

ADVANCED MONOGRAPH SERIES IN
SUSTAINABLE POLYMERIC MATERIALS

VEGETABLE OIL BIOEPOXY VITRIMERS

Design, Transesterification Kinetics,
Dynamic Covalent Networks, and
Industrial Circularity

Core Scientific Scope: Dynamic Transesterification • Topology
Freezing Transitions (T_g) • Triglyceride Architectures • Closed-
Loop Closed-Die Thermocompression • Fiber-Reinforced Green

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Monograph Synopsis

Classical thermosetting epoxy resins (primarily diglycidyl ether of bisphenol A; DGEBA) provide structural rigidity, heat resistance, and thermal tolerance. However, their permanent covalently crosslinked architectures render them intractable post-cure, preventing remolding, reshaping, and circular mechanical recycling. They inevitably accumulate in terrestrial landfills or enter destructive down-cycling protocols upon reaching end-of-life.

Vitrimers, introduced theoretically and demonstrated experimentally by Ludwik Leibler and co-

workers in 2011, represent a paradigm shift. Operating through associative dynamic covalent bond exchanges, vitrimers retain absolute network integrity, solvent insolubility, and constant crosslink density across operating temperatures, while exhibiting Arrhenius-type fluidity at elevated processing temperatures. By substituting petroleum-derived aromatics with chemically epoxidized plant triglycerides—derived from soybean, linseed, castor, and tung oils—a sustainable, bio-based class of structural plastics emerges: **Vegetable Oil Bioepoxy Vitrimers**. This text offers a comprehensive chemical and mechanical treatment of this sustainable materials platform.

Fundamentals of Vitrimers and Covalent Adaptable Networks (CANs)

1.1 The Crosslinking Paradox: Thermoplastics vs. Thermosets

Macromolecular materials have historically been bisected into two distinct thermal and structural regimes: thermoplastics and thermosets. Thermoplastics consist of linear or branched macromolecular chains held together by physical entanglements and secondary intermolecular interactions (van der Waals, dipole-dipole, hydrogen bonding). When thermally excited above their glass transition temperature (T_g) or crystalline melting temperature (T_m), they transition into a viscoelastic fluid capable of flow, allowing extrusion, injection molding, and repeated thermo-mechanical reprocessing. However, this fluid vulnerability severely limits their dimensional stability, creep resistance, and solvent tolerance under mechanical load at elevated temperatures.

Thermosetting resins, conversely, are synthesized via covalent step-growth or chain-growth polymerizations of multifunctional monomers, producing an infinite three-dimensional crosslinked percolation network. While this rigid covalent framework provides outstanding modulus, chemical resilience, and dimensional stability at operating temperatures, it introduces a definitive performance bottleneck: post-gelation thermal intractability. Covalent bonds cannot be reformed once cleaved via thermal degradation; consequently, thermosetting polymers cannot be remelted, re-welded, or mechanically recycled.

THE VITRIMER DISTINCTION: ASSOCIATIVE EXCHANGE VS. DISSOCIATIVE CANS

Covalent Adaptable Networks (CANs) are categorized mechanistically by their exchange pathways:

- **Dissociative CANs (e.g., retro-Diels-Alder networks):** The system undergoes bond cleavage prior to subsequent bond reformation ($\text{A-B} \rightleftharpoons \text{A} + \text{B}$). At elevated temperatures, the equilibrium constant shifts toward bond rupture, inducing transient loss of crosslink density, catastrophic drop in viscosity, and risk of structural creep or premature matrix collapse.
- **Associative CANs (Vitrimer):** Exchange occurs through a concerted addition-elimination intermediate ($\text{A-B} + \text{C}^* \rightleftharpoons [\text{A-B-C}]^\ddagger \rightleftharpoons \text{A} + \text{B-C}$). The active bond cleavage is synchronized with fresh bond creation. Crosslink density remains constant throughout topological reconfiguration ($\Delta \nu \equiv 0$).

1.2 The Topology Freezing Transition Temperature (T_v)

Vitrimer introduces an intrinsic transition threshold: the *topology freezing transition temperature* (T_v). Historically, conventional glass-forming liquids transition from an ergodic liquid state to an out-of-equilibrium vitreous state at the glass transition temperature (T_g), driven by steric hindrance and molecular jamming of segmental motions. In vitrimers, two independent transition phenomena govern material behavior:

$$\eta(T) = \eta_0 \exp\left(\frac{E_a}{RT}\right) \quad (\text{Eq. 1.1})$$

Leibler defined T_v arbitrarily as the temperature at which the internal melt viscosity of the covalent network reaches the conventional processing threshold of $10^{12} \text{ Pa} \cdot \text{s}$. Below T_v , transesterification or exchange kinetics are frozen on human-scale observation times; the vitrimer responds mechanically as a classical, static thermoset. Above T_v , the rate of dynamic bond exchange accelerates sufficiently to allow macroscopic stress relaxation, yielding shear flow while maintaining an intact crosslinked architecture.

Depending on molecular formulation, two distinct regimes emerge relative to the structural glass

transition:

- **Regime I ($T_g > T_v$):** Observed frequently in hyper-rigid, high-aromatic networks. Below T_g , segmental chain mobility is locked, freezing exchange reactions despite catalyst activation. Flow is achieved immediately upon passing T_g .
- **Regime II ($T_v > T_g$):** Characteristic of high-entropy, flexible aliphatic networks—such as those synthesized from vegetable oils. Above T_g , the material enters an elastomeric rubbery plateau; it cannot flow until thermal energy provides sufficient activation energy (E_a) to cross the higher T_v barrier.

1.3 Viscoelastic Contrast: Arrhenius vs. Williams-Landel-Ferry (WLF)

The definitive rheological hallmark of vitrimeric behavior is its high-temperature flow mechanism. Linear polymer melts relax stress through snake-like reptation dynamics; their viscosity scales near T_g according to the non-Arrhenius Williams-Landel-Ferry (WLF) or Vogel-Fulcher-Tammann (VFT) models governed by free volume availability:

$$\log a_T = \frac{-C_1 (T - T_{\text{ref}})}{C_2 + (T - T_{\text{ref}})} \quad (\text{Eq. 1.2})$$

Conversely, vitrimers undergo topological reconfiguration controlled directly by chemical transesterification kinetics. Because bond exchange is limited by the chemical reaction activation barrier rather than conformational free-volume creation, high-temperature viscosity displays an Arrhenius trajectory, as described in Equation 1.1. This fundamental difference enables vitrimers to be reshaped with precision, avoiding the sudden thermal sag and flash running characteristic of uncrosslinked thermoplastic melts.

Vegetable Oils as Precursors: Epoxidation and Macromolecular Structures

2.1 Fatty Acid Profiles and Structural Triglyceride Heterogeneity

Natural plant-derived oils represent renewable tri-esters of glycerol condensed with three fatty acid chains. Their chemical utility for high-performance polymeric crosslinking depends heavily on the average degree of unsaturation (carbon-carbon double bonds, $C=C$) per triglyceride molecule, quantified via the industrial *Iodine Value* ($\frac{g\ I_2}{100\ g\ oil}$).

Table 2.1: Fatty Acid Compositions and Physicochemical Metrics of Primary Industrial Vegetable Oils

VEGETABLE OIL SOURCE	IODINE VALUE (G I ₂ /100G)	DOMINANT UNSATURATION	AVERAGE C=C PER TRIGLYCERIDE	THEORETICAL MAX EEW (G/EQ)
Linseed Oil (LO)	170 – 205	Linolenic (18:3, ~55%)	6.2 – 6.6	155 – 175
Soybean Oil (SBO)	120 – 142	Linoleic (18:2, ~53%)	4.5 – 4.8	220 – 250
Tung Oil (TO)	160 – 175	α-Eleostearic (18:3 conj., ~80%)	5.8 – 6.2	170 – 190
Castor Oil (CO)	82 – 90	Ricinoleic (18:1-OH, ~88%)	2.7 – 3.0	280 – 320
Palm Oil (PO)	50 – 55	Oleic (18:1, ~40%)	1.6 – 1.8	380 – 430

2.2 Industrial Epoxidation Chemistries

Triglyceride $C=C$ unsaturations lack the intrinsic reactivity needed for rapid step-growth crosslinking with nucleophilic or electrophilic hardeners. They must undergo chemical transformation into oxirane (epoxy) three-membered rings. The dominant commercial method remains the **Prilezhaev epoxidation**, operating via an in-situ generated peroxyacetic acid:

SCHEME 2.1: CATALYTIC MECHANISM OF IN-SITU PEROXYFORMIC/PERACETIC PRILEZHAEV EPOXIDATION

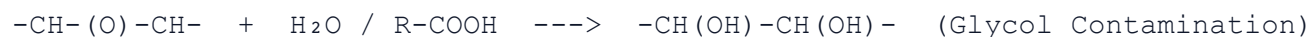
1. Formic/Acetic Acid Oxidation:



2. Electrophilic Alkene Oxygenation (Concerted Transition State):



3. Parasitic Side-Reaction (Hydrolytic Oxirane Ring Cleavage):



Maintaining strict temperature control (typically between 50°C and 65°C) and utilizing heterogeneous acid catalysts, such as sulfonated crosslinked polystyrene resins (Amberlyst-15), effectively suppresses parasitic ring-opening hydrolyses. Modern greener syntheses utilize biocatalytic routes driven by immobilized *Candida antarctica* Lipase B (Novozym 435), achieving high oxirane selectivity without mineral-acid-induced secondary cleavage.

2.3 Macromolecular Architecture: The Challenge of Internal Oxiranes

An essential structural difference separates vegetable-oil-derived epoxies (e.g., Epoxidized Soybean Oil [ESBO], Epoxidized Linseed Oil [ELO]) from standard aromatic petro-epoxies (e.g., DGEBA):

- **Terminal vs. Internal Positioning:** DGEBA features unhindered terminal oxiranes. In contrast, ESBO and ELO bear oxirane groups positioned centrally along aliphatic fatty acid backbones, creating steric hindrance that reduces electrophilic reactivity toward

amine curing agents.

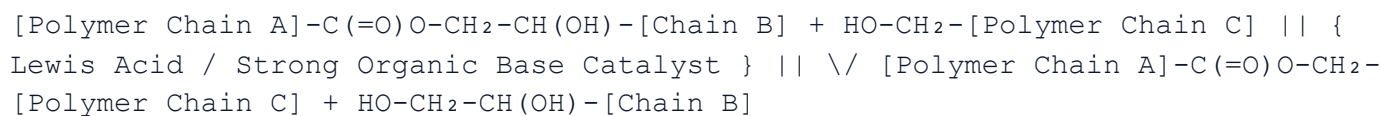
- **Dangling Aliphatic Chains:** Saturated fractions (palmitic, stearic acids) along with unreacted or single-functional terminal tail groups fail to form crosslinks. These free chain ends act as internal plasticizers, driving down glassy storage moduli and depressive thermodynamic T_g .

Dynamic Exchange Chemistries and Catalytic Formulations

3.1 Transesterification Mechanics in Bio-Epoxy Networks

Vitrimers derived from epoxidized triglycerides rely primarily on catalyzed or autocatalyzed associative transesterification. When an epoxidized vegetable oil reacts with a carboxylic acid anhydride or dicarboxylic acid hardener, ring-opening polyaddition yields an ester linkage accompanied by a β -hydroxy ester motif:

SCHEME 3.1: CLASSICAL ASSOCIATIVE TRANSESTERIFICATION PATHWAY IN EPOXIDIZED TRIGLYCERIDES



Because the incoming free nucleophilic hydroxyl group attacks the electrophilic carbonyl carbon while the original leaving group remains covalently bound to the network backbone, network connectivity is maintained. The transient intermediate is a pentacoordinate carbon state; total crosslink density remains invariant throughout this structural exchange.

3.2 Catalytic Suites: Coordination Complexes vs. Organocatalysts

Uncatalyzed transesterification typically proceeds slowly below 200°C. To lower the operational T_v into a workable processing window (130°C – 170°C), suitable catalyst systems must be formulated into the resin matrix prior to cure:

Table 3.1: Comparative Catalytic Efficiencies for Bio-Based Transesterification Vitrimers

CATALYST CATEGORY	REPRESENTATIVE SPECIES	ACTIVATION ENERGY (EA)	PROCESSING TEMP (TV)	DRAWBACKS / VULNERABILITIES
Metal Acetylacetonates	Zn(acac)_2 , Co(acac)_2	85 – 110 kJ/mol	140 – 160 °C	Hygroscopic aggregation; moisture poisoning
Zinc Carboxylates	Zinc 2-ethylhexanoate	90 – 125 kJ/mol	150 – 175 °C	Phase separation at elevated fractions
Bicyclic Amidines/Guanidines	TBD, DBU	65 – 95 kJ/mol	110 – 130 °C	Thermal decomposition above 190 °C; volatile
Phosphonium Salts	Ph_4PBr , EtPh_3PI	115 – 140 kJ/mol	170 – 195 °C	High temperatures trigger Hofmann-type elimination

3.3 Catalyst-Free Design Protocols

A persistent limitation of metal catalysts (e.g., zinc, tin octoates) is their tendency to leach into solvents and deactivate over time through atmospheric hydrolytic oxidation. Researchers have overcome this by designing *catalyst-free vitrimer networks* using neighboring-group participation. By incorporating tertiary amines directly into the hardener backbone (e.g., utilizing hardeners synthesized from triethanolamine or bio-based secondary amine precursors), the unshared electron pair coordinates intramolecularly with the ester carbonyl, accelerating transesterification internally without added organometallic dopants.

Network Design, Stoichiometry, and Thermomechanical Properties

4.1 Stoichiometric Formulations: The R-Ratio and Hydroxyl Density

In conventional non-dynamic epoxy formulations, chemists target an exact stoichiometric equivalence between electrophilic oxirane moieties and active nucleophilic hardener protons ($R = [\text{Oxirane}] / [\text{Hardener H}] = 1.0$) to maximize gel fractions, crosslink density, and storage modulus while minimizing dangling ends.

In vitrimeric formulations, this classic paradigm is intentionally modified. Transesterification requires an excess population of nucleophilic free hydroxyl groups (-OH) to attack dynamic ester bonds. The crosslinking stoichiometry must be calibrated using the formulation parameter R :

$$R_{\text{stoich}} = \frac{n_{\text{epoxy}}}{n_{\text{COOH}} \text{ or } 2 \times n_{\text{anhydride}}} \quad (\text{Eq. 4.1})$$

Operating off-stoichiometrically (e.g., $R = 0.70\text{--}0.85$ or $R = 1.15\text{--}1.30$, depending on whether a diacid or anhydride curing agent is selected) guarantees the persistent presence of pendant hydroxyl functional handles. If all hydroxyls are consumed in irreversible esterification without regeneration, exchange pathways shut down, increasing topological relaxation times toward infinity.

4.2 Bio-Based Crosslinking Hardeners

Replacing toxic petroleum curing agents (e.g., methylhexahydrophthalic anhydride [MHHPA] or isophoronediamine [IPDA]) with plant-derived hardeners enables high bio-carbon contents (approaching 100% per ASTM D6866):

- **Dimer Fatty Acids (Pripol series):** Dimeric C_{36} aliphatic diacids provide exceptional chain compliance and impact toughness, but yield lower T_g values (ranging from $-10^{\circ}C$ to $35^{\circ}C$).
- **Citric Acid / Malic Acid:** Polycarboxylic organic acids offering compact stereocenters that improve crosslink densities; however, their hydrophilic character demands careful processing to suppress early hydrolytic phase separation.
- **Rosin-Derived Acids (Maleopimaric / Abietic Acids):** Phenanthrene ring architectures that yield rigid, high- T_g matrices ($>100^{\circ}C$), directly competing with traditional bisphenol-based performance profiles.

Table 4.2: Thermomechanical Properties of Representative Vegetable Oil Vitrimer Formulations				
MATRIX SYSTEM	HARDENERS / CATALYST SYSTEM	GLASS TRANSITION (TG)	TENSILE MODULUS (MPa)	TENSILE STRENGTH (MPa)
ESBO / Dimer Acid	C_{36} Dimer Acid / 5 mol% $Zn(acac)_2$	12 °C	42 ± 5	4.8 ± 0.6
ELO / Citric Acid	Bio-Citric Acid / 2.5 mol% TBD	58 °C	850 ± 35	28.4 ± 2.1
ELO / Rosin Derivative	Maleopimaric Anhydride / $Zn(acac)_2$	115 °C	2,150 ± 90	58.2 ± 3.4
Castor Oil Hybrid	Sebacic Acid / Imidazole Complex	34 °C	320 ± 20	16.5 ± 1.2

Stress Relaxation, Rheology, and Viscoelastic Scaling

5.1 Maxwellian Relaxation Kinetics in Covalent Networks

The definitive method for characterizing dynamic crosslink exchange kinetics is step-strain transient stress relaxation via shear or torsional dynamic mechanical rheometry. An instantaneous shear or axial strain (γ_0 or ϵ_0) is imposed on the sample above T_g , and the decay of the relaxation modulus $G(t)$ or $E(t)$ is monitored over time:

$$G(t) = G_0 \exp\left[-\left(\frac{t}{\tau^*}\right)^\beta\right] \quad (\text{Eq. 5.1})$$

When the stretched exponential parameter $\beta = 1$, the system exhibits an ideal, monodisperse Maxwell behavior. In bio-based epoxies, structural polydispersity and uneven distribution of crosslink nodes usually yield a Kohlrausch-Williams-Watts (KWW) exponent in the range of $0.65 < \beta < 0.90$.

QUANTIFYING CHARACTERISTIC RELAXATION TIMES (T^*)

The characteristic relaxation time (τ^*) is defined as the time point at which the initial normalized relaxation modulus decays to $1/e$ (approximately 36.8%) of its initial value:

$$\frac{G(\tau^*)}{G_0} = \frac{1}{e} \approx 0.368$$

Plotting $\ln(\tau^*)$ versus $1000/T$ across isothermal steps constructs a linear Arrhenius plot. The slope reveals the precise apparent activation energy (E_a) of the dynamic transesterification exchange reaction within the bulk polymer network.

5.2 Creep Resistance vs. Flowability Trade-offs

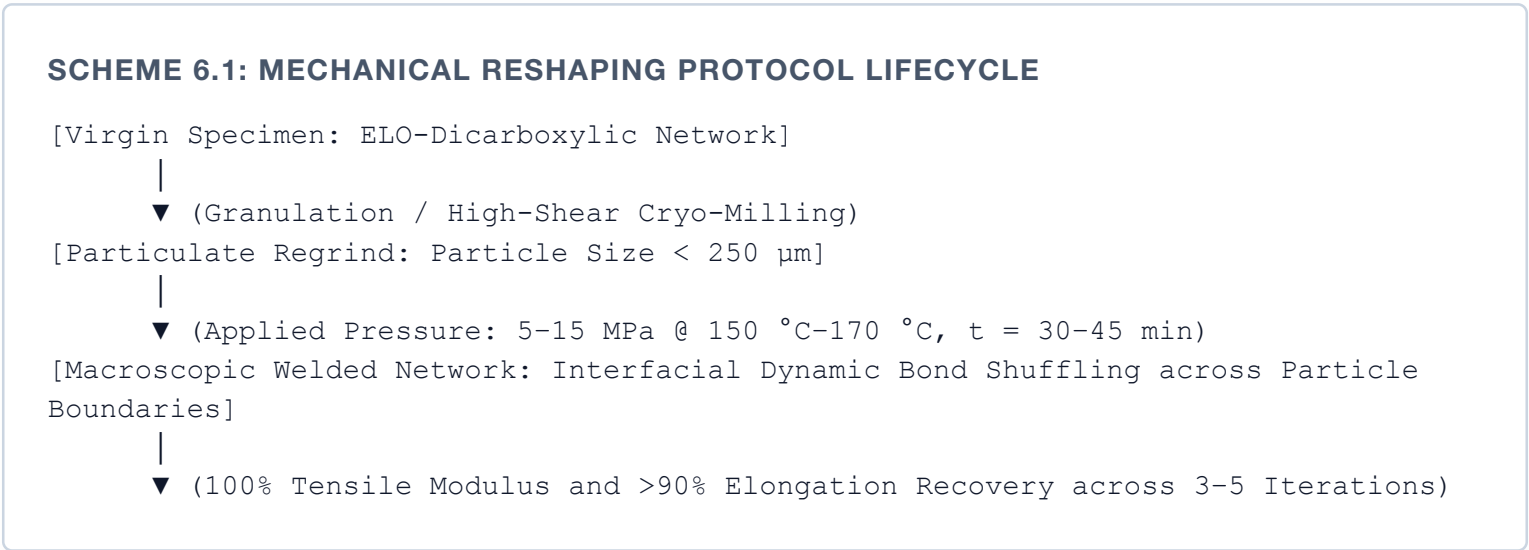
A central challenge in vitrimer engineering is the delicate trade-off between thermal reprocessability and high-temperature dimensional creep resistance:

- **Creep Resistance:** Under operational loads below T_v , the network must preserve structural tolerances without exhibiting irreversible plastic distortion. If T_v is engineered too close to room temperature, vegetable oil vitrimers can exhibit continuous creep over long loading cycles, compromising structural reliability.
- **Reprocessing Flowability:** Conversely, if T_v is shifted higher than 200°C to suppress creep, thermal degradation of the plant-derived fatty acid backbones can occur through β -elimination and radical homolysis before the matrix relaxes quickly enough for processing.

Reprocessing, Closed-Loop Recycling, and Fiber-Reinforced Composites

6.1 Mechanical Recycling via Thermocompression Protocols

Unlike conventional thermosets, vegetable oil bioepoxy vitrimers can undergo multiple mechanical recycling sequences through grinding, chipping, and subsequent closed-die high-pressure consolidation:



6.2 Closed-Loop Solvolytic Deconstruction

In addition to thermoforming and welding, bioepoxy vitrimers can undergo chemical closed-loop recycling via catalytic solvolysis. When immersed in an excess volume of a reactive, low-molecular-weight protic solvent (such as ethylene glycol, glycerol, or bio-ethanol) at temperatures near 160°C , transesterification shifts from intra-network exchange to solvent exchange.

This exchange progressively depolymerizes the covalent network, decomposing the solid matrix into oligomeric polyols and functional diesters. Once dissolved, the liquid resin precursor can be purified, blended with fresh stoichiometric curing agents, and re-crosslinked into virgin-grade structural components without down-cycling.

6.3 Sustainable Fiber-Reinforced Composites

Vitrimeric vegetable-oil matrices are well suited for sustainable fiber-reinforced polymer composites (FRPs). Combining these matrices with woven flax, hemp, or basalt fibers yields structural, fully bio-derived laminates. At end-of-life, the composite undergoes solvolysis, breaking down the polymer network without damaging delicate reinforcing fibers, enabling both fiber and oligomer recovery:

Table 6.1: Retained Performance Metrics of Flax/ELO Vitrimer Composites Post-Recycling Cycles			
PROCESSING ITERATION	TENSILE STRENGTH (MPa)	FLEXURAL MODULUS (GPa)	INTERLAMINAR SHEAR STRENGTH (ILSS)
Virgin Composite	178 ± 8	14.2 ± 0.6	24.8 ± 1.1 MPa
Recycled (Cycle 1: Compression)	171 ± 9	13.8 ± 0.5	23.5 ± 1.3 MPa
Recycled (Cycle 2: Compression)	165 ± 11	13.4 ± 0.8	22.1 ± 1.2 MPa
Recovered Fiber + Virgin Resin	175 ± 7	14.0 ± 0.7	24.2 ± 1.0 MPa

Industrial Scalability, Hydrolytic Durability, and Future Perspectives

7.1 Chemical Vulnerability: Hydrolysis vs. Dynamic Exchange

A central chemical challenge for bio-based polyester vitrimers is their environmental hydrolytic stability. The active dynamic motifs that enable transesterification—namely β -hydroxy ester bonds—are inherently vulnerable to water-induced ester cleavage:



Under hot and humid conditions (e.g., 85°C / 85% RH), atmospheric water ingress can shift this equilibrium, inducing network de-crosslinking, matrix swelling, microcracking, and premature mechanical failure. Incorporating hydrophobic barrier monomers—such as cardanol-derived modifiers, fluorinated co-monomers, or dense aliphatic fatty acid architectures (e.g., tung oil conjugated networks)—helps shield vulnerable ester linkages from moisture penetration.

7.2 Industrial Implementation: Scalability Barriers

Before vegetable-oil vitrimers can compete commercially with standard bisphenol-A (DGEBA) resins in aerospace, automotive, and wind-energy sectors, several manufacturing hurdles must be addressed:

- **Thermal Cycle Times:** While traditional thermoset matrices cure rapidly in automated resin transfer molding (HP-RTM) cycles in under 3 minutes, vitrimer composites often

require extended curing and stress-relaxation windows (15 to 45 minutes) to ensure uniform bond exchange.

- **Raw Material Batch-to-Batch Heterogeneity:** Plant-derived triglycerides exhibit natural variations in fatty acid distribution due to seasonal climate conditions, soil composition, and crop genetics, requiring adaptive industrial formulation protocols.
- **Long-Term Creep under Dynamic Loads:** Structural components subject to sustained load at elevated service temperatures must resist premature plastic creep, requiring precise formulation to decouple creep resistance at operational temperatures from rapid exchange at processing temperatures.

7.3 Concluding Scientific Roadmap

Vegetable oil bioepoxy vitrimers offer a compelling route to sustainable materials by bridging the historical divide between thermoset performance and thermoplastic reprocessability. By leveraging the internal architecture of plant triglycerides and pairing them with associative exchange chemistries, polymer engineers can target high mechanical properties alongside genuine end-of-life circularity. As advances in catalyst latency, moisture-resistant network architectures, and additive manufacturing converge, these bio-based dynamic networks provide a clear pathway toward a circular, non-petroleum polymer economy.

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