohydrin (ECH) to produce polyglycidyl esters<sup>13</sup>. A potential side reaction during this glycidylation step involves the premature ring-opening of the glycidyl ether groups by residual carboxylic acid species, which can slightly increase the molecular weight and viscosity of the resulting monomer<sup>17</sup>. Nevertheless, this architectural modification places highly reactive, terminal glycidyl ester groups at the molecular chain ends<sup>13</sup>. The resulting HOEP monomer possesses a shorter average distance between dynamic linkages and significantly enhanced oxirane reactivity, leading to cured network architectures with substantially higher cross-link densities, stiffness, and thermal properties<sup>13</sup>.

| Precursor Metric         | Hempseed Oil Fatty Acids (HOFA) | Conjugate d HOFA      | HO-Polyacid (Triacid)    | Epoxidized Hempseed Oil (EHSO/EVO 9) | Terminally Glycidylated Epoxy (HOEP) |
|--------------------------|---------------------------------|-----------------------|--------------------------|--------------------------------------|--------------------------------------|
| Primary Synthesis Method | Saponification & Acidification  | Thermal Isomerization | Diels-Alder & Hydrolysis | <i>In Situ</i> Peracetic Epoxidation | Glycidylation with Epichlorohydrin   |
| Oxirane Oxygen Content   | 0.0%                            | 0.0%                  | 0.0%                     | 6.8% -- 8.6%                         | 7.2% -- 8.4%                         |
| Epoxy Equivalent Weight  | N/A                             | N/A                   | N/A                      | 179 g · eq <sup>-1</sup>             | 195 -- 210 g · eq <sup>-1</sup>      |
| Acid Value (             | 199 -- 201                      | 195 -- 198            | 362 -- 423               | < 2.0                                | < 1.0                                |

|                                   |             |             |              |                     |                     |
|-----------------------------------|-------------|-------------|--------------|---------------------|---------------------|
| mg KOH · )                        |             |             |              |                     |                     |
| <b>Dynamic Viscosity ( 25°C )</b> | 0.02 Pa · s | 0.03 Pa · s | 14.83 Pa · s | 0.40 -- 0.60 Pa · s | 0.85 -- 1.10 Pa · s |

## Catalog of Hempseed Oil-Based Bioepoxy Vitrimer Chemistries

A comprehensive evaluation of chemical pathways reveals that hempseed oil-derived monomers and hardeners can be integrated into several distinct dynamic covalent networks. These chemistries utilize transesterification, Schiff-base (imine) metathesis, and disulfide exchange reactions to achieve topological adaptability<sup>5</sup>.

### 1. Internally Catalyzed Transesterification Networks

The most widely researched class of hempseed oil vitrimers relies on the dynamic transesterification reaction (DTER) occurring between ester linkages and free hydroxyl groups<sup>3</sup>.

The transesterification pathway is thermally activated, requiring temperatures above 150°C to overcome the activation energy barrier ( $E_a \approx 80\text{--}120 \text{ kJ/mol}$ )<sup>3</sup>.



A room-temperature curable, high-performance coating was designed by blending HOEP with a petro-based bisphenol A-based epoxy (DGEBA, DER 331) and curing the mixture with a standard aliphatic amine hardener, diethylenetriamine (DETA), in the presence of triethanolamine (TEOA)<sup>3</sup>. The system contains up to 67.5 wt% of renewable HOEP in the total resin composition<sup>3</sup>. The resulting cross-linked network contains a high density of flexible ester linkages (originating from the HOEP monomer) and polar hydroxyl groups (generated via the epoxy-amine ring-opening reaction)<sup>3</sup>.

A unique feature of this system is that the tertiary amines within the TEOA catalyst, alongside the secondary and tertiary amine structures formed within the cured network, function as internal catalysts for the transesterification reaction<sup>3</sup>. These internal amine sites coordinate with nearby hydroxyl and ester groups, accelerating the kinetics of dynamic transesterification

above  $150^{\circ}\text{C}$  without requiring toxic, external heavy metal catalysts<sup>3</sup>.

When cured at room temperature for 7 days, this epoxy vitrimer exhibits a glass transition temperature ( $T_g > 40^{\circ}\text{C}$ ), a scratch hardness of 5H, a gouge hardness of 6H, an adhesive strength of 5B on tin plates, and outstanding solvent resistance<sup>3</sup>. At elevated temperatures, the system displays rapid stress relaxation and self-healing properties<sup>3</sup>.

## 2. Rosin-Derived Anhydride/Acid Co-Cured Transesterification Systems

To eliminate petro-based components entirely, fully bio-based vitrimers were synthesized by pairing hempseed oil-derived monomers with rosin-derived rigid curing agents<sup>13</sup>. Two complementary, 100% bio-based systems were evaluated:

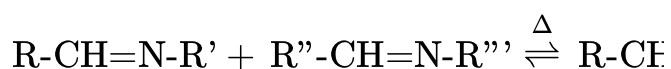
- **HO-EP/MPA System:** Terminally glycidylated hempseed oil epoxy (HO-EP) cured with maleopimaric acid (MPA), a rigid, tricyclic rosin derivative<sup>13</sup>.
- **MPA-EP/HO-Polyacid System:** A rigid, rosin-derived epoxy monomer (MPA-EP) cured with the flexible HO-polyacid hardener<sup>13</sup>.

These vitrimers utilize ester-hydroxyl pathways activated during a two-stage thermal cure cycle:  $150^{\circ}\text{C}$  for 2 hours, followed by a post-cure at  $200^{\circ}\text{C}$  for 1 hour<sup>11</sup>. The stoichiometry of the rigid rosin segments to the flexible aliphatic chain segments governs the resulting dynamic and mechanical performance<sup>13</sup>.

In the HO-EP/MPA system, a molar ratio of 2:1 (epoxy to acid equivalents) yields optimal stress relaxation and self-healing, whereas a 1.5:1 molar ratio promotes superior shape-memory properties due to the increased elastic contribution of the network<sup>13</sup>. For the MPA-EP/HO-polyacid system, a 1:1 molar ratio optimizes dynamic self-healing, while a 2:1 ratio enhances shape-memory characteristics<sup>13</sup>.

## 3. Catalyst-Free Schiff-Base (Imine) / Ester Dual Adaptable Networks

Imine-based vitrimers (Schiff-base networks) undergo dynamic exchange reactions—including imine metathesis, transamination, and hydrolysis—under thermal or mild chemical stimuli<sup>18</sup>. Unlike transesterification networks, imine chemistry does not require heavy metal or toxic organic catalysts, avoiding issues of catalyst leaching and premature thermal aging<sup>1</sup>.



This dynamic network is synthesized by curing EHSO with vanillin-based imine cross-linkers<sup>23</sup>. The cross-linkers are prepared by reacting vanillin (a lignin-derived aromatic aldehyde) with aliphatic diamines to form dynamic imine ( $\text{-C=N-}$ ) linkages<sup>23</sup>.

An alternative formulation utilizes a ternary Schiff-base system, where EHSO is cured with a

terpene-derived diamine, specifically limonene diamine (also known as limonene amine), and a bio-based dialdehyde<sup>18</sup>. Throughout the curing process, the diamine exhibits dual reactivity: it reacts with the aldehyde to form dynamic imine linkages, and it reacts with the oxirane groups of EHSO to form a cross-linked network<sup>18</sup>.

This hybrid architecture incorporates two distinct classes of chemically adaptable linkages: dynamic ester bonds from the epoxidized hempseed oil backbone, and dynamic imine linkages<sup>18</sup>. The rigid aromatic structures derived from vanillin compensate for the high flexibility of the aliphatic EHSO chains, yielding a vitrimer with balanced thermal stability, high self-healing efficiency, and rapid stress relaxation<sup>23</sup>.

#### 4. Dynamic Disulfide / Transesterification Dual Covalent Adaptable Networks

Disulfide metathesis is a highly responsive dynamic chemistry capable of thermal activation without the addition of catalysts<sup>1</sup>. This chemistry can be coupled with carboxylate transesterification to form a dual-dynamic network with enhanced reprocessing capabilities<sup>19</sup>.



In this system, epoxidized hempseed oil (EVO 9) is copolymerized with an aromatic dicarboxylic acid containing dynamic disulfide bonds, 2,2'-dithiodibenzoic acid (DTBA), as the hardener<sup>19</sup>. The curing reaction between the carboxylic acid groups of DTBA and the oxirane rings of EVO 9

produces  $\beta$ -hydroxy ester linkages<sup>19</sup>. Consequently, the cross-linked network contains two distinct dynamic pathways: disulfide metathesis and carboxylate transesterification<sup>19</sup>.

The dual-exchange mechanism significantly accelerates network rearrangement<sup>24</sup>. To study the role of catalysis in this dual system, investigators evaluated a series of initiators<sup>24</sup>. Imidazole emerged as the highly efficient initiator, lowering the curing temperature and substantially enhancing solid-state reprocessability<sup>24</sup>. Imidazole-catalyzed EVO 9/DTBA vitrimers exhibit excellent recovery of tensile strength and mechanical properties, maintaining approximately 100% of their original tensile performance even after 10 consecutive grinding and hot-press recycling cycles<sup>24</sup>.

Furthermore, these vitrimers demonstrate chemical recyclability, dissolving completely in a 1 N NaOH aqueous solution at 80°C over 3 days via selective ester saponification, avoiding the hazardous organic solvents typical of thermoset degradation<sup>24</sup>.

#### 5. UV-Curable Dimethacrylate Dimer-Acid (eMDA) Transesterification Systems

To accommodate advanced manufacturing techniques such as digital light processing (DLP) 3D printing and high-speed UV-curable inks, a dynamic photopolymerizable vitrimer chemistry

was developed<sup>18</sup>. While standard vegetable-oil vitrimers require long thermal curing cycles (  $> 5$  hours at  $> 100^{\circ}\text{C}$  ), this formulation integrates high-speed UV-initiated free-radical polymerization with subsequent thermal transesterification<sup>18</sup>.

The synthesis is conducted via a two-step process<sup>26</sup>:

1. An intermediate methacrylate monomer (MDA) is prepared by reacting a vegetable-oil-derived dimer acid (DA)—obtained through the Diels-Alder dimerization of unsaturated fatty acids—with glycidyl methacrylate (GMA)<sup>26</sup>.
2. The MDA intermediate is reacted with a diepoxy compound—such as ethylene glycol diglycidyl ether (EGDE), resorcinol diglycidyl ether (RDGE), or DGEBA (DER 331)—to produce a chain-extended dimethacrylate monomer (eMDA)<sup>26</sup>.



When blended with a terpene-derived photoinitiator (such as biogenic acylphosphine oxides synthesized from *p*-cymene), the eMDA monomer undergoes rapid free-radical photopolymerization under  $365\text{ nm}$  UV light within 80 seconds at room temperature<sup>15</sup>. The resulting cured network exhibits a tensile strength of up to 9.2 MPa and an elongation at break of 66.4%<sup>26</sup>.

Because the network contains a high density of  $\beta$ -hydroxyl groups and ester linkages, it undergoes efficient dynamic transesterification at temperatures above  $160^{\circ}\text{C}$ <sup>26</sup>. This thermal activation enables post-cure welding, thermal reshaping, and mechanical repair of 3D-printed components<sup>18</sup>.

## 6. Structural High-Performance Dual-Dynamic Matrix

To target advanced structural applications requiring thermal and mechanical properties comparable to aerospace-grade resins, a complex 13-component, 100% bio-based vitrimer platform was developed<sup>15</sup>. Designated as the "Trideca-Hemp" or "Sovereign Vitrimer" architecture, this system coordinates multiple hemp-derived fractions to form a dual-dynamic network with high specific strength<sup>15</sup>.

The matrix formulation utilizes a precise stoichiometry<sup>15</sup>:

- **Polymeric Base:** Epoxidized hempseed oil (EHSO, SOP 01) combined with Furfuryl Glycidyl Ether (FGE, SOP 04) derived from hemp hurd hemicellulose, which acts as a reactive diluent to lower the infusion viscosity to  $0.4\text{--}0.6\text{ Pa} \cdot \text{s}$ <sup>15</sup>.
- **Dual-Dynamic Hardener:** Quadruple-Function Modified Hemp Lignin (QF-MHL, SOP 02), which is synthesized from hemp shive lignin via demethylation, phenolation, maleic anhydride grafting, and amination with DETA<sup>15</sup>. The QF-MHL provides covalent

cross-linking sites, compatibilization, and both amine and aldehyde functional groups for catalyst-free imine exchange<sup>2</sup>.

- **Primary Bio-Hardener:** Hemp-Derived Amine (HDA, SOP 03), synthesized from seed cake protein via reductive amination over a Raney-Nickel catalyst at  $120^{\circ}\text{C}$  and 5 MPa  $\text{H}_2$ <sup>15</sup>.
- **Functional Additives:** Phytic acid (SOP 13) extracted from seed cake to provide flame retardancy (achieving a UL-94 V0 rating and a limiting oxygen index of 31.2% to 33.5%), biogenic silica (SOP 10) for mechanical reinforcement, and terpene-derived photoinitiators (SOP 12)<sup>12</sup>.

Oxirane-to-Amine Stoichiometric Ratio = 1 : 1.1 [cite]

Curing is conducted via a triple-stage curing profile<sup>15</sup>:

1. **Phase 1 (Surface Stabilization):** A 30-second flash of 365 nm UV light initiates surface stabilization via the photoinitiator<sup>15</sup>.
2. **Phase 2 (Bulk Network Formation):** Thermal curing at  $80^{\circ}\text{C}$  for 2 hours initiates primary epoxy-amine and amine-aldehyde reactions to build the cross-linked network<sup>15</sup>.
3. **Phase 3 (Vitrimer Activation):** Post-curing at  $140^{\circ}\text{C}$  for 4 hours activates dynamic transesterification and imine exchange pathways, establishing the self-healing and reprocessability characteristics of the matrix<sup>15</sup>.

## Physical Properties, Curing Profiles, and Coating Application Parameters

The viscosity and curing profiles of hempseed oil-based vitrimers directly govern their processing window and application<sup>5</sup>. Because of the highly flexible aliphatic backbone of epoxidized vegetable oils, specialized formulation parameters and curing cycles are required to achieve satisfactory thermal and mechanical properties<sup>3</sup>.

### Coating Deposition and Parameters

For surface-protection applications, hempseed oil-based vitrimer coatings are typically deposited onto substrates (such as tin plates or steel panels) using specialized industrial techniques<sup>3</sup>. The rheological properties of the vitrimer must be carefully adjusted to match the requirements of each deposition method<sup>5</sup>.

- **Spray Coating:** The coating mixture is diluted or heated to achieve a viscosity of 50 to 200 mPa · s at the application temperature, ensuring uniform atomization and smooth film formation over large surfaces<sup>5</sup>.
- **Dip Coating:** Used for complex geometries, where the substrate is withdrawn from a 5

to 20 wt% vitrimer solution at a controlled speed of 1 to 10  $\text{cm} \cdot \text{s}^{-1}$  to yield dry film thicknesses of 10 to 500  $\mu\text{m}$ <sup>5</sup>.

- **Spin Coating:** Utilized for high-precision microelectronic applications, where spin-coating at 1000 to 3000 rpm yields ultra-thin hydrophobic films ( $< 1000 \text{ nm}$ ) after vacuum curing at  $120^\circ\text{C}$  for 12 hours<sup>5</sup>.
- **Electrostatic Powder Coating:** Used for vitroc ceramic formulations on metallic substrates, where a single-layer process at 800 to  $900^\circ\text{C}$  incorporating 0.1 to 1 wt% spodumene additives produces highly thermal shock-resistant coatings<sup>5</sup>.

The final film thickness governs the performance trade-off of the coating<sup>5</sup>. Thin coatings ( $< 100 \mu\text{m}$ ) exhibit rapid self-healing kinetics due to shorter molecular diffusion distances, whereas thick coatings ( $> 500 \mu\text{m}$ ) provide superior chemical resistance and physical barrier properties<sup>5</sup>.

| Coating Method                           | Target Viscosity                       | Key Process Parameters                                    | Target Thickness         | Primary Industrial Application                            |
|------------------------------------------|----------------------------------------|-----------------------------------------------------------|--------------------------|-----------------------------------------------------------|
| <b>Spray Coating</b><br>[cite: 5]        | 50 -- 200 $\text{mPa} \cdot \text{s}$  | Diluent addition or thermal heating                       | 50 -- 150 $\mu\text{m}$  | Automotive panels, large-area infrastructure <sup>5</sup> |
| <b>Dip Coating</b><br>[cite: 5]          | 200 -- 500 $\text{mPa} \cdot \text{s}$ | Withdrawal speed: 1 -- 10 $\text{cm} \cdot \text{s}^{-1}$ | 10 -- 500 $\mu\text{m}$  | Heat exchangers, complex electronic housings <sup>5</sup> |
| <b>Spin Coating</b><br>[cite: 5]         | 10 -- 50 $\text{mPa} \cdot \text{s}$   | Spin speed: 1000 -- 3000 rpm                              | $< 1000 \text{ nm}$      | Microelectronics, precision optical devices <sup>5</sup>  |
| <b>Electrostatic Powder</b><br>[cite: 5] | Dry Powder                             | Temp: 800 -- $900^\circ\text{C}$ ; 0.1 -- 1 wt%           | 100 -- 300 $\mu\text{m}$ | Vitroc ceramic metal protection, high-temperat            |

|  |  |           |  |                        |
|--|--|-----------|--|------------------------|
|  |  | spodumene |  | ure pipes <sup>5</sup> |
|--|--|-----------|--|------------------------|

## Stoichiometry, Catalysis, and Dynamic Viscoelastic Behavior

The mechanical durability and thermal transitions of hempseed oil vitrimers are directly governed by the stoichiometric balance of reactive functional groups and the selected catalyst systems<sup>28</sup>.

In traditional thermosets, curing is conducted at a strict 1:1 stoichiometric ratio of epoxy to

hardener to maximize cross-link density, glass transition temperature ( $T_g$ ), and mechanical properties<sup>4</sup>. In vitrimer formulations, however, deviations from this stoichiometric balance are frequently engineered to tune dynamic adaptability<sup>6</sup>.

For transesterification vitrimers, off-stoichiometric formulations containing an excess of epoxy groups (e.g., a 20% stoichiometric excess) are common<sup>6</sup>. The excess epoxy reacts to form a

higher concentration of free, secondary  $\beta$ -hydroxyl groups ( $-\text{OH}$ ) within the network<sup>3</sup>.

These free hydroxyl groups are the active nucleophiles in the transesterification exchange

pathway<sup>6</sup>. Increasing the concentration of free  $-\text{OH}$  groups reduces the activation energy ( $E_a$ ) of the exchange reaction and significantly accelerates stress relaxation and self-healing

rates, although it typically induces a modest decrease ( $10\text{--}15^\circ\text{C}$ ) in  $T_g$  due to the minor reduction in net cross-link density<sup>6</sup>.

The dynamic exchange rate is modeled using stress relaxation experiments, where the decay of stress under a constant applied strain is quantified via a Maxwell-type decay equation<sup>23</sup>:

$$\sigma(t) = \sigma_0 \cdot \exp\left(-\frac{t}{\tau^*}\right)$$

where  $\tau^*$  is the characteristic relaxation time, defined as the time required for the initial stress to relax to  $1/e$  ( $\approx 37\%$ ) of its original value<sup>30</sup>. The temperature dependence of the characteristic relaxation time follows the Arrhenius law:

$$\ln(\tau^*) = \ln(\tau_0) + \frac{E_a}{R \cdot T}$$

where  $\tau_0$  is a pre-exponential factor,  $E_a$  is the activation energy of the bond exchange

reaction,  $R$  is the universal gas constant, and  $T$  is the absolute temperature in Kelvin<sup>25</sup>.

The cross-linking density ( $\nu_e$ ) of the cured and reprocessed vitrimers is calculated from the elastic storage modulus ( $E'$ ) in the rubbery plateau region using Flory's theory of rubber elasticity<sup>19</sup>:

$$\nu_e = \frac{E'}{3 \cdot R \cdot T}$$

where  $E'$  is the storage modulus at  $T_g + 50^\circ\text{C}$ ,  $R$  is the gas constant, and  $T$  is the absolute temperature in Kelvin<sup>19</sup>. High-performance hempseed oil vitrimers balance a high cross-linking density in the service state with rapid relaxation at processing temperatures, as detailed in the thermomechanical matrix below.

| Formulation & Architecture ID                        | Glass Transition Temp (T <sub>g</sub> ) | Tensile / Flexural Strength                            | Elongation at Break   | Characteristic Relaxation (τ*)                    | Reference Standards & Performance                                                    |
|------------------------------------------------------|-----------------------------------------|--------------------------------------------------------|-----------------------|---------------------------------------------------|--------------------------------------------------------------------------------------|
| HOEP / DETA / DGEBA (Room-Temp Coating) [cite: 3, 6] | 40 -- 52°C [cite: 3, 6]                 | Scratch: 5H<br>Gouge: 6H <sup>3</sup>                  | 5% -- 8% <sup>5</sup> | 1200 s at 180°C [cite: 25]                        | Room-temperature curable; 5B adhesion; excellent solvent resistance <sup>3</sup>     |
| HO-EP / MPA (Rosin-Based Vitramer, 2:1) [cite: 13]   | 40 -- 89°C [cite: 12]                   | High rigidity; variable by rosin content <sup>13</sup> | 3% -- 6% <sup>5</sup> | Tunable by acid-epoxy stoichiometry <sup>13</sup> | 100% bio-based; 2:1 ratio optimizes stress relaxation and self-healing <sup>13</sup> |

|                                                                     |                                  |                                                       |                         |                                                          |                                                                                  |
|---------------------------------------------------------------------|----------------------------------|-------------------------------------------------------|-------------------------|----------------------------------------------------------|----------------------------------------------------------------------------------|
| <b>EVO 9 / DTBA (Dynamic Disulfide Vitrimer)</b><br>[cite: 19]      | 34 -- 111 °C<br>[cite: 31, 32]   | Modulus correlates with oxirane density <sup>31</sup> | 10% -- 40% <sup>5</sup> | 32 -- 210 s at 170 °C<br>[cite: 30]                      | 10-cycle reprocessability; chemical recycling in 1 N NaOH at 80 °C<br>[cite: 24] |
| <b>EHSO / Limonene Amine (Dual-Dynamic Matrix)</b><br>[cite: 4, 33] | 72.6 -- 73.9 °C<br>[cite: 4, 33] | ≈<br>[cite: 4, 33]                                    | 8% -- 12%               | Rapid catalyst-free imine metathesis <sup>2</sup>        | Complete chemical degradation in ethanolamine at 100 °C in 3 h <sup>18</sup>     |
| <b>EPV-VP-1.5 (Vanillin Schiff-Bas e Vitrimer)</b><br>[cite: 22]    | 132.7 °C<br>[cite: 22]           | 82.4 MPa <sup>22</sup>                                | 5.5% <sup>22</sup>      | Rapid imine exchange; catalyst-free <sup>22</sup>        | Retains 62.8 MPa tensile strength after 3 recycling cycles <sup>22</sup>         |
| <b>Sovereign Vitrimer (Trideca-Hemp SOP 14)</b><br>[cite: 15]       | >                                | > (neat matrix) <sup>2</sup>                          | 4% -- 6%                | Rapid transesterification & imine exchange <sup>15</sup> | Titanium-equivalent specific strength when reinforced with carbon <sup>15</sup>  |

## Structural Biocomposites and Sustainable End-of-Life Mechanisms

The integration of hempseed oil-based vitrimers into natural fiber-reinforced composites (NFRCs) has emerged as a key strategy to develop fully circular structural materials<sup>27</sup>. By pairing natural reinforcements—such as hemp bast, flax, or jute fibers—with recyclable

hempseed oil vitrimer matrices, researchers have manufactured high-strength, lightweight biocomposites that address the end-of-life challenges of traditional petrochemical composites<sup>27</sup>.

## Interfacial Compatibility and Toughness Enhancement

A historical bottleneck of natural fiber-reinforced composites is the poor interfacial adhesion between the hydrophilic natural fibers (rich in polar cellulose hydroxyl groups) and hydrophobic polymer matrices, which typically leads to high moisture absorption and premature delamination<sup>4</sup>. Hempseed oil vitrimers inherently mitigate this issue. The high abundance of polar secondary hydroxyl and ester groups generated during epoxy-acid or epoxy-amine curing facilitates strong hydrogen bonding and chemical compatibility at the fiber-matrix interface<sup>3</sup>.

In advanced formulations, such as the *hemp fiber-reinforced dual dynamic network vitrimer*, compatibility is optimized through the direct incorporation of amino silanes<sup>18</sup>. The trialkoxysilane groups of the coupling agent covalently bind to the hydroxyl ends of the crystalline and amorphous regions of the cellulose fibers<sup>18</sup>. This reaction opens up a portion of the hydrogen-bonded cellulose chains, generating new amorphous cellulose at the crystalline chain ends<sup>37</sup>.

The primary amine tails of the silane coupling agent participate directly in the epoxy-curing and imine-exchange reactions of the matrix<sup>18</sup>. The highly pliant silane interface significantly improves mechanical load transfer, enhancing both the interfacial shear strength and the ultimate fracture toughness of the biocomposite<sup>18</sup>.

## Dynamic Reconfigurability and Solid-State Recycling

Under thermal stimulus ( $140\text{--}180^\circ\text{C}$ ), the associative bond exchange reactions within the hempseed vitrimer matrix become kinetically rapid, allowing the composite to be reshaped, welded, or repaired in the solid state<sup>5</sup>.

- **Self-Healing and Repair:** Micro-cracks and delamination zones within structural composite panels can be healed by applying localized heat and contact pressure<sup>2</sup>. The dynamic network rearranges across the damage interface, restoring up to 90% of the initial mechanical properties<sup>2</sup>.
- **Solid-State Reprocessing:** Damaged or end-of-life biocomposites can be physically ground into fine powders<sup>19</sup>. This powder is then consolidated under a hydraulic thermal press (typically at  $150\text{--}180^\circ\text{C}$  and  $5\text{--}10\text{ MPa}$ ) to thermoform new, high-performance second-life structural components, completely bypassing the landfill or energy-intensive pyrolysis processes typical of traditional carbon/glass-epoxy waste<sup>4</sup>.

## Mild Chemical Solvolysis and Fiber Reclamation

When physical reprocessing is no longer viable, hempseed oil vitrimers can undergo clean chemical recycling under exceptionally mild conditions, a process termed chemical solvolysis<sup>35</sup>.

The chemical degradation mechanisms are tailored to the dynamic chemistry of the matrix:

- **Transesterification in Glycols:** Polyester-based vitrimer matrices are chemically recycled via glycolytic dissolution<sup>25</sup>. When heated in a glycol solvent (such as ethylene glycol) at 150–180°C, the ester linkages undergo rapid transesterification with the solvent molecules, leading to complete dissolution and recovery of high-quality reinforcement fibers and matrix oligomers with zero degradation of fiber properties<sup>25</sup>.
- **Acid-Mediated Solvolysis:** Schiff-base polyimine vitrimers are highly susceptible to acid-catalyzed hydrolysis<sup>18</sup>. These matrices dissolve completely in a mild acidic solution (e.g., 0.5 M HCl in dimethylformamide at 50°C) over 2 days, allowing the undamaged fibers to be reclaimed and the aldehyde monomers to be precipitated and reused in a closed-loop cycle<sup>22</sup>.
- **Selective Aminolysis:** For EHSO/limonene amine-derived dual dynamic network composites, both the ester and imine linkages are cleaved via aminolysis in an ethanolamine solution at 100°C within 3 hours<sup>18</sup>. Because this process operates below the thermal degradation threshold of natural fibers, the hemp or flax fibers are reclaimed with zero loss in structural integrity, enabling their direct integration into a second generation of high-value structural biocomposites<sup>18</sup>.

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