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VEGETABLE OIL BIOEPOXY VITRIMERS FOR COMPOSITE MATERIALS

Fundamental Chemistry, Processing, and Industrial Applications

MARIE SESHAT LANDRY

LANDRY INDUSTRIES INC. · MONCTON, NEW BRUNSWICK



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VEGETABLE OIL BIOEPOXY VITRIMERS FOR COMPOSITE MATERIALS: FUNDAMENTAL CHEMISTRY, PROCESSING, AND INDUSTRIAL APPLICATIONS

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PREFACE

A thermoset that can be repaired, reshaped and recovered — made from a plant oil and reinforced with fibres — is no longer a contradiction. This book explains how, and how far the idea has really travelled.

Fibre-reinforced epoxies combine the stiffness of carbon, glass or plant fibres with the toughness, adhesion and chemical resistance of a crosslinked matrix. That crosslinked matrix is also their weakness at end of life: a conventional epoxy cannot be melted, so a damaged part is difficult to repair and a retired one is difficult to recycle. Wind-turbine blades are the most visible example; coverage of one industry announcement reported that wind turbines account for about a tenth of Europe's fibre-reinforced composite waste, most of it historically landfilled [1].

Vitrimers change that premise. First described in 2011 for epoxy–acid networks, they are permanently crosslinked yet able to rearrange their topology through associative bond exchange, so they can flow, heal and be reprocessed when hot while behaving as thermosets in service [2]. Epoxidized vegetable oils are an unusually good fit for the most common vitrimer chemistry, because their preferred hardeners — acids and anhydrides — generate exactly the ester and hydroxyl groups that transesterification exchange requires. Combining the two ideas offers a matrix that is both largely renewable in origin and designed for a second life.

Who this book is for

The book is written for materials scientists, polymer chemists, composite manufacturing engineers and sustainability researchers in academia and industry. It assumes familiarity with basic polymer chemistry but builds the vitrimer-specific ideas — topology freezing, stress relaxation, exchange catalysis — from first principles.

Scope and structure

Part I sets out the principles: why thermosets are hard to recycle, what distinguishes associative from dissociative dynamic networks, how plant oils are epoxidized and characterized, and which dynamic covalent chemistries are available. **Part II** covers formulation and properties: hardeners, stoichiometry, rigid bio-based partners, catalysts, and the mechanical, thermal, self-healing and shape-memory behaviour that results. **Part III** moves to composites: fibres and interfaces, processing routes and their rheological windows, and functional composites with nanocarbons and flame retardants. **Part IV** addresses circularity: reshaping, remoulding, chemical recycling with fibre recovery, and degradation in the environment. **Part V** examines applications, techno-economics, life-cycle assessment, regulation, and the open technical problems that will decide how quickly these materials reach the market.

Conventions and evidence

- **Abbreviations.** EVO = epoxidized vegetable oil; ESO, ELO, EHO = epoxidized soybean, linseed and hemp oils; VOEV = vegetable oil epoxy vitrimer; T_g = glass transition; T_v = topology-freezing temperature; τ^* = characteristic relaxation time; E_a = activation energy. A glossary appears in the back matter.
- **Evidence levels.** Values attributed to a source are reported as published. Worked examples are labelled and calculated from stated inputs. Application chapters distinguish documented demonstrations from design scenarios, so that readers can see where the field is proven and where it is still projecting.
- **Companion volume.** Feedstock and epoxidation chemistry are covered more extensively in the companion book, *Bio-Based Epoxy Resins*; Chapter 2 here summarizes what a vitrimer formulator needs.

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Moncton, New Brunswick · October 2026



PRINCIPLES OF BIOBASED EPOXIES AND VITRIMER PHYSICS

Why permanent networks can flow, and how plant oils become the building blocks of networks that can be remade.

CH. 1 · INTRODUCTION TO VITRIMERS AND SUSTAINABLE COMPOSITES

CH. 2 · SYNTHESIS AND EPOXIDATION OF VEGETABLE OIL FEEDSTOCKS

CH. 3 · DYNAMIC COVALENT CHEMISTRIES IN BIOEPOXY NETWORKS

INTRODUCTION TO VITRIMERS AND SUSTAINABLE COMPOSITES

The property that makes a thermoset valuable – a network that never lets go – is the same property that makes it so hard to repair, reshape or recycle. Vitrimers keep the network and let it rearrange.

IN THIS CHAPTER

- Why conventional epoxy composites are difficult to recycle, and what current end-of-life routes achieve.
- Covalent adaptable networks: dissociative versus associative exchange.
- The two transitions of a vitrimer – T_g and T_v – and the Arrhenius flow that follows.
- Plant oils as vitrimer feedstocks: scale, variability and the right way to talk about sustainability.

1.1 THE THERMOSET RECYCLING DILEMMA

An epoxy matrix is a single, covalently connected molecule that fills the whole part. That is why it does not creep under load, does not dissolve in solvents and does not soften until its glass transition. It is also why it cannot be melted, re-shaped or separated cleanly from the fibres it surrounds. For thermoplastics, recycling begins with melting; for thermosets, there is no melt to begin with.

The consequences are most visible in large composite structures. Wind-turbine blades combine glass and carbon fibres, foam or balsa cores and a thermoset matrix. Coverage of Siemens Gamesa's 2021 recyclable-blade announcement reported that wind turbines account for about 10 % of Europe's fibre-reinforced composite waste, which had mostly gone to landfill, and that several European countries had banned landfilling such waste [1]. Similar end-of-life questions confront aerospace scrap, automotive parts, boat hulls and printed circuit boards.

What existing routes achieve

Recycling technologies for carbon- and glass-fibre composites have been reviewed extensively [3]. They fall into four families, summarized in Table 1.1. None is ideal: the routes that preserve fibre quality tend to consume energy and chemicals, and the matrix itself is almost always downgraded or destroyed.

Table 1.1 End-of-life routes for conventional thermoset composites (qualitative).

Route	What happens	Fibre outcome	Matrix outcome	Main drawback
Mechanical	Shredding and grinding to powders and short fibres	Short, low-value filler	Filler	Severe downcycling
Thermal (pyrolysis, fluidized bed)	Matrix burned or pyrolysed off at high temperature	Long fibres, often with reduced strength or surface char	Fuel, gases, oils	Energy demand; fibre damage (especially glass)
Chemical (solvolytic)	Matrix depolymerized in hot solvents, often under pressure	Clean fibres, good properties	Mixed chemicals, rarely reused as resin	Harsh conditions for conventional epoxies; solvent handling
Disposal	Landfill, incineration, cement-kiln co-processing	Lost (or mineral credit in cement)	Lost or energy	Increasingly restricted; no material recovery

Repair is the other half of the dilemma. A cracked or delaminated epoxy laminate cannot heal; damaged regions are scarfed out and patched with new resin and fibre, leaving a bonded joint rather than a continuous material. Designing a matrix that can be healed in place, reshaped after cure and dissolved selectively at end of life addresses both problems at once.

1.2 DEFINING VITRIMERS

Covalent adaptable networks

Polymer networks whose crosslinks can rearrange under a stimulus are called covalent adaptable networks (CANs). They divide into two classes according to the mechanism of exchange:

- **Dissociative networks** break a bond first and re-form it later. The classic example is the thermally reversible Diels–Alder adduct between furan and maleimide groups: a crosslinked material built on this chemistry was shown in 2002 to be re-mendable by heating, because the adducts dissociate at elevated temperature and re-form on cooling [4]. Because bonds are lost before they are regained, crosslink density falls on heating; above a certain temperature such networks can lose their integrity entirely and flow like a liquid.
- **Associative networks** exchange bonds through a pathway in which a new bond forms before, or at the same time as, the old one breaks. The number of crosslinks is conserved at every temperature, so the network never dissolves in a good solvent and never becomes a low-viscosity liquid — yet its topology can rearrange, and so it can flow.

The term *vitriimer* was introduced for associative networks of the second kind. Montarnal, Capelot, Tournilhac and Leibler showed in 2011 that epoxy networks cured with acids or anhydrides and containing a transesterification catalyst could be reshaped and repaired at high temperature while remaining insoluble — behaviour they compared to that of silica glass, whose viscosity falls gradually and predictably with temperature [2]. Many associ-

ative chemistries have since been developed, including transamination of vinylogous urethanes [5] and metathesis of dioxaborolanes, which converted commodity thermoplastics into vitrimers [6]; these have been reviewed in depth [7].

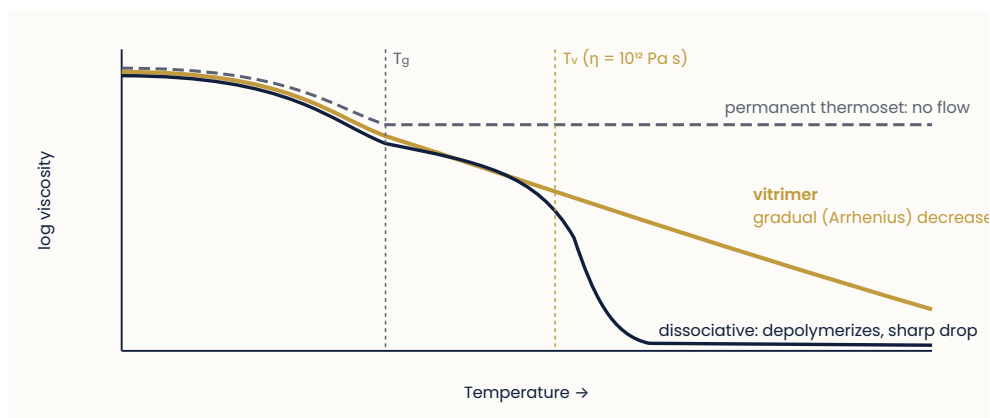


Figure 1.1 Schematic (not measured) viscosity–temperature behaviour. A permanent thermoset never flows above T_g ; a dissociative network loses crosslinks and its viscosity collapses over a narrow range; an associative vitrimer keeps its crosslinks and its viscosity falls gradually, following an Arrhenius law governed by the exchange reaction.

Table 1.2 Dissociative and associative covalent adaptable networks compared (qualitative).

Feature	Dissociative (e.g., Diels–Alder)	Associative (vitrimer)
Crosslink density on heating	Falls; may reach zero	Constant
Solubility when hot	Can dissolve or depolymerize	Insoluble (swells)
Viscosity–temperature	Sharp drop near dissociation temperature	Gradual Arrhenius decrease
Processing window	Narrow, near the dissociation temperature	Broad; controlled by exchange kinetics and catalyst
Typical chemistries	Furan–maleimide, some disulfide and imine systems depending on conditions	Transesterification, vinylogous urethane transamination, dioxaborolane and boronic–ester metathesis, imine metathesis
Main risk	Loss of integrity at high temperature	Creep at service temperature if exchange is too fast

1.3 TOPOLOGY FREEZING TRANSITION (T_v) AND T_g

A vitrimer has two characteristic temperatures. The **glass transition**, T_g , marks the onset of cooperative segmental motion, as in any polymer. The **topology-freezing temperature**, T_v , marks the point at which bond exchange becomes fast enough for the network to flow on practical timescales; by convention it is defined as the temperature at which the viscosity reaches 10^{12} Pa s. The catalyst concentration shifts T_v , as Capelot and co-workers demonstrated by measuring it directly [8].

Two orderings, two behaviours

- $T_g < T_v$. On heating, the material passes from glass to rubber at T_g , behaves as an elastic thermoset in a rubbery plateau, and only above T_v begins to flow. This is the usual case for low- T_g networks, including most vegetable-oil vitrimers.
- $T_v < T_g$. The exchange chemistry would be fast enough, but the network is glassy; segments cannot move to bring reactive groups together. Flow appears only above T_g , and its temperature dependence first follows the steep, free-volume-controlled (WLF-type) behaviour near T_g before crossing over to the Arrhenius regime of the exchange reaction.

Exchange kinetics and flow

Above both transitions, the characteristic relaxation time of the network, τ^* , is set by the rate of the exchange reaction and follows an Arrhenius law:

$$\tau^*(T) = \tau_0 \exp(E_a / RT) \quad (1.1)$$

Through the Maxwell relation between viscosity, modulus and relaxation time,

$$\eta \approx G \tau^* \quad (1.2)$$

the viscosity inherits the same temperature dependence. The rheology of vitrimers — including departures from single-exponential relaxation and the role of network structure — has been analysed theoretically and experimentally [9]; Chapter 3 develops the measurement methods.

WORKED EXAMPLE · WHAT TEMPERATURE DO YOU NEED TO REPROCESS?

Suppose a vitrimer relaxes with $\tau^* = 1000$ s at 473 K (200 °C) and $E_a = 110$ kJ mol⁻¹. A compression-moulding cycle of about ten minutes needs τ^* of order 100 s, ten times shorter. From Eq. 1.1, $\ln(1000/100) = (E_a/R)(1/473 - 1/T)$, so $1/T = 2.114 \times 10^{-3} - 2.303 \times 8.314/110\,000 = 1.940 \times 10^{-3}$ K⁻¹, giving $T \approx 515$ K (242 °C). A modest acceleration of processing requires a 40 K increase in temperature — which brings ester pyrolysis and oxidation into play. Inputs are illustrative; the lesson is that catalyst activity, not just temperature, must carry the processing window.

The central design tension

Every vitrimer design must reconcile two requirements that pull in opposite directions: exchange must be *fast* at processing temperature, yet *negligibly slow* at service temperature, or the part will creep. Because the Arrhenius law links the two through a single activation energy, a high E_a is desirable — it gives a steep change in rate between service and processing conditions. Strategies to suppress creep without sacrificing processing speed are an active research front; one approach traps the catalytic amine reversibly so that it is released only at high temperature [10]. Chapter 12 returns to this as one of the field's principal open challenges.

1.4 VEGETABLE OILS AS RENEWABLE FEEDSTOCKS

Economic scalability

Epoxidized soybean and linseed oils are already manufactured at industrial scale and sold against defined specifications — for example, ESO with oxirane oxygen above 6.8 % and ELO with 9.2 % oxirane content — primarily as plasticizers and stabilizers for PVC [11, 12]. A vitrimer built on these intermediates therefore starts from an existing supply chain rather than a laboratory synthesis, which is a decisive advantage over many specialty bio-based monomers.

Chemical variability

Oils are natural mixtures, and their composition varies with cultivar, climate and processing. Table 1.3 summarizes the four oils named in this book's scope. Soybean oil is dominated by linoleic acid; linseed by α -linolenic acid; castor by ricinoleic acid, whose hydroxyl group adds a second reactive handle; tung by α -eleostearic acid, a conjugated triene.

Table 1.3 Key compositional features of four vitrimer feedstock oils. Soybean ranges are Codex ranges [13]; linseed, castor and tung values are single analyses with iodine values calculated from composition [14].

Oil	Dominant fatty acid	Share	Iodine value	Significance for vitrimers
Soybean	Linoleic (18:2)	48.0–59.0 %	124–139	Commodity ESO; ~4 epoxides per molecule
Linseed	α -Linolenic (18:3)	50.3 %	181 (calc.)	Highest epoxide density among common oils; stiffer networks
Castor	Ricinoleic (12-OH 18:1)	88.2 %	87.9 (calc.)	Built-in hydroxyls aid transesterification; low epoxide content
Tung	α -Eleostearic (conj. 18:3)	78.4 %	226 (calc.)	Conjugated diene/triene for Diels–Alder chemistry; poor epoxidation; Wijs IV underestimates unsaturation [14]

Variability matters more for vitrimers than for conventional thermosets. The exchange rate depends on the concentration of hydroxyl and ester groups and on catalyst availability, all of which shift with the epoxide content of the oil and with the extent of ring opening during epoxidation. Lot-to-lot control of oxirane content, hydroxyl value and acid value is therefore part of the vitrimer specification, not merely of the resin specification (Chapter 2).

Sustainability metrics, honestly stated

Three distinct claims are often blurred together. *Bio-based content* describes origin and is measured by radiocarbon analysis (ASTM D6866) or by radiocarbon plus elemental analysis (EN 16785-1) [15, 16]. *Recyclability* describes what can be done with the material after use, and depends on chemistry and infrastructure rather than origin. *Environmental impact* requires a life-cycle assessment; a cradle-to-gate comparison of bio-epoxies found triglyceride-based epoxy the best of three bio-based options studied, but also cautioned that bio-sourced epoxies should not be assumed environmentally friendly without full assessment [17]. Vegetable-oil vitrimers can score well on all three, but each must be demonstrated separately (Chapters 9 and 11).

CHAPTER SUMMARY

- Conventional thermoset composites cannot be melted; existing recycling routes recover fibres at a cost in energy, chemicals or fibre quality, and rarely recover the matrix.
- Vitrimers are associative covalent adaptable networks: crosslink density is conserved while topology rearranges, giving gradual, Arrhenius flow above T_v .
- Processing speed and creep resistance are linked through the exchange activation energy; catalyst design must deliver fast exchange hot and negligible exchange cold.
- Epoxidized soybean and linseed oils are commodity intermediates; oil variability must be controlled because it changes exchange kinetics as well as network density.

SYNTHESIS AND EPOXIDATION OF VEGETABLE OIL FEEDSTOCKS

A vitrimer formulator needs more from an epoxidized oil than a high oxirane number. The hydroxyls, esters and acids it carries are not impurities to be minimized blindly – they are the raw material of bond exchange.

IN THIS CHAPTER

- Triglyceride architecture and how many reactive sites each molecule carries.
- Peracid, chemo-enzymatic and heterogeneous catalytic epoxidation – with a vitrimer-specific view of side reactions.
- Acrylation, maleination, glycidylation, isomerization and high-functionality derivatives.
- Characterization by NMR, FTIR, titration and MALDI-TOF mass spectrometry.

2.1 TRIGLYCERIDE ARCHITECTURE

A vegetable oil is a mixture of triglycerides: glycerol esterified with three fatty acids. Three ester groups are therefore present in every molecule before any chemistry is done — a fact that matters for transesterification vitrimers, because these esters can take part in exchange once the network is formed. The reactive sites for epoxidation are the carbon–carbon double bonds of the unsaturated chains (Table 2.1).

Table 2.1 Fatty-acid profiles (% of total fatty acids) and iodine values (g I₂/100 g). Soybean: Codex ranges [13]; hemp: multi-location ranges [18]; linseed, castor, tung: single analyses with calculated IV [14].

Oil	Saturated (16:0 + 18:0)	18:1	18:2	18:3	Other	IV
Soybean	10.0–18.9	17–30	48.0–59.0	4.5–11.0	—	124–139
Hemp seed	7.9–11.1	10.2–14.0	56.5–60.5	16.9–20.0	γ-18:3 0.6–1.7	154–165
Linseed	10.0	21.8	17.9	50.3	—	181 (calc.)
Castor	—	4.3	7.5	—	ricinoleic 88.2	87.9 (calc.)
Tung	5.8	6.8	9.0	—	α-eleostearic 78.4	226 (calc.)

Saturated totals for soybean and hemp are sums of the published palmitic and stearic ranges (calculated).

Unsaturation and functional-site distribution

Average double bonds per triglyceride can be calculated from composition: about 4.6 for soybean, 5.6 for hemp seed and 6.3 for linseed oil (calculated from the compositions above; see the companion volume for the method). After epoxidation the average number of oxiranes per molecule is somewhat lower, because conversion is incomplete and some rings open. It can be estimated directly from a product's epoxide equivalent weight (EEW).

WORKED EXAMPLE · EPOXIDES PER MOLECULE OF COMMERCIAL ESO AND ELO

The EEW of an epoxide is 1600 divided by its oxirane-oxygen percentage. Commercial ESO (OOC > 6.8 %) therefore has $\text{EEW} \leq 235 \text{ g eq}^{-1}$, and ELO (9.2 %) about 174 g eq^{-1} [11, 12]. Taking the parent triglyceride as $\approx 874 \text{ g mol}^{-1}$ and adding the oxygen (oil mass $\times 1.073$ for ESO, $\times 1.101$ for ELO), the epoxidized molecules weigh about 938 and 963 g mol^{-1} . Dividing by EEW gives about **4.0 epoxides per ESO molecule** and **5.5 per ELO molecule** (calculated). These numbers set the functionality f used for gel-point calculations in Chapter 6.

Two features of the distribution matter for vitrimer networks. First, functionality is statistical: some molecules carry two epoxides, others six or more, and the low-functionality fraction contributes dangling chains and sol. Second, the epoxides are *internal* — positioned mid-chain on 1,2-disubstituted carbons — so they react sluggishly with amines but well with carboxylic acids and anhydrides under base or metal catalysis. Those hardeners create β -hydroxy esters, the native exchange unit of transesterification vitrimers (Chapter 3).

2.2 EPOXIDATION PATHWAYS

The Prileschajew reaction via peroxyacids

Prileschajew reported the oxidation of unsaturated compounds by organic peroxy acids in 1909 [19]. Industrially, the peracid is generated in situ from hydrogen peroxide and formic or acetic acid, in a two-phase system with the oil; peracetic acid formation is catalysed by mineral acids or sulfonic-acid ion-exchange resins. Kinetic studies with ion-exchange resins and with liquid acids map the process in detail [20, 21], and the side reactions — opening of the oxirane by water, carboxylic acids and peroxide to give diols, hydroxy esters and oligomers — have been characterized for soybean oil [22].

A VITRIMER VIEW OF SIDE REACTIONS

For a conventional thermoset, ring opening during epoxidation is simply a yield loss. For a transesterification vitrimer it is more nuanced. The hydroxyls it creates are potential exchange partners and can accelerate stress relaxation; the hydroxy-ester groups formed by acid attack are themselves exchangeable. But every opened ring is an epoxide that will not form a crosslink, and oligomers raise viscosity. The practical rule is to *measure* hydroxyl value, acid value and oxirane content on every lot and to formulate against them, rather than assuming a theoretical structure.

Chemo-enzymatic epoxidation using lipases

Immobilized lipases — notably *Candida antarctica* lipase B — catalyse the perhydrolysis of fatty acids with hydrogen peroxide to give peroxy fatty acids, which then epoxidize double bonds. The approach was demonstrated for unsaturated carboxylic acids in 1995 and extended to the complete and partial epoxidation of plant oils [23, 24]; optimization for soybean oil has been reported [25]. Mild, mineral-acid-free conditions give high oxirane selectivity, at the cost of enzyme deactivation by peroxide, enzyme price and slower rates.

Heterogeneous and metal-catalysed strategies

Metal catalysts that activate hydrogen peroxide directly avoid the carboxylic acid and its ring-opening chemistry. Quaternary ammonium peroxotungstophosphates act as phase-transfer epoxidation catalysts with H_2O_2 [26]; methyltrioxorhenium is a highly active homogeneous benchmark [27]. True heterogeneous catalysts — titanium-containing mesoporous silicas, supported tungstates, acidic resins for in situ peracid generation — offer easy separation and reuse but must overcome pore-size limits (triglycerides are large), leaching of the active metal and fouling by viscous products. For vitrimer producers, a key advantage of heterogeneous systems is that they leave no residual metal or acid that might act as an uncontrolled exchange catalyst in the final network.

Table 2.2 Epoxidation routes compared from a vitrimer-formulation perspective (qualitative).

Route	Selectivity	Residues that affect exchange	Scale status
In situ peracid, mineral acid	Moderate; ring opening increases with T and time	Hydroxyls, hydroxy esters, residual acid (must be washed out)	Industrial
In situ peracid, ion-exchange resin	Higher; resin removed by filtration	Fewer hydroxyls; low residual acid	Industrial / pilot
Chemo-enzymatic (lipase)	High	Free fatty acids from perhydrolysis substrate	Pilot / specialty
Metal/ H_2O_2 (W, Re, Ti)	High with suitable additives	Possible trace metals (potential unintended catalysts)	Laboratory / specialty

2.3 CHEMICAL MODIFICATIONS FOR ADVANCED REACTIVITY

Acrylation

Ring opening of the oxiranes with acrylic acid produces acrylated epoxidized oils such as AESO, multifunctional acrylates that cure by radical or UV polymerization; they were developed systematically for liquid moulding and composites [28] and have been used in photoprinted shape-memory scaffolds [29]. Each acrylation event also creates a β -hydroxy ester, so acrylated oils carry an intrinsic exchange motif; combined with a transesterification catalyst, radical-cured AESO networks can in principle relax stress, a route explored in vitrimer photopolymers (Chapter 12).

Maleination

Maleic anhydride grafts onto oil unsaturation through ene and Diels–Alder reactions, giving succinic-anhydride-bearing oils that act as flexible, oil-derived anhydride hardeners. Combined with epoxidized hemp oil and methyl nadic anhydride, maleinized hemp oil lowered stiffness, increased impact absorption by about 180 % and roughly halved the curing time at a 25 % share of the hardener blend [30]. Because anhydride–epoxy cure yields ester-rich networks, maleinized-oil hardeners are natural partners for vitrimer formulations.

Glycidylation of fatty-acid hydroxyls

Hydroxyl groups — native in castor oil’s ricinoleic acid, or created by ring opening — can be glycidylated with epichlorohydrin to install terminal epoxides, which react far more readily with amines than internal oxiranes. Epichlorohydrin can itself be made from glycerol [31]. Excess ECH and control of hydrolysable chlorine are the key process requirements (see the companion volume).

Isomerization and high-functionality derivatives

Methylene-interrupted dienes and trienes can be isomerized into conjugated systems with base or metal catalysts. Conjugation does not help epoxidation — tung oil, naturally conjugated, is a poor epoxidation feedstock — but it opens Diels–Alder chemistry with maleimides and maleic anhydride, useful both for anhydride hardeners and for dissociative, thermally reversible crosslinks of the furan–maleimide type [4]. To raise functionality, fatty acids can be re-esterified onto larger polyol cores: epoxidized sucrose esters of soybean fatty acids carry many more epoxides per molecule than a triglyceride and give high-bio-content anhydride thermosets [32]. High functionality lowers the gel point (Chapter 6) and raises crosslink density, but it also reduces the free hydroxyl-to-ester balance per junction, which must be considered when designing exchange.

2.4 CHARACTERIZATION TECHNIQUES

Oxirane content titrations

Direct titration with HBr in acetic acid (AOCS Cd 9-57) gives oxirane oxygen in epoxidized fatty materials [33]; ASTM D1652 covers epoxy content of epoxy resins between 0.1 and 26 % epoxide [34]. For vitrimer work, three further titrations belong in the standard package: **hydroxyl value** (exchange partners), **acid value** (catalysis and side reactions), and **residual iodine value** (unreacted double bonds that may oxidize during hot reprocessing).

NMR

^1H NMR shows the disappearance of olefinic protons ($\approx 5.3\text{--}5.4$ ppm) and appearance of oxirane methine protons ($\approx 2.9\text{--}3.1$ ppm). The four glycerol $\text{CH}_2\text{--O}$ protons ($\approx 4.1\text{--}4.3$ ppm) are unaffected and serve as an internal standard, so the epoxide-to-glycerol integral ratio yields oxiranes per triglyceride directly. Ring-opened species appear between about 3.4 and 3.9 ppm. In ^{13}C NMR, olefinic carbons ($\approx 127\text{--}132$ ppm) give way to oxirane carbons ($\approx 54\text{--}58$ ppm). Shifts are approximate and should be confirmed with references.

FTIR

ATR-FTIR tracks loss of the =C–H stretch near 3010 cm^{-1} , appearance of oxirane bands near $820\text{--}845\text{ cm}^{-1}$, and growth of O–H near $3400\text{--}3500\text{ cm}^{-1}$. In cured vitrimers, the same technique follows ester ($\approx 1735\text{--}1740\text{ cm}^{-1}$) and hydroxyl bands before and after reprocessing cycles — a quick check for degradation or side reactions.

MALDI-TOF mass spectrometry

Titration and NMR give averages; matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry resolves the *distribution*. Triglycerides are typically detected as cation adducts (for example with sodium), and each added oxirane oxygen shifts a peak by 16 Da, so a spectrum of an epoxidized oil shows families of peaks corresponding to molecules with different numbers of epoxides on each parent fatty-acid combination. Ring-opened products appear at characteristic increments (+18 Da for water addition, for example), and dimers and oligomers appear at roughly twice the parent mass and beyond. For vitrimer design, MALDI-TOF answers questions averages cannot: what fraction of molecules is mono- or difunctional, and how much oligomer will raise processing viscosity. It is semi-quantitative, because ionization efficiency varies with structure, and is best used comparatively between lots.

Table 2.3 Characterization package for epoxidized oils destined for vitrimers.

Measurement	Answers	Why it matters for vitrimers
Oxirane oxygen / EEW	Epoxide content	Stoichiometry; crosslink density
Hydroxyl value	OH from ring opening or native (castor)	Exchange partner concentration
Acid value	Residual carboxylic acid	Uncontrolled catalysis; pot life
Residual iodine value	Unreacted C=C	Oxidation and yellowing during hot reprocessing
^1H NMR	Average epoxides per molecule; side products	Functionality f for gel-point design
MALDI-TOF MS	Distribution of epoxides; oligomers	Low-functionality and high-viscosity fractions
Trace metals (ICP)	Catalyst residues	Unintended exchange catalysis; electrical properties

CHAPTER SUMMARY

- Commercial ESO and ELO carry about 4.0 and 5.5 internal epoxides per molecule (calculated from EEW), plus three native ester groups.
- Peracid, enzymatic and metal-catalysed epoxidation differ in selectivity and in the residues — hydroxyls, acids, metals — that later influence exchange.
- Acrylation, maleination, glycidylation, isomerization and polyol-core derivatives tune reactivity and functionality.
- Titrations, NMR, FTIR and MALDI-TOF together specify an oil for vitrimer formulation; hydroxyl and acid values are as important as oxirane content.

DYNAMIC COVALENT CHEMISTRIES (DCC) IN BIOEPOXY NETWORKS

The choice of exchange reaction decides everything that follows: the processing temperature, the catalyst, the sensitivity to moisture, the creep at service temperature — and how a part will be recycled.

IN THIS CHAPTER

- Transesterification vitrimers and their catalysts: metal salts, organic bases, and catalyst-free designs.
- Imine, disulfide, boronic-ester, dioxaborolane and anhydride exchange — and dual dynamic networks.
- Measuring exchange: stress relaxation, Arrhenius analysis, activation energy and T_v .

3.1 TRANSESTERIFICATION-BASED VITRIMERS

The exchange reaction

In a transesterification vitrimer, a hydroxyl group attacks the carbonyl of an ester, passing through a tetrahedral intermediate, and a new ester is formed as the original alcohol is released. When acids or anhydrides cure epoxides, each reaction produces an ester with a hydroxyl on the adjacent carbon — the β -hydroxy ester — so the network contains both partners in close proximity. This was the chemistry of the original vitrimers [2], and it is the most natural chemistry for epoxidized vegetable oils, whose preferred hardeners are exactly acids and anhydrides.



associative ester-hydroxyl exchange; one ester is created as another is consumed, so crosslink count is conserved

Uncatalysed transesterification is slow at practical processing temperatures, so most vitrimers use catalysts. Capelot and co-workers showed that, with a transesterification catalyst, epoxy-acid and epoxy-anhydride thermosets can be healed and joined at high temperature, while exchange is too slow at lower temperatures for the material to lose thermoset behaviour — and that catalyst concentration controls welding and assembly [35].

Metal carboxylates and acetylacetonates

Zinc salts — acetate and acetylacetonate in particular — are the most widely used catalysts and were central to the original work [2]. In a bio-based example, ESO cured with lignin-derived divanillic acid used zinc acetylacetonate hydrate at 5 mol % relative to carboxylic acid groups; stress relaxed at 170–200 °C with activation energies of about

112–119 kJ mol⁻¹ [36]. Zinc is preferred over tin compounds on toxicity grounds, but metal salts raise their own questions: solubility in the resin, migration or leaching over time, effects on electrical properties, and residual catalytic activity at service temperature. Other Lewis-acidic metal compounds have been explored in the literature; selection should weigh activity, solubility in the oil matrix, toxicity and regulatory status. Immobilizing zinc in an ionomer is one route to retain the catalyst in the network [37].

Organic bases

Strong organic bases catalyse transesterification without metals. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), a bicyclic guanidine, is a highly active organocatalyst for many polymer-forming and exchange reactions, as a recent comprehensive review documents [38]. Imidazoles act both as cure catalysts and exchange catalysts: in DGEBA networks crosslinked with dicarboxylic acids and citric acid, 1-methylimidazole catalysed the epoxy–acid reaction, epoxy homopolymerization and subsequent transesterification [39]. Organic bases can be volatile or can migrate, and strongly basic catalysts can promote side reactions at reprocessing temperatures; their loading must be optimized against shelf life and pot life (Chapter 4).

Catalyst-free and internally catalysed networks

Three strategies avoid an added catalyst:

- **Bonded tertiary amines.** Reacting a primary or secondary amine with excess epoxy generates tertiary amines covalently bonded to the network, which then catalyse transesterification; the bonded amines are less likely to leach. A statistical analysis estimated that 28.3 % of the tertiary amine resided in the sol fraction when dibutylamine was used versus 5.6 % with butylamine [40].
- **Hydroxyl- and acid-rich hardeners.** ESO crosslinked with aqueous citric acid, without any added catalyst or solvent, gave networks that self-healed through transesterification of the β -hydroxy esters formed during cure [41]. Citric acid's own hydroxyl groups were also proposed to accelerate exchange in DGEBA vitrimers [39].
- **Neighbouring-group participation.** Placing activating groups close to the ester (for example, adjacent hydroxyls or amines) can accelerate exchange intramolecularly. Reversibly “trapping” an amine catalyst so that it is released only at high temperature has been used to suppress creep while keeping reprocessing fast [10].

Table 3.1 Catalyst strategies for transesterification vitrimers based on epoxidized oils (qualitative).

Strategy	Example	Advantages	Concerns
Zinc salts	Zn(acac) ₂ , Zn(OAc) ₂ [2, 36]	Well studied; effective; low toxicity relative to tin	Solubility; leaching; electrical properties
Zinc ionomer	Zn ²⁺ ionomer [37]	Catalyst retained in network	Formulation complexity
Organic guanidine base	TBD [38]	Metal-free; very active	Basicity-driven side reactions; migration
Imidazole	1-Methylimidazole [39]	Dual role: cure + exchange	Volatility; pot life
Bonded tertiary amine	In situ from amine + excess epoxy [40]	No added catalyst; low leaching	Lower activity than metal salts in some systems
Hydroxyl-rich hardener, no catalyst	Citric acid + ESO [41]	Simple; fully bio-based possible	Slower exchange; water handling

3.2 ALTERNATIVE EXCHANGE MECHANISMS

Imine / Schiff base exchange

Imines (C=N) form reversibly from aldehydes and primary amines with loss of water, and exchange with amines (transimination) or with other imines (metathesis), often without a catalyst and at moderate temperatures. Polyimine networks can be made malleable by heat or even by water, and recycled by dissolving them in excess amine — a property demonstrated in an early highly recyclable covalent network [42]. The aldehyde need not be petrochemical: vanillin, produced from lignin, is a key intermediate for bio-based polymers [43], and vanillin-derived polyimine vitrimers have been developed as malleable, recyclable structural adhesives [44]. Imines combine naturally with epoxides when an epoxy is built from a vanillin-derived imine-containing precursor or when an amine hardener carries imine groups. Their main weakness is hydrolytic sensitivity, which must be designed for in humid service.

Disulfide and boronic-ester exchanges

Aromatic disulfides exchange through radical or anionic pathways at moderate temperature. Using a hardener that contains an aromatic disulfide, Ruiz de Luzuriaga and co-workers made epoxy networks with exchangeable disulfide crosslinks and used them to produce fibre-reinforced composites that could be reprocessed, repaired and recycled [45]; networks with high contents of aromatic disulfide have since been reported to reprocess rapidly and degrade, enabling recyclable carbon-fibre composites [46]. Vanillin-based epoxy vitrimers cured with cystamine, a disulfide-containing diamine, illustrate how a bio-based epoxy and a dynamic hardener can be combined [47].

Boronic esters form from boronic acids and diols and exchange with other diols or esters, often at room temperature, which gives fast self-healing but also makes networks sensitive to water and prone to creep. They are frequently combined with a second, slower dynamic or permanent crosslink.

Dual dynamic networks combine two exchange chemistries — for example, transesterification with disulfide or imine exchange — so that one provides rapid healing or relaxation at moderate temperature and the other governs high-temperature reprocessing, or so that one provides a permanent load-bearing skeleton while the other provides malleability.

Dioxaborolane and anhydride exchange systems

Dioxaborolanes undergo a metathesis that swaps substituents between boron-containing rings without breaking the network. Röttger and co-workers used dioxaborolane metathesis to convert commodity thermoplastics such as polystyrene, poly(methyl methacrylate) and polyethylene into vitrimers with improved solvent and mechanical resistance, processable by standard methods [6]. The reaction is fast and catalyst-free; for epoxy systems, dioxaborolane-containing hardeners or crosslinkers are the route of entry.

Anhydride-based exchange relies on transacylation between anhydride and carboxylic acid groups, which can rearrange acyl groups between chains. It is relevant to anhydride-cured oils because residual anhydride and acid groups are present after cure; designing networks in which this exchange operates deliberately is an emerging area, and its kinetics relative to ester–hydroxyl exchange should be established for each formulation.

Table 3.2 Dynamic chemistries for bioepoxy networks (qualitative overview).

Chemistry	Typical trigger	Catalyst	Strength	Weakness
Transesterification	Heat (often > 150 °C)	Zn, organic bases, internal amines	Native to acid/anhydride-cured EVOs; high E_a	High processing T; catalyst issues
Vinylogous urethane	Heat	Often none; acids/bases accelerate [5]	Fast exchange	Requires acetoacetate chemistry
Imine	Heat, water, amines	Usually none	Low-energy reprocessing; vanillin-derived [43]	Hydrolysis in humid service
Aromatic disulfide	Heat, light	None	Composites demonstrated [45, 46]	Odour, sulfur chemistry; creep
Boronic ester	Ambient–moderate T, water	None	Room-temperature healing	Water sensitivity; creep
Dioxaborolane metathesis	Heat	None	Fast; demonstrated in commodity polymers [6]	Boron-containing building blocks
Diels–Alder (dissociative)	Heat	None	Thermally re-mendable [4]	Integrity loss at high T

3.3 KINETICS AND RHEOLOGY

Stress relaxation

The signature test for a vitrimer is stress relaxation: a small step strain, within the linear viscoelastic range, is applied above T_g and the decay of the relaxation modulus $G(t)$ is recorded at several temperatures. The simplest description is single-exponential (Maxwell) relaxation:

$$\frac{G(t)}{G_0} = \exp(-t/\tau^*) \quad (3.1)$$

Real networks with distributed environments often relax more broadly and are better fitted by a stretched exponential,

$$\frac{G(t)}{G_0} = \exp[-(t/\tau^*)^\beta], \quad 0 < \beta \leq 1 \quad (3.2)$$

where $\beta < 1$ indicates a distribution of relaxation times. Vegetable-oil networks, built from statistically mixed molecules, commonly show such breadth. Theory and experiment on the origins of this behaviour are reviewed in the literature on vitrimer rheology [9]. A practical, model-free definition of τ^* is the time at which $G/G_0 = 1/e \approx 0.37$.

Arrhenius analysis and activation energy

Plotting $\ln \tau^*$ against $1/T$ gives a straight line of slope E_a/R if a single exchange mechanism controls relaxation (Eq. 1.1). Curvature signals a change of mechanism, catalyst deactivation, or the influence of T_g at the low-temperature end. Reported activation energies for bio-based transesterification systems include about 112–119 kJ mol⁻¹ for zinc-catalysed ESO–divanillic acid vitrimers [36] and about 89–119 kJ mol⁻¹ for imidazole-catalysed DGEBA–diacid vitrimers, for which T_v values of 105–117 °C were reported [39].

WORKED EXAMPLE · ACTIVATION ENERGY FROM TWO RELAXATION TIMES

Suppose $\tau^* = 2400$ s at 443 K (170 °C) and 300 s at 473 K (200 °C). Then $E_a = R \ln(\tau_1/\tau_2) / (1/T_1 - 1/T_2) = 8.314 \times \ln 8 / (1/443 - 1/473) = 8.314 \times 2.079 / 1.432 \times 10^{-4} \approx 121$ kJ mol⁻¹. Two points define a line but not its linearity; at least four temperatures are recommended. Inputs are illustrative.

From relaxation to T_v

Combining the Arrhenius fit with the Maxwell relation $\eta = G\tau^*$ (with $G \approx E'/3$ from the rubbery plateau) allows the temperature at which $\eta = 10^{12}$ Pa s to be estimated by extrapolation. Because this usually lies below the measured range, it is sensitive to the Arrhenius slope and should be reported with its uncertainty. Direct measurement — for example by dilatometry, where the slope of thermal expansion changes when topology freezes — was used in establishing catalytic control of T_v [8].

Table 3.3 Rheological and thermomechanical tests for vitrimers.

Test	Output	Notes
Stress relaxation (step strain)	τ^* , β , Arrhenius E_a	Stay in linear range; check for sample slip; several temperatures
Creep (constant stress)	Strain–time curves at service and processing T	Most relevant to dimensional stability
Frequency sweep (SAOS)	G' , G'' , crossover frequency	Crossover $\approx 1/\tau^*$; complements relaxation
Dilatometry / TMA	Expansion slope change at T_v	Direct T_v estimate [8]
DMA temperature ramp	T_g , rubbery plateau, onset of flow	Plateau decline at high T indicates exchange
Swelling / gel fraction before and after reprocessing	Network integrity	Associative networks remain insoluble

CHAPTER SUMMARY

- Transesterification of β -hydroxy esters is the native exchange chemistry for acid- and anhydride-cured EVOs; zinc salts, organic bases (TBD, imidazoles) and bonded tertiary amines catalyse it.
- Imine, disulfide, boronic-ester, dioxaborolane and anhydride exchanges offer lower processing temperatures or faster healing at the cost of moisture sensitivity or creep; dual dynamic networks combine strengths.
- Stress relaxation (Maxwell or stretched exponential), Arrhenius analysis and T_v estimation are the core measurements; reported bio-based E_a values cluster around 90–120 kJ mol^{−1}.



FORMULATION, NETWORK PHYSICS, AND PROPERTY TUNING

*Hardeners, stoichiometry, rigid partners and catalysts – and the mechanical, thermal
and self-healing performance they produce.*

CH. 4 · FORMULATING VEGETABLE OIL EPOXY VITRIMERS

CH. 5 · THERMO-MECHANICAL, THERMAL, AND SELF-HEALING PERFORMANCE

FORMULATING VEGETABLE OIL EPOXY VITRIMERS (VOEVs)

A vitrimer formulation has to satisfy two chemistries at once: the cure that builds the network, and the exchange that later lets it move. The hardener, the stoichiometry and the catalyst serve both.

IN THIS CHAPTER

- Bio-based curing agents and co-monomers: diacids, anhydrides, lignin-derived phenols and plant-based amines.
- Stoichiometry for exchange: how hydroxyl and ester densities depend on hardener type and ratio.
- Raising T_g and stiffness with rigid bio-based partners and multifunctional crosslinkers.
- Choosing, retaining and controlling the exchange catalyst.

4.1 CURING AGENTS AND CO-MONOMERS

Dicarboxylic and polycarboxylic acids

Carboxylic acids open epoxides to give β -hydroxy esters — one ester and one hydroxyl per reaction — which makes them the most direct route to transesterification vitrimers. Many are available from renewable sources: sebacic acid is produced from castor oil, azelaic acid from oxidative cleavage of oleic acid, succinic acid by fermentation, and dimerized fatty acids from tall-oil and vegetable-oil fatty acids. Long aliphatic diacids give flexible, low- T_g networks; short or aromatic diacids give stiffer ones. Polyfunctional acids raise crosslink density: citric acid, applied to ESO as an aqueous solution, crosslinked the oil without added catalyst and gave self-healing networks [41]; in DGEBA systems, blending citric with sebacic acid raised T_g while speeding relaxation [39]. Lignin-derived aromatic diacids such as divanillic acid supply rigidity: cured with ESO under zinc catalysis, they gave $\tan \delta$ peak temperatures of 20–62 °C depending on the acid and stoichiometry [36].

Bio-anhydrides

Anhydrides cure epoxides in an alternating, base-catalysed copolymerization that produces two esters per anhydride. Oil-derived options include maleinized oils, which act as flexible hardeners [30], and rosin-derived anhydrides, which supply rigid alicyclic structure [48]. Anhydride networks are ester-rich but, as shown below, hydroxyl-poor — a significant consideration for exchange.

Lignin-derived phenols

Phenolic hydroxyls react with epoxides under basic catalysis to form aryl ethers and secondary hydroxyls. Lignin and its depolymerization products bring aromatic rigidity and char-forming ability, but also heterogeneity, viscosity and limited solubility in oil matrices [49]. Vanillin, the best-established single-molecule lignin derivative, is a versatile intermediate that can be converted into epoxies, diacids and amines [43]. Phenol–epoxy links are ethers, not esters, so phenolic co-hardeners add rigidity without adding exchange sites; they must be combined with an ester-forming hardener or a different dynamic chemistry.

Plant-based amines

Amines are the most common epoxy hardeners but react slowly with internal oxiranes and create C–N bonds that do not undergo transesterification. In vitrimer formulations they are therefore used in three ways: as minor co-hardeners that generate tertiary-amine catalytic sites [40]; as carriers of a second dynamic chemistry — for example cystamine, a disulfide-containing diamine used with vanillin-based epoxies [47], or diamines that form exchangeable imines with bio-based aldehydes [44]; or as amine-functional oils prepared by thiol–ene coupling [50]. Fatty-acid-derived diamines are commercially available and give hydrophobic, flexible segments.

Table 4.1 Hardener families for vegetable-oil epoxy vitrimers (qualitative).

Hardener	Links formed	Exchange role	Network effect
Aliphatic diacids (sebacic, azelaic, dimer acids)	β -Hydroxy esters	Supplies ester + OH 1:1	Flexible, low T_g
Citric acid	β -Hydroxy esters; own OH	Extra OH accelerates exchange	Higher crosslink density
Aromatic diacids (divanillic)	β -Hydroxy esters	Ester + OH 1:1	Stiffer, higher T_g
Anhydrides (maleinized oil, rosin)	Diesters	Ester-rich, OH-poor	Depends on anhydride rigidity
Phenols (lignin, vanillin derivatives)	Aryl ethers + OH	OH only (no ester)	Rigidity, char
Amines (dynamic-bearing)	C–N; plus disulfide/imine	Second dynamic chemistry	Depends on amine

4.2 STOICHIOMETRIC OPTIMIZATION

In a conventional thermoset, stoichiometry is set to maximize conversion and T_g . In a transesterification vitrimer, it also sets the concentrations of the exchange partners — esters and hydroxyls — and the fraction of permanent, non-exchangeable links. Three points govern the choice.

- **Acid versus anhydride.** Each acid–epoxy reaction creates one ester and one hydroxyl. Each anhydride–epoxy cycle creates two esters and no new hydroxyl; free hydroxyls come only from initiation, ring-opened oil species or added polyols.
- **Epoxy excess and etherification.** Excess epoxide homopolymerizes (especially with imidazole or amine catalysts), forming ether links that raise T_g but cannot exchange. A modest excess may be beneficial for properties;

a large one locks in permanent topology. Citric acid has been used to reduce the required epoxy excess while maintaining a high T_g and fast relaxation [39].

- **Acid excess.** Unreacted carboxylic acids can catalyse exchange and hydrolysis, but they also lower crosslink density and may promote corrosion or moisture uptake.

WORKED EXAMPLE · EXCHANGE-PARTNER DENSITIES IN TWO ESO FORMULATIONS

Formulation A — sebacic acid. 100 g ESO (EEW 235; 0.4255 eq) with a stoichiometric amount of sebacic acid ($C_{10}H_{18}O_4$, 202.25 g mol⁻¹, 101.1 g per COOH) = 43.0 g. At full conversion, cure creates 0.4255 mol ester and 0.4255 mol hydroxyl. The ESO molecules (≈ 938 g mol⁻¹) contribute $3 \times 0.1066 = 0.320$ mol native triglyceride esters. In 143.0 g of network: esters ≈ 5.2 mmol g⁻¹, hydroxyls ≈ 3.0 mmol g⁻¹.

Formulation B — MHHPA anhydride at A/E = 0.9: 64.4 g MHHPA (0.383 mol) gives 0.766 mol esters; with native esters, ≈ 6.6 mmol g⁻¹ in 164.4 g — but almost no hydroxyls from cure.

Formulation B has more esters but very few exchange partners; without added hydroxyls or an acid co-hardener, it will relax far more slowly. All values are calculated from stated assumptions; they show why acid hardeners, or deliberate hydroxyl sources, are favoured for transesterification vitrimers.

The practical target is not a single “correct” ratio but a balance: enough crosslinks for stiffness and T_g , enough hydroxyl–ester pairs for exchange, and few permanent ether links if full reprocessability is required. Gel content and stress relaxation should be measured across a ratio series (for example, the COOH/epoxy ratios of 0.7, 1.0 and 1.5 used in the ESO–divanillic acid study [36]) rather than predicted from theory alone.

4.3 OVERCOMING LOW T_g AND MECHANICAL SOFTNESS

Vegetable-oil networks are soft because their fatty chains are long and flexible and leave dangling ends beyond the last crosslink. For structural composites, T_g must sit comfortably above service temperature, and the matrix must be stiff enough to support the fibres in compression. Three families of remedy exist.

Blending with rigid bio-based epoxies

- **Isosorbide-based epoxies.** Isosorbide, a bicyclic diol from sorbitol (and thus from starch), can be glycidylated to a compact difunctional epoxy whose fused rings add rigidity. Its hydrophilicity requires attention to moisture uptake.
- **Vanillin-based epoxies.** Vanillin’s aromatic ring, aldehyde and phenol give access to rigid diepoxides and to imine-containing dynamic building blocks [43, 47].
- **Tannic acid.** This polyphenol, extracted from plant tissues, carries many aromatic hydroxyls; it can act as a multifunctional hardener or be glycidylated into a highly functional epoxy. Its high functionality raises crosslink density sharply, and its many hydroxyls are potential exchange partners.
- **Furan-based epoxies.** Carbohydrate-derived furan diepoxides offer aromatic-like rigidity [51] and have been used to make intrinsically flame-retardant bio-based epoxy vitrimers for recyclable carbon-fibre composites [52].

- **Itaconic-acid and sucrose-based epoxies** provide high epoxide density per mass [32, 53].

As a first estimate for miscible co-networks, the Fox equation ($1/T_g = \sum w_i/T_{g,i}$) predicts the blend T_g ; large positive deviations indicate genuine co-network formation.

Hyperbranched crosslinkers and aromatic rigid-rod structures

Hyperbranched polyesters and polyols with many terminal hydroxyls or carboxyls act as compact, high-functional-ity junctions: they raise crosslink density, add exchange partners and can toughen through their globular architecture. Rigid-rod aromatic segments — biphenyl-, naphthalene- or vanillin-derived — stiffen the network and may promote local ordering. Both strategies trade higher viscosity and, often, lower bio-based content for performance; their effect on T_v must also be checked, because a stiffer network with higher T_g may push the flow regime into the $T_v < T_g$ case (Chapter 1).

Table 4.2 Strategies to raise T_g and stiffness in VOEVs, with their side effects on exchange (qualitative).

Strategy	Effect on T_g / modulus	Effect on exchange	Watch-out
Higher-functionality oil (ELO vs ESO)	↑	Slightly slower (denser network)	Brittleness
Aromatic diacid hardener	↑	OH/ester preserved	Solubility of diacid in oil
Rigid bio-epoxy co-monomer	↑↑	Diluted ester density unless co-monomer also forms esters	Phase separation
Polyphenol (tannic) co-hardener	↑↑	Adds OH; ether links are permanent	Colour; viscosity
Epoxy excess (etherification)	↑	↓ Permanent links	Loss of full reprocessability
Hyperbranched junctions	↑	↑ if hydroxyl-terminated	Viscosity

4.4 CATALYST SELECTION AND LEACHING DYNAMICS

Homogeneous versus heterogeneous incorporation

Homogeneous catalysts — zinc acetylacetonate, TBD, imidazoles — are dissolved in the resin before cure. They are effective and easy to dose, but they remain mobile: they can be extracted by solvents or water, migrate to surfaces, volatilize during hot processing, or be lost with the sol fraction. Heterogeneous or immobilized strategies anchor the catalyst: zinc ionomers retain the metal within ionic aggregates [37], and tertiary amines generated in situ from primary or secondary amines become covalently bonded to the network, with the bonded fraction depending on the amine used [40].

Measuring leaching

Leaching should be tested under realistic conditions: immersion in water, solvents or simulants at service temperature; extraction of the sol fraction; and analysis by ICP for metals or by NMR/chromatography for organic catalysts. Stress relaxation before and after ageing shows whether lost catalyst translates into lost reprocessability. For food-contact, medical or electronic applications, catalyst migration is also a regulatory question (Chapter 12).

Latency control

An ideal vitrimer catalyst is inactive during storage and in service, and highly active during processing. Approaches include:

- **Concentration control.** Catalyst concentration directly controls welding and assembly kinetics [35] and shifts T_v [8]; using the minimum effective loading improves creep resistance.
- **Reversibly trapped catalysts.** Amine catalysts trapped in a reversible adduct are released only at high temperature, suppressing creep while keeping reprocessing fast [10].
- **Catalyst-controlled tuning.** In bio-based epoxy vitrimers for carbon-fibre composites, the choice of transesterification catalyst has been used to tune reprocessability and recyclability [54].

Because many exchange catalysts also catalyse cure (zinc salts and imidazoles accelerate epoxy–acid reactions), the catalyst affects pot life, gel time and exotherm as well as exchange. Shelf life of one-component systems — resin, hardener and catalyst premixed — is often limited by this cure activity rather than by exchange.

Table 4.3 Catalyst selection checklist for VOEV composites.

Criterion	Question to answer
Exchange activity	What τ^* is achieved at the intended processing temperature?
Service-temperature activity	What is the creep rate at maximum service temperature and load?
Cure interaction	How does the catalyst change gel time, exotherm and pot life?
Solubility	Does it dissolve in the oil-rich resin without phase separation?
Retention	How much leaches in water, solvents or simulants over the service life?
Thermal stability	Does it survive repeated reprocessing cycles without volatilizing or degrading?
Toxicity and regulation	Is it acceptable for the application (REACH, food contact, electronics)?
Interaction with fibres and sizing	Does it adsorb on fibres, react with sizing, or corrode metal inserts?

CHAPTER SUMMARY

- Diacids give equal numbers of esters and hydroxyls; anhydrides give ester-rich, hydroxyl-poor networks; phenols and amines add rigidity or second dynamic chemistries but not esters.
- Stoichiometry sets exchange-partner densities and the fraction of permanent ether links; calculated examples show acid hardeners favour exchange.
- Rigid bio-based partners (isosorbide, vanillin, tannic acid, furans, itaconic and sucrose derivatives) and hyper-branched junctions raise T_g , with side effects on exchange.
- Catalysts must be active, retained and latent; immobilization, bonded amines and reversible trapping address leaching and creep.

THERMO-MECHANICAL, THERMAL, AND SELF-HEALING PERFORMANCE

A vitrimer has to be judged twice: once as a thermoset that must carry load, and again as a material that must heal, reshape and survive reprocessing without losing what made it useful.

IN THIS CHAPTER

- Tensile, flexural, impact and DMA metrics — and how to report them for dynamic networks.
- Thermal stability, degradation pathways, and the processing window between flow and decomposition.
- Healing efficiency, scratch recovery and light- or heat-triggered healing.
- Shape memory, permanent reshaping and vitrimeric welding.

5.1 MECHANICAL METRICS

Static properties

Tensile (modulus, strength, elongation), flexural and impact tests are performed as for any thermoset, but two vitrimer-specific practices apply. First, test temperature must be stated relative to T_g : many vegetable-oil networks have glass transitions near or below room temperature, so “room-temperature” properties may describe a rubber rather than a glass. Second, properties should be reported for virgin material *and* after each reprocessing or healing cycle, because retention is part of the material’s performance.

Published data show the range typical of bio-based systems. ESO crosslinked with lignin-derived divanillic acids under zinc catalysis gave Young’s moduli from about 3 to 286 MPa, depending on the acid and stoichiometry [36]. In anhydride-cured epoxidized hemp oil, replacing a quarter of a rigid anhydride with maleinized hemp oil raised impact energy absorption by about 180 % while sharply lowering modulus [30]. Both illustrate the same trade-off: oil-derived networks are tough and extensible but soft unless rigid partners are added (Chapter 4).

Dynamic mechanical analysis

DMA ramps give the glass transition (by onset, E'' peak or $\tan \delta$ peak — the definition must be stated) and the rubbery-plateau modulus, from which crosslink density follows via rubber elasticity:

$$\nu_e \approx \frac{E'_{\text{rubbery}}}{3RT} \quad (5.1)$$

In a vitrimer, the rubbery plateau has a finite length: as temperature approaches the flow regime, exchange relaxes stress during each oscillation and E' falls. The plateau should therefore be read at a temperature well above T_g but where τ^* is still much longer than the oscillation period. For DGEBA–diacid–citric acid vitrimers, DMA transition temperatures were 15–20 °C higher than DSC glass transitions, which ranged from about 30 to 62 °C [39] — a reminder that DSC and DMA values are not interchangeable.

Table 5.1 Recommended reporting set for vitrimer mechanical performance.

Property	Method	Report also
Tensile modulus, strength, elongation	ASTM D638 / ISO 527	Test T relative to T_g ; values after each cycle
Flexural modulus and strength	ASTM D790 / ISO 178	Composite fibre content and orientation
Impact	Izod or Charpy	Notch geometry; temperature
Fracture toughness	ASTM D5045	Before and after healing
T_g	DSC and DMA	Definition used (onset, E'' , $\tan \delta$)
Crosslink density	Rubbery E' ; swelling	Temperature of reading; gel fraction
Creep	Constant stress at service T	Strain after defined time

5.2 THERMAL STABILITY

Degradation mechanisms

Vegetable-oil vitrimers degrade through overlapping pathways: loss of volatiles and sol species; elimination and pyrolysis of ester links, especially β -hydroxy esters; oxidation of residual unsaturation and allylic sites; and scission of aliphatic chains at higher temperatures. ESO–divanillic acid vitrimers showed 5 % mass-loss temperatures above 300 °C [36], comfortably above typical service temperatures. The more relevant limit is the *reprocessing* temperature: in the same study, films hot-pressed repeatedly at 230 °C lost 50–60 % of their tensile strength and modulus over five cycles, and one formulation showed signs attributed to thermal degradation [36].

The processing window

The useful window for reprocessing lies between the temperature at which τ^* becomes short enough for the intended process (Chapter 1) and the temperature at which degradation becomes significant over the process time. Isothermal TGA at the candidate processing temperature, in air and nitrogen, is a more meaningful test than a dynamic ramp: a material that loses 1 % of its mass in an hour at 220 °C may still be unsuitable for five reprocessing cycles. Antioxidants, an inert atmosphere during pressing, and catalysts that allow lower processing temperatures all widen the window.

Char yield enhancement

Aliphatic oil networks form little char, which limits fire performance (Chapter 7). Aromatic co-monomers raise char yield: lignin, vanillin and tannic-acid derivatives, and furan-based epoxies. Phosphorus is especially effective, promoting char formation in the condensed phase; incorporating a phosphine oxide monomer into an epoxy vitrimer enabled reprocessability and fire protection simultaneously [55], and a furan-derived bio-based epoxy vitrimer was reported to be intrinsically flame retardant [52].

5.3 SELF-HEALING MECHANICS

Measuring healing

Healing efficiency is defined as the ratio of a property after healing to that of the virgin material:

$$\eta_{\text{heal}} = \frac{P_{\text{healed}}}{P_{\text{virgin}}} \times 100 \% \quad (5.2)$$

where P may be fracture toughness, tensile strength, lap-shear strength or interlaminar shear strength. The choice of P matters: recovering stiffness is easy; recovering fracture toughness across a fully separated crack is hard. Conditions — temperature, time, pressure and whether the crack faces were held in contact — must accompany every efficiency.

Crack and scratch healing

In transesterification vitrimers, healing requires the two crack faces to be brought into intimate contact and held above T_g long enough for exchange reactions to create bonds across the interface — typically several relaxation times. Scratch healing is easier, because the material on either side of a shallow scratch can flow into it. In ESO–divanillic acid vitrimers at 100 °C, a scratch about 53 μm wide narrowed to about 7 μm in one hour in one formulation, while a closely related formulation barely healed [36] — showing how strongly healing depends on network mobility and T_g . Catalyst-free citric acid–ESO networks also showed thermally activated healing, assessed by stress relaxation and lap-shear tests [41].

Thermal and light-stimulated reconfiguration

Heat can be delivered globally (oven, press) or locally. Local, light-triggered heating is attractive for repair in place: carbon nanotubes dispersed in an epoxy vitrimer absorb near-infrared light and convert it to heat, enabling efficient photo-welding and healing confined to the illuminated region [56]. Aromatic disulfide networks can also respond to light through photo-induced exchange. Electrical (Joule) heating of conductive fibre or filler networks offers a third trigger, discussed in Chapter 7.

5.4 SHAPE MEMORY AND WELDABILITY

Shape memory versus permanent reshaping

Vitrimers combine two distinct shape-changing behaviours:

- **Shape memory** operates above T_g but below the flow regime. The material is deformed while rubbery, cooled to fix a temporary shape, then reheated to recover its permanent shape, driven by network elasticity.
- **Permanent reshaping (plasticity)** operates in the flow regime. Held deformed long enough for exchange to relax stress, the network adopts the new shape as its permanent one.

Shape-memory performance is quantified by the fixity ratio R_f (how much of the programmed strain is retained on unloading) and the recovery ratio R_r (how much is recovered on reheating):

$$R_f = \frac{\epsilon_{\text{fixed}}}{\epsilon_{\text{programmed}}} \times 100 \%, \quad R_r = \frac{\epsilon_{\text{programmed}} - \epsilon_{\text{residual}}}{\epsilon_{\text{programmed}}} \times 100 \% \quad (5.3)$$

For DGEBA networks crosslinked with dicarboxylic acids and citric acid, fixity of about 99.5–100 % and recovery of about 98.4–100 % were reported over five cycles at 5 % strain, with fixity remaining near 99.5–100 % at strains up to 30 % [39]. Because the same networks had T_v values of 105–117 °C, they could also be reshaped permanently — the combination that enables “program, use, re-program” cycles for adaptive parts.

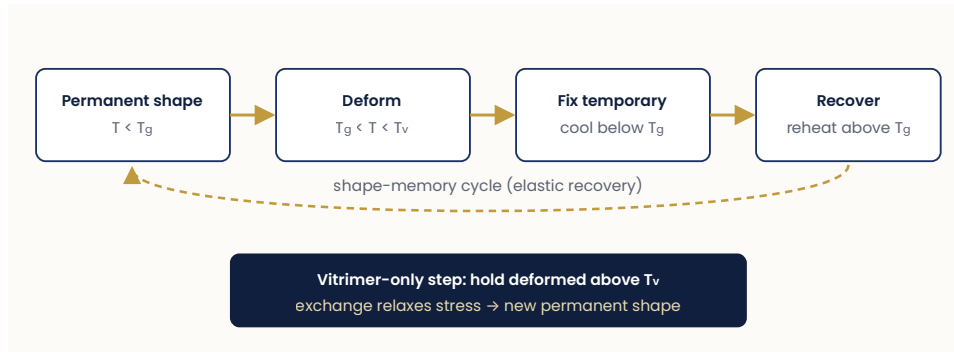


Figure 5.1 Shape memory (elastic, above T_g) and permanent reshaping (plastic, above T_v) in a vitrimer. The second step, unavailable to conventional shape-memory thermosets, lets the permanent shape itself be re-programmed.

Interfacial vitrimeric welding

Two vitrimer parts pressed together above T_v exchange bonds across the interface and become a single network. Capelot and co-workers demonstrated healing and assembly of epoxy–acid and epoxy–anhydride thermosets by metal-catalysed transesterification and showed that catalyst concentration controls the kinetics of welding [35]. The interfacial strength develops over a time comparable to several relaxation times, so the same Arrhenius analysis that predicts reprocessing also predicts welding schedules. For composites, welding offers adhesive-free joining of laminates and repair patches; Chapter 6 discusses its limits when fibres bridge the joint.

CHAPTER SUMMARY

- Report mechanical properties relative to T_g and after every reprocessing or healing cycle; DSC and DMA T_g values differ.
- ESO-based vitrimers are thermally stable well above service temperature, but repeated reprocessing near 230 °C cost about half their strength and stiffness over five cycles in one study.
- Healing efficiency (Eq. 5.2) depends on contact, temperature and time; scratch healing is easier than crack healing; NIR-absorbing nanotubes enable local photo-welding.
- Vitrimers combine shape memory (reported fixity and recovery near 100 %) with permanent re-programming above T_v , and weld across interfaces at rates set by catalyst concentration.



VEGETABLE OIL VITRIMER COMPOSITES: MANUFACTURING AND PERFORMANCE

Fibres, interfaces, processing windows and functional fillers for composites that can be repaired and recovered.

CH. 6 · REINFORCEMENTS, INTERFACES, AND COMPOSITE PROCESSING

CH. 7 · FUNCTIONAL COMPOSITES AND ADVANCED NANOMATERIALS

REINFORCEMENTS, INTERFACES, AND COMPOSITE PROCESSING

A vitrimer composite is processed twice in its life: once when the resin first wets the fibres, and again – perhaps many times – when the cured part is reshaped, repaired or recovered. The fibres must survive both.

IN THIS CHAPTER

- Natural and synthetic fibres, their surfaces, and their compatibility with oil-based dynamic matrices.
- RTM, VARTM, prepreg, automated fibre placement, compression moulding and RIM for VOEVs.
- The rheological window before gelation – and the second window that vitrimers open after it.

6.1 FIBER SELECTION AND SURFACE INTERPHASE

Natural fibres: flax, hemp and jute

Bast fibres combine good specific stiffness with low density and a renewable origin, and they pair naturally with vegetable-oil matrices to make composites with high overall bio-based content. AESO-type resins were developed with natural-fibre composites in mind [28], and hemp-fibre composites with epoxidized soybean oil matrices continue to be reported [57]. Compatibilization addresses the polarity mismatch between hydrophilic, hydroxyl-rich fibre surfaces and hydrophobic oil networks: alkali treatment removes waxes and hemicellulose and roughens the surface; silanes and acetylation reduce polarity; fibres must be dried immediately before impregnation.

For vitrimers, natural fibres raise two specific issues:

- **Thermal budget.** Published reprocessing and relaxation temperatures for transesterification vitrimers are often in the range 160–230 °C (Chapters 3 and 5), a range in which natural fibres begin to discolour and lose strength with time. Lower-temperature dynamic chemistries (imine, disulfide, highly catalysed transesterification) or short, well-controlled cycles are therefore preferred for natural-fibre vitrimer composites.
- **Moisture and exchange.** Absorbed water plasticizes fibres and can hydrolyse esters or imines at reprocessing temperatures. Drying before every hot-processing step is essential.

Synthetic fibres: carbon and glass

Carbon and glass fibres are supplied with *sizing* — thin polymer coatings that protect the fibre and promote adhesion. Glass fibres are sized with silane coupling agents (epoxy- or amino-functional silanes) that bond to the glass surface and react with the matrix; carbon fibres are typically sized with epoxy-compatible polymers. Standard

epoxy sizings are generally compatible with EVO-based matrices, but their reactive groups can consume hardener or catalyst locally, and the interphase they form may not participate in exchange. Fibres recovered from vitrimer composites by solvolysis (Chapter 8) may have lost their sizing and need re-sizing before reuse.

Recyclable fibre-reinforced vitrimer composites have been demonstrated with several chemistries: carbon-fibre composites whose epoxy vitrimer matrix was dissolved in ethylene glycol to recover clean fibres and repolymerizable matrix [58]; fibre-reinforced composites with exchangeable aromatic disulfide crosslinks that were reprocessable, repairable and recyclable [45, 46]; and bio-based epoxy vitrimers whose carbon-fibre composites were tuned for reprocessability and recyclability through catalyst choice [54].

Load transfer

The critical fibre length for full load transfer in short-fibre composites follows the Kelly–Tyson relation $l_c = \sigma_f d / (2\tau)$ [59]. It matters doubly for vitrimers: recycled composites made by chopping and remoulding (Chapter 8) contain short fibres, and their performance depends on whether the fibre length after chopping exceeds l_c for the interfacial strength achieved on remoulding.

WORKED EXAMPLE · WILL CHOPPED RECYCLATE CARRY LOAD?

Carbon fibres with $\sigma_f = 3.5$ GPa and $d = 7$ μm in a matrix that develops $\tau = 30$ MPa on remoulding give $l_c = (3500 \times 7) / (2 \times 30) \approx 408$ $\mu\text{m} \approx 0.4$ mm. Chopping to 5 mm leaves fibres more than ten times l_c , so most of each fibre can be loaded to near its strength; chopping to 0.5 mm would not. If remoulding weakens the interface to $\tau = 10$ MPa, l_c rises to 1.2 mm. Inputs are illustrative.

6.2 PROCESSING METHODS FOR VOEV COMPOSITES

Resin transfer moulding and vacuum infusion

RTM and VARTM require a low-viscosity resin throughout filling. Epoxidized oils are favourable here: commercial ESO has a viscosity of 320–500 cP and ELO about 800 cP at 25 °C [11, 12], compared with 110–150 P for a standard liquid DGEBA [60]. The difficulty lies with the hardener. Many vitrimer-forming diacids — sebacic, divanillic, citric — are crystalline solids that must be melted or dissolved, while liquid anhydrides give hydroxyl-poor networks (Chapter 4). Practical options include:

- pre-reacting a diacid with part of the epoxy to form a liquid, acid- or epoxy-terminated prepolymer;
- using liquid anhydrides with a dissolved polyacid or polyol co-hardener to supply hydroxyls;
- heated injection, with the catalyst chosen for latency at injection temperature.

Fill time scales with viscosity through Darcy's law, $t_{\text{fill}} = \phi \mu L^2 / (2K \Delta P)$ for one-dimensional flow at constant pressure, so a temperature that halves viscosity halves fill time — provided pot life allows.

Prepregs and automated fibre placement

Prepregs are fibres pre-impregnated with partly reacted (B-staged) resin, stored cold, laid up and then cured. Automated fibre placement (AFP) lays narrow prepreg tows by robot and relies on tack and consolidation under heat and pressure. Vitrimer chemistry offers two potential advantages: plies of a fully or partly cured vitrimer prepreg can, in principle, be consolidated and welded by exchange at high temperature rather than by co-cure, and out-of-life or misplaced material can be re-formed rather than scrapped. The challenges are out-life (latent catalysts are essential), tack (oil-based B-stages can be either too tacky or too dry), and the long times needed for exchange-driven consolidation compared with conventional cure.

Compression moulding

Compression moulding — of sheet or bulk moulding compounds, or of chopped recyclate — is the most natural process for vitrimers, because it is also the main reprocessing route. Heat and pressure drive both flow and exchange; mould temperature and dwell time are set from the relaxation-time data (Chapter 3). For first moulding, resin and fibres can be compounded and cured in the mould; for subsequent cycles, cured parts are granulated and re-pressed (Chapter 8).

Reaction injection moulding

RIM mixes two fast-reacting liquid streams and injects them into a mould where cure occurs within seconds to minutes. Conventional EVO cure is too slow for classic RIM cycle times; hybrid chemistries (for example, fast amine or thiol co-reactions that gel the part, followed by slower ester formation) or highly active catalysts are required. Structural RIM with preplaced fibre mats adds the infusion constraints above.

Table 6.1 Processing routes for VOEV composites (qualitative).

Process	Key resin requirement	VOEV advantage	VOEV challenge
RTM / VARTM	Low viscosity; long pot life	Low-viscosity oils	Solid diacid hardeners; slow cure
Prepreg / AFP	Controlled B-stage, tack, out-life	Exchange-driven consolidation and rework	Latency; long consolidation times
Compression moulding	Flow under heat and pressure	Same process for first moulding and recycling	Thermal budget of fibres and matrix
RIM / SRIM	Very fast reaction	Hybrid chemistries possible	Intrinsically slow EVO cure
Filament winding / pultrusion	Fast gel; low viscosity	Post-forming of cured profiles	Cure speed; die temperature

6.3 RHEOLOGICAL PROCESSING WINDOWS

Before gelation

During impregnation, viscosity rises with both falling temperature and increasing conversion. A widely used chemorheological description is the Castro–Macosko form:

$$\eta(T, \alpha) = \eta_0 \exp(E_\eta / RT) \left(\frac{\alpha_{\text{gel}}}{\alpha_{\text{gel}} - \alpha} \right)^{(A + B\alpha)} \quad (6.1)$$

where α is conversion, α_{gel} the conversion at gelation, E_η the flow activation energy, and A, B fitted constants. The process window is the time before η exceeds the limit the process can tolerate.

Estimating the gel point

For an ideal step-growth reaction between an epoxy of functionality f_e and a hardener of functionality f_a , with stoichiometric ratio r (reactive groups of the minor component divided by those of the major), Flory–Stockmayer theory gives the conversion of the minor component at gelation:

$$\alpha_{\text{gel}} = \frac{1}{\sqrt{r(f_e - 1)(f_a - 1)}} \quad (6.2)$$

WORKED EXAMPLE · GEL POINTS OF OIL–DIACID SYSTEMS

For ESO ($f_e \approx 4.0$, Chapter 2) with a diacid ($f_a = 2$) at $r = 1$: $\alpha_{\text{gel}} = 1/\sqrt{3} = 0.577$. For ELO ($f_e \approx 5.5$): $\alpha_{\text{gel}} = 1/\sqrt{4.5} = 0.471$. With the acid in deficit at $r = 0.8$, ESO gels when the acid is 0.645 converted and the epoxide 0.516 converted. Higher-functionality oils gel earlier, shortening the impregnation window. The theory ignores etherification, intramolecular loops and the statistical spread of oil functionality, so measured gel points (by rheology, $G' - G''$ crossover) should always be used for process design. Calculated values.

After gelation: the vitrimer's second window

For a conventional thermoset, gelation ends all flow: whatever has not been impregnated or consolidated stays that way. A vitrimer behaves differently. Above T_v , the gelled — even fully cured — network can still flow and relax stress, at a rate set by τ^* . This opens a second processing window for consolidating plies, closing voids, joining parts and correcting geometry after cure. The window is slow compared with liquid-resin flow (relaxation times of minutes to hours rather than seconds) and is bounded by thermal degradation, but it changes how composite manufacturing can be planned: defects become repairable, and scrap becomes feedstock.

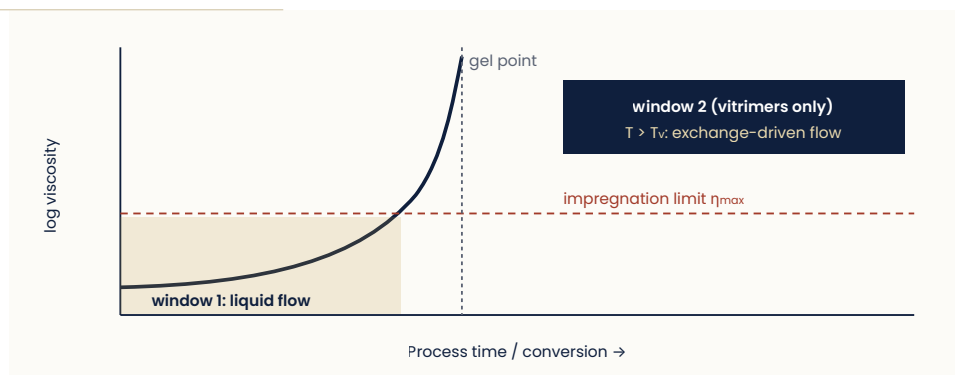


Figure 6.1 Schematic processing windows. Conventional thermosets are processable only before the viscosity limit and the gel point (window 1). Vitrimerers add a second, slower window after cure, in which exchange allows consolidation, welding and reshaping above T_v .

CHAPTER SUMMARY

- Natural fibres suit bio-based vitrimers but limit reprocessing temperature and require strict drying; carbon and glass fibres need sizings compatible with exchange and may need re-sizing after recovery.
- Low-viscosity oils favour infusion, but solid diacid hardeners and hydroxyl-poor anhydrides complicate liquid moulding; compression moulding is the most natural VOV process.
- Castro–Macosko and Flory–Stockmayer models frame the pre-gel window (calculated $\alpha_{gel} \approx 0.58$ for ESO, 0.47 for ELO with diacids); vitrimers add a post-cure window for consolidation and repair.

FUNCTIONAL COMPOSITES AND ADVANCED NANOMATERIALS

Fillers that conduct, sense, heat and resist fire can turn a recyclable matrix into a functional material – and some of them can also switch on the exchange reactions exactly where repair is needed.

IN THIS CHAPTER

- Carbon nanotube and graphene vitrimer composites for conduction, strain sensing and electro- or photo-thermal healing.
- Flame retardancy through phosphorus, silicon and char-forming bio-aromatics – without losing reprocessability.
- The fibre-matrix interphase as a dynamic, exchangeable region.

7.1 CARBON NANOTUBE AND GRAPHENE VITRIMER COMPOSITES

Conductive networks

Carbon nanotubes (CNTs) and graphene platelets make an insulating matrix conductive once they form a connected network at the percolation threshold. Above it, conductivity follows a power law in the excess filler fraction:

$$\sigma \propto (\phi - \phi_c)^t \quad (7.1)$$

where ϕ_c is the percolation threshold and t a critical exponent. High-aspect-ratio fillers percolate at low loadings, which preserves processability.

In vitrimer matrices, filler networks must survive reprocessing. Hot pressing and remoulding can re-disperse, align or break filler contacts, so conductivity should be measured after each cycle, just as mechanical properties are (Chapter 5). Graphene oxide adds a chemical subtlety: its acidic surface groups can catalyse oxirane ring opening in epoxidized fatty esters [61], and could therefore influence cure, side reactions and possibly exchange; formulations should be re-characterized after adding it. Bio-derived carbons are emerging alternatives; interconnected carbon nanosheets prepared from hemp bast fibre, for example, were reported for high-rate supercapacitors [62], although their use in vitrimer matrices remains to be demonstrated.

Piezoresistive sensing

Near the percolation threshold, small strains change the distances between conductive particles and hence the tunnelling resistance across gaps, giving a strain-dependent resistance. Sensitivity is expressed by the gauge factor,

$$GF = \frac{\Delta R / R_0}{\varepsilon} \quad (7.2)$$

A conductive vitrimer laminate can therefore monitor its own strain and damage. The vitrimer adds a distinctive possibility: after damage is detected and repaired by heating, the sensing network can be partly restored, so that structural health monitoring and repair use the same filler.

Photo- and electro-thermal healing

Local heating avoids exposing a whole structure to reprocessing temperatures. Two filler-based routes exist:

- **Photothermal.** CNTs absorb near-infrared light and convert it to heat. CNT–vitrimer composites have been welded and healed efficiently by light, with heating confined to the illuminated region [56].
- **Electrothermal (Joule) heating.** Passing current through a percolated CNT or graphene network, or through carbon fibres themselves, heats the matrix from within. Power dissipated is $P = V^2/R$; at steady state it balances heat loss to the surroundings.

WORKED EXAMPLE · JOULE POWER TO BRING A REPAIR ZONE ABOVE T_v

Consider a 100 mm × 20 mm repair zone on a 2 mm laminate, losing heat from both faces by convection with $h \approx 10 \text{ W m}^{-2} \text{ K}^{-1}$, to be held 150 K above ambient. Heat loss $\approx h A \Delta T = 10 \times (2 \times 0.1 \times 0.02) \times 150 = 6 \text{ W}$ at steady state (edges and conduction into the surrounding laminate neglected — real values will be higher). With a zone resistance of 20 Ω , the required voltage is $\sqrt{(6 \times 20)} \approx 11 \text{ V}$. Insulating blankets reduce power; conduction into cold surroundings increases it. Inputs are illustrative.

7.2 FLAME RETARDANCY

Aliphatic oil-based networks burn readily and form little char. Composites for transport, construction and electronics must nonetheless meet fire standards, typically assessed by limiting oxygen index, vertical burning classification and cone calorimetry. Three families of strategy are compatible with vitrimers.

Phosphorylation

Phosphorus-containing groups act mainly in the condensed phase, promoting dehydration and char formation that shields the underlying material, and in some cases also in the gas phase by scavenging radicals. They can be built into epoxides, hardeners or co-monomers. Incorporating a phosphine oxide monomer into an epoxy vitrimer enabled reprocessability and fire protection simultaneously [55]. Because some phosphorus species are acidic or ester-forming, they can influence transesterification and hydrolysis; their effect on τ^* and on long-term ageing should be measured.

Silicon-modified vegetable-oil resins

Silanes and siloxanes grafted onto oils or co-cured with them form silica-rich residues during combustion that act as protective barriers, and they often improve thermal stability and hydrophobicity. Alkoxysilanes can be introduced through the oxirane (for example by reaction with amino- or mercapto-silanes) or through hydroxyl groups. Their hydrolysis–condensation chemistry adds a second, inorganic network that is generally permanent, which must be accounted for if full reprocessability is required.

Bio-char generation

Aromatic and polyphenolic bio-based components — lignin, tannins, vanillin and furan derivatives — increase char yield and can be combined with phosphorus for synergistic, partly intumescent behaviour. A bio-based epoxy vitrimer made from furan derivatives was reported to be intrinsically flame retardant and was used in recyclable carbon-fibre composites [52].

Table 7.1 Flame-retardant strategies for VOV composites (qualitative).

Strategy	Main mode of action	Effect on exchange	Consideration
Phosphorus in network	Condensed-phase char; some gas-phase action	May catalyse or participate in exchange	Hydrolytic stability; reprocessability demonstrated [55]
Silicon modification	Silica-rich barrier layer	Adds permanent inorganic links	Moisture during processing
Bio-aromatic char formers	Char yield	Neutral to slightly slowing	Colour; viscosity
Intrinsically FR bio-epoxy	Combined char and structure	Designed in	Furan-based example [52]
Additive mineral fillers	Heat sink, dilution, water release	Neutral	High loadings raise viscosity; may hinder reprocessing

7.3 FIBER–MATRIX INTERFACIAL TRANSESTERIFICATION

In a conventional composite, the interphase — the thin region around each fibre where sizing and matrix meet — is fixed at cure. If it debonds, the damage is permanent. In a vitrimer composite, the interphase can be designed to participate in exchange, so that interfacial bonds can rearrange, relax residual stress and re-form after debonding.

Mechanisms

- **Hydroxyl-rich fibre surfaces.** Cellulosic fibres carry abundant hydroxyl groups. In a transesterification vitrimer, matrix esters near the surface could, in principle, exchange with fibre hydroxyls, forming covalent ester links between matrix and fibre.
- **Exchange-active sizings.** Sizings containing esters and hydroxyls (or other dynamic groups such as disulfides) can be designed to co-react with the matrix and continue exchanging after cure, making the interphase part of the dynamic network.

- **Catalyst at the interface.** Catalyst can be concentrated in the sizing, accelerating exchange where adhesion is most needed.

STATUS OF THE EVIDENCE

Interphase exchange is a design concept with strong chemical logic but limited direct experimental demonstration for vegetable-oil vitrimers. Claims of covalent fibre–matrix exchange should be supported by surface-sensitive analysis (for example XPS or ToF-SIMS of debonded fibres) and by interfacial mechanical tests before and after healing, not inferred from bulk healing alone.

Measuring interfacial performance and healing

Table 7.2 Tests for interfacial strength and its recovery.

Test	Measures	Use for vitrimer interphases
Single-fibre pull-out / microbond	Interfacial shear strength τ	Compare virgin, debonded and healed states
Single-fibre fragmentation	Critical length $\rightarrow \tau$ (Kelly–Tyson)	Interface quality in situ
Short-beam shear (ILSS)	Interlaminar shear strength	Laminate-level healing efficiency
Mode I / II fracture	Delamination toughness	Recovery after thermal healing
Surface analysis of fibres	Chemistry of debonded surfaces	Evidence of covalent exchange

Enhanced interfacial shear transfer translates directly into composite performance through the critical-length relation (Chapter 6): doubling τ halves l_c , improving the efficiency of short and recycled fibres. A healable interphase would also slow the accumulation of fatigue damage — one of the most attractive, and least proven, promises of vitrimer composites.

CHAPTER SUMMARY

- CNT and graphene networks add conductivity, strain sensing and local heating; their properties must be re-checked after reprocessing, and GO can affect cure chemistry.
- Photothermal (NIR) welding of CNT–vitrimer composites is demonstrated; Joule heating offers in-service repair with modest power for small zones.
- Phosphorus, silicon and bio-aromatic char formers provide flame retardancy; phosphine oxide and furan-based vitrimers combine fire protection with reprocessability.
- Exchange-active interphases are a promising but still largely unproven route to healable fibre–matrix adhesion.



CIRCULARITY: REPAIR, REPROCESSING, AND DEGRADATION

Reshaping, remoulding, dissolving and degrading: what really happens to a vitrimer composite at the end of its first life.

CH. 8 · REPAIRABILITY, THERMOFORMING, AND RECYCLING STRATEGIES

CH. 9 · BIODEGRADATION AND ENVIRONMENTAL LIFECYCLE

REPAIRABILITY, THERMOFORMING, AND RECYCLING STRATEGIES

Circularity is not a property of a molecule. It is a sequence of operations – reshape, remould, dissolve, recover – each with its own energy, chemistry and losses. This chapter follows that sequence.

IN THIS CHAPTER

- Thermoforming and re-shaping of cured vitrimer composite sheets.
- Closed-loop remoulding of chopped composites by hot pressing.
- Chemical recycling by alcoholysis, acidolysis and swelling, with intact fibre recovery.
- Quantifying property retention across recycling generations.

8.1 POST-FABRICATION RE-SHAPING

Solid-state thermoforming

A cured vitrimer sheet heated above T_v can be bent, twisted or formed in a mould and held until exchange relaxes the internal stress; on cooling, the new geometry becomes permanent. The required hold time follows from the stress-relaxation kinetics (Chapter 3). For single-exponential relaxation, the fraction of stress remaining after time t is $\exp(-t/\tau^*)$:

Table 8.1 Stress remaining after holding at constant deformation (calculated from Eq. 3.1).

Hold time	$1 \tau^*$	$2 \tau^*$	$3 \tau^*$	$5 \tau^*$
Stress remaining	37 %	14 %	5 %	0.7 %

Residual stress at release determines springback: a part released after $1 \tau^*$ will spring back noticeably, one released after $3 \tau^*$ only slightly. For networks with stretched-exponential relaxation ($\beta < 1$), the slowest fraction relaxes considerably more slowly, and longer holds are needed.

WORKED EXAMPLE · THERMOFORMING SCHEDULE

A vitrimer laminate has $\tau^* = 1200$ s at 180°C . To leave no more than 5 % residual stress, hold for $3\tau^* = 3600$ s (1 h). If the forming press can only dwell 20 min, the target is $\tau^* \leq 400$ s, requiring either a higher temperature (with $E_a = 110$ kJ mol⁻¹, about 198°C from Eq. 1.1) or a more active catalyst. Inputs are illustrative.

The fibre constraint

Continuous fibres do not stretch. Reshaping a fibre-reinforced laminate therefore relies on bending, inter-ply shear and fibre re-orientation rather than in-plane extension — the same deformation modes used in thermoforming thermoplastic composites. Sharp radii can cause fibre wrinkling or buckling on the compressive side. Simulating and testing formability with the actual lay-up is essential; matrix flow alone does not guarantee that the fibre architecture can follow.

8.2 THERMOMECHANICAL RECYCLING

The simplest closed-loop route for a vitrimer composite is to chop or granulate a retired part and hot-press the pieces into a new one. Above T_v , the matrix flows between fragments and exchange bonds them into a continuous network. Fibre-reinforced composites with exchangeable aromatic disulfide crosslinks were shown to be reprocessable, repairable and recyclable in this sense [45], and highly disulfide-rich networks were designed specifically for rapid reprocessing [46].

The outcome is a short-fibre or discontinuous-fibre composite, typically with lower stiffness and strength than the original continuous-fibre laminate. Its performance depends on:

- **fragment and fibre length** relative to the critical length (Chapter 6);
- **fibre orientation**, which becomes random or flow-induced;
- **void content**, governed by pressure, temperature and degassing;
- **matrix degradation**, accumulated over each hot-pressing cycle (Chapter 5);
- **fragment welding quality**, set by exchange kinetics at the fragment interfaces.

Mixing granulated recycle with fresh resin, or using it as a core between virgin skins, are practical ways to place recycled material where its properties are adequate.

8.3 CHEMICAL RECYCLING AND FIBER RECOVERY

Alcoholysis and acidolysis under mild conditions

Because transesterification vitrimers exchange esters with hydroxyls, flooding them with a small-molecule alcohol drives the same reaction toward small fragments: the network dissolves without harsh reagents. Yu and co-workers immersed a carbon-fibre epoxy vitrimer composite in ethylene glycol at elevated temperature; ethylene glycol took part in bond exchange and broke the network into small segments, clean carbon fibres were recovered with dimensions and mechanical properties comparable to fresh fibres, and the dissolved epoxy was repolymerized by heating and combined with the recycled fibres to make a new composite — a closed loop described as near 100 % recyclability [58].

Acidolysis uses acids to cleave ester linkages. At industrial scale, Siemens Gamesa's recyclable wind-turbine blade was designed so that, at end of life, the blade can be immersed in a heated, mildly acidic solution that separates the resin from the other components for reuse; the announcement did not name the resin chemistry [1]. Other dynamic chemistries have their own dissolution routes: imine networks dissolve in excess amine [42], and disulfide-rich networks can be degraded to recover carbon fibres [46].

Swelling-based separation

A gentler alternative to depolymerization is to swell the vitrimer with small-molecule solvents until it releases the components it holds. Vitrimer-based printed circuit boards (vPCBs) were recycled this way: the process recovered 98 % of the polymer, 100 % of the glass fibre and 91 % of the solvent, and the recovered materials were used to make new boards [63].

Table 8.2 Chemical recycling routes for dynamic-network composites (qualitative unless cited).

Route	Chemistry	Demonstration	Fibre outcome	Matrix outcome
Alcoholysis (e.g., ethylene glycol)	Ester exchange with solvent	CF vitrimer composite [58]	Clean, near-virgin properties	Repolymerizable oligomers
Acidolysis / mild acid	Acid cleavage of esters	Wind blade concept [1]	Separated for reuse	Separated for reuse
Swelling	Physical separation without depolymerization	vPCB: 98 % polymer, 100 % fibre [63]	Fully recovered	Re-used in new boards
Amine-driven dissolution	Transimination (imine networks)	Polyimine networks [42]	Recovered	Monomers / oligomers
Thiol-mediated / disulfide degradation	Disulfide exchange	Disulfide CF composites [46]	Recovered	Degraded fragments

Non-destructive fibre recovery

The value of recovered fibres depends on length, surface condition and mechanical properties. Carbon fibre is the main economic driver, but glass-fibre recovery matters for volume (wind, marine, electronics). Chemical routes that operate below the temperatures of pyrolysis avoid oxidative and thermal damage, and fibres recovered as aligned fabrics, rather than as tangled mats, retain far more value. Recovered fibres should be characterized for single-fibre tensile strength, surface chemistry and sizing residues before reuse; re-sizing is often required. Recycling options for carbon- and glass-fibre composites, including matrix and filler recovery, have been reviewed [3].

8.4 UPCYCLING AND RE-CURE EFFICIENCY

Retention across generations

The figure of merit for closed-loop recycling is retention of key properties across generations. If each cycle retains a fraction k of a property, after n cycles

$$P_n = P_0 k^n \quad (8.1)$$

WORKED EXAMPLE · IMPLIED PER-CYCLE RETENTION

ESO-divanillic acid vitrimer films hot-pressed five times at 230 °C retained about 40–50 % of their tensile strength and modulus [36]. Solving $k^5 = 0.40\text{--}0.50$ gives $k \approx 0.83\text{--}0.87$ per cycle (calculated). Raising k to 0.95 would leave 77 % after five cycles. Small per-cycle gains compound strongly — which is why reprocessing temperature, atmosphere and catalyst stability matter so much.

Levers for higher retention

- **Lower reprocessing temperature** through more active or latent catalysts (Chapter 4), reducing thermal and oxidative damage.
- **Inert atmosphere and antioxidants** during hot pressing.
- **Catalyst replenishment** where catalyst is lost by volatilization or extraction.
- **Stoichiometric correction**: adding fresh hardener or epoxide to restore network balance after side reactions.
- **Blending with virgin material** to set a guaranteed minimum property level.
- **Cascading use**: placing each generation in a less demanding application.

Upcycling

Chemical recycling can do better than restore: recovered oligomers and polyols can be re-formulated, for example with rigid co-monomers or flame retardants, into a material suited to a higher-value application than the one it came from. The vPCB study reported that recovered materials were used to make new boards [63], and the ethylene-glycol route regenerated a composite from recovered matrix and fibres [58] — both demonstrations of re-cure rather than downcycling.

CHAPTER SUMMARY

- Thermoforming schedules follow from τ^* : about $3\tau^*$ leaves 5 % residual stress; continuous fibres restrict reshaping to bending and shear.
- Hot-press recycling of chopped vitrimer composites gives discontinuous-fibre materials whose properties depend on fibre length, voids and matrix degradation.
- Alcoholysis (ethylene glycol), mild acidolysis and swelling recover clean fibres and reusable matrix; vPCBs recovered 98 % polymer, 100 % fibre and 91 % solvent.
- Per-cycle retention compounds (Eq. 8.1): an implied $\approx 0.83\text{--}0.87$ per cycle in one ESO vitrimer study shows the value of lower-temperature reprocessing.

BIODEGRADATION AND ENVIRONMENTAL LIFECYCLE

A material designed to come apart on command must not come apart by accident. The same ester bonds that enable recycling also expose vegetable-oil vitrimers to water, enzymes and weather.

IN THIS CHAPTER

- Enzymatic and soil biodegradation of triglyceride-based networks, and how to test it properly.
- UV, moisture and chemical weathering — and their specific consequences for dynamic networks.
- Comparing end-of-life scenarios: composting, chemical monomer recovery and thermal conversion.

9.1 ENZYMATIC AND SOIL BIODEGRADATION

Hydrolytic cleavage of triglyceride-based networks

Every vegetable-oil vitrimer contains the ester bonds of the original triglyceride, plus the esters formed during acid or anhydride cure. Lipases, esterases and cutinases hydrolyse such bonds, and the fatty acids and glycerol they release are readily metabolized by microorganisms. In a crosslinked network, however, enzymes cannot penetrate the bulk; they act at the surface, so degradation proceeds by slow surface erosion. Its rate depends on:

- **Accessibility** — water uptake, surface area, porosity and the presence of hydrophilic domains;
- **Mobility** — degradation is faster above T_g , which for many oil networks lies near ambient temperature;
- **Crosslink density** — tighter networks require more bond cleavage before fragments become soluble and assimilable;
- **Chemical composition** — aromatic co-monomers, ether links from homopolymerization and inorganic phases (silicon, phosphorus) slow or block degradation.

Testing biodegradation

Three outcomes are often confused. *Disintegration* is physical fragmentation into small pieces. *Primary degradation* is chemical change, such as loss of molecular weight or crosslinks. *Ultimate biodegradation* (mineralization) is conversion of organic carbon into CO_2 , water and biomass by microorganisms, measured respirometrically against a positive reference material under standardized conditions — for example ISO 14855 for controlled composting or ISO 17556 for soil. Only the last supports a biodegradability claim. Methods for evaluating biological degrada-

tion of crosslinked, partly bio-based polymers have been reviewed in depth for polyurethanes [64]; the same principles — combining mass loss, surface analysis, spectroscopy, enzyme assays and respirometry — apply to oil-based vitrimers.

COMPOSITES CHANGE THE PICTURE

In a fibre-reinforced vitrimer, the fibres dominate the mass. Carbon and glass fibres do not biodegrade; natural fibres do, but at rates that depend on retting, treatment and encapsulation by the matrix. A “biodegradable matrix” therefore does not make a biodegradable composite. For carbon- and glass-fibre parts, biodegradation is the wrong end-of-life goal; for natural-fibre parts, it must be demonstrated on the composite itself.

9.2 ENVIRONMENTAL DEGRADATION PATHWAYS

UV stability

Ultraviolet light drives photo-oxidation, especially at residual double bonds and allylic positions left after incomplete epoxidation, and at aromatic co-monomers that absorb UV. Consequences are yellowing, surface embrittlement and micro-cracking. For vitrimers, photo-oxidation has an added effect: chain scission and new oxidized groups change the exchange chemistry and may reduce reprocessability. Low residual iodine value in the epoxidized oil (Chapter 2), UV absorbers, hindered-amine light stabilizers and protective coatings or gel coats are the standard defences.

Moisture absorption

Water diffuses into polymer networks and, in thin laminates, typically follows Fickian kinetics. For a plate of thickness b exposed on both faces, half of the equilibrium uptake is reached at

$$t_{1/2} \approx 0.049 \frac{b^2}{D} \quad (9.1)$$

where D is the diffusion coefficient.

WORKED EXAMPLE · HOW FAST DOES A LAMINATE TAKE UP WATER?

For $h = 2 \text{ mm}$ and $D = 1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$: $t_{1/2} \approx 0.049 \times (2 \times 10^{-3})^2 / 10^{-12} \approx 1.96 \times 10^5 \text{ s} \approx 2.3 \text{ days}$. A 10 mm section, with the same D , takes 25 times longer — about eight weeks. Inputs are illustrative; D for a given formulation must be measured.

Absorbed water affects dynamic networks in three ways. It plasticizes the matrix, lowering T_g and increasing creep. It can hydrolyse esters (slowly at ambient temperature, faster when hot) and, much more readily, imines — polyimine networks can even be made malleable by water [42]. And it can extract or deactivate catalysts. Hot-wet conditioning followed by stress-relaxation and creep testing is therefore part of qualification, and laminates must be dried before any reprocessing.

Chemical weathering

Alkaline environments (concrete, some cleaning agents, marine sediments) saponify esters; acidic ones catalyse ester hydrolysis and exchange. Fuels and solvents swell oil-based networks to an extent that depends on crosslink density and polarity. Vitrimers are, by design, insoluble — dioxaborolane vitrimers, for example, improved solvent resistance relative to their thermoplastic precursors [6] — but swelling still reduces stiffness, and a swollen dynamic network can creep and relax faster. Exposure tests should therefore combine fluid immersion with mechanical loading at the expected temperature.

Table 9.1 Environmental stressors and their vitrimer-specific effects (qualitative).

Stressor	Generic effect	Vitrimer-specific effect	Mitigation
UV	Photo-oxidation, yellowing	Altered exchange chemistry; reduced reprocessability	Low residual unsaturation; UV absorbers; coatings
Humidity / immersion	Plasticization; swelling	Faster creep; hydrolysis of esters or imines; catalyst loss	Hydrophobic formulation; barrier layers; dry before reprocessing
Heat	Softening above T_g	Exchange activates near T_v ; creep	High E_a ; latent catalysts; margin to T_v
Alkali / acid	Ester hydrolysis	Exchange catalysis by acids/bases	Protective coatings; chemistry choice
Solvents / fuels	Swelling	Accelerated relaxation in swollen state	Higher crosslink density; aromatic content

9.3 END-OF-LIFE SCENARIOS

Three broad end-of-life outcomes are available for a vegetable-oil vitrimer composite, after repair and remoulding (Chapter 8) have been exhausted.

Composting and biodegradation

Composting returns carbon to the biosphere but recovers no material value. It is relevant only for natural-fibre composites whose matrix and fibres are both shown to biodegrade under the relevant standard, and only where industrial composting infrastructure accepts such products. For durable composites, a material that composts quickly may also degrade prematurely in service — an inherent tension.

Chemical monomer and fibre recovery

Alcoholysis, acidolysis and swelling-based separation recover fibres and matrix components for reuse (Chapter 8). For carbon-fibre composites this is the outcome that preserves the most value: recovered fibres can be re-used in new composites, and the matrix can be repolymerized [58]. The environmental benefit depends on solvent recovery and energy use; the vPCB example recovered 91 % of its solvent alongside 98 % of the polymer [63].

Thermal conversion

Incineration with energy recovery, pyrolysis and cement-kiln co-processing extract energy (and, in cement kilns, a mineral contribution from glass fibres) but destroy the matrix and usually damage the fibres. For bio-based matrices, the carbon released is biogenic, which changes its accounting in life-cycle assessment but does not recover material. Thermal routes remain the fallback when contamination, mixed materials or lack of collection make other routes impractical.

Table 9.2 End-of-life scenarios for VOEV composites compared (qualitative).

Scenario	Material value recovered	Suitable for	Prerequisites	Position in waste hierarchy
Repair / reshape	Whole part	All vitrimer composites	Access, heating, design for repair	Highest (reuse)
Hot-press remoulding	Matrix + short fibres	All; best for glass/natural fibres in lower-grade uses	Collection, size reduction	Recycling
Chemical recovery	Clean fibres + matrix chemicals	Carbon-fibre and high-value glass-fibre parts	Solvent handling and recovery	Recycling
Composting	None (returns carbon to soil)	Natural-fibre, demonstrated-biodegradable composites	Standardized certification; infrastructure	Organic recycling
Thermal conversion	Energy; possibly fibres (damaged)	Contaminated or mixed waste	Emissions control	Recovery (energy)

CHAPTER SUMMARY

- Oil-based vitrimer networks biodegrade, if at all, by slow surface erosion; only standardized respirometric tests support biodegradability claims, and fibres change the picture entirely.
- UV, moisture and chemicals affect vitrimers in specific ways — altered exchange, faster creep, ester or imine hydrolysis — that must be tested under load.
- Fickian uptake (Eq. 9.1) shows that thick sections take weeks to saturate; drying before reprocessing is essential.
- For carbon-fibre composites, chemical recovery preserves most value; composting suits only demonstrated-biodegradable natural-fibre parts; thermal conversion is the fallback.



INDUSTRIAL APPLICATIONS, TECHNO-ECONOMICS, AND OUTLOOK

Markets that need recyclable thermosets, the economics of getting there, and the rules and research that will decide the pace.

CH. 10 · INDUSTRIAL CASE STUDIES AND MARKET DEPLOYMENT
CH. 11 · TECHNO-ECONOMIC ANALYSIS AND LIFE CYCLE ASSESSMENT
CH. 12 · FUTURE PERSPECTIVES AND REGULATORY LANDSCAPE

INDUSTRIAL CASE STUDIES AND MARKET DEPLOYMENT

Where would a recyclable, repairable, plant-based thermoset matter most? This chapter answers sector by sector – and separates what has been demonstrated from what is still a design scenario.

IN THIS CHAPTER

- Automotive interior, under-hood and crash components.
- Wind-turbine blades: manufacturing and end-of-life recycling.
- Recyclable printed circuit boards and flame-retardant vitrimer laminates.
- Sporting goods and consumer products where repairability creates value.

HOW TO READ THIS CHAPTER

Each section lists the sector's requirements, the documented demonstrations that exist (with references), and a *design scenario* for a vegetable-oil epoxy vitrimer (VOEV). Design scenarios are engineering reasoning, not reports of products; any performance they mention is a target to be validated.

10.1 AUTOMOTIVE COMPONENTS

Requirements

Table 10.1 Automotive component classes and matrix requirements (qualitative).

Component class	Key requirements	VOEV fit
Interior panels (door, trim, parcel shelf)	Low weight, low emissions/odour, formability, modest heat resistance	Good: natural-fibre reinforcement; thermoformable; bio-content
Under-hood structural parts	Heat (well above 100 °C), oil/coolant resistance, creep resistance	Challenging: needs high T_g , high E_a , low creep
Crash structures and bumpers	Energy absorption, toughness, repair after minor impacts	Promising: oil networks are tough; healing and reshaping of minor damage
Bonded assemblies	Structural adhesion, disassembly at end of life	Promising: vitrimer adhesives can be reprocessed and debonded

Documented building blocks

No vegetable-oil vitrimer automotive part has, to our knowledge, been documented in series production. The relevant demonstrations are at the material level: recyclable and reprocessable epoxy vitrimer adhesives [65]; malleable, recyclable structural adhesives based on vanillin polyimine vitrimers [44]; and hemp-fibre composites with epoxidized soybean oil matrices [57].

DESIGN SCENARIO · THERMOFORMABLE NATURAL-FIBRE DOOR PANEL

A hemp- or flax-mat composite with an ESO-diacid vitrimer matrix is compression-moulded flat, then thermoformed to shape in a second operation above T_v (Chapter 8). Scrap and end-of-life panels are granulated and re-pressed into lower-grade parts. Key validation targets: fogging and odour, dimensional stability at cabin temperatures, creep under clip loads, and the thermal budget of the natural fibres during each forming cycle.

10.2 WIND ENERGY

Manufacturing large blades

Blades are made by vacuum infusion of glass- or carbon-fibre laminates around foam or balsa cores, in moulds tens of metres long. The resin must stay fluid for hours, cure without excessive exotherm in thick root sections, and deliver a T_g and fatigue performance that survive decades of cyclic loading outdoors. Epoxidized oils are attractive for their low viscosity (Chapter 6), but their low T_g , the solid nature of many vitrimer-forming diacids and the creep risk of dynamic networks under sustained gravitational and aerodynamic loads are serious hurdles for primary structure.

End-of-life recycling: a documented industrial step

In September 2021 Siemens Gamesa announced the RecyclableBlade, which uses a resin that can be separated from the other blade components at end of life by immersion in a heated, mildly acidic solution, allowing the materials to be recovered for reuse. Six 81 m blades had been manufactured, with first installation planned at RWE's Kaskasi offshore wind plant in Germany and energy production expected from 2022 [1]. The announcement did not identify the resin as a vitrimer or as bio-based; it nonetheless shows that matrix chemistries designed for separation are entering the wind industry.

DESIGN SCENARIO · REPAIRABLE VITRIMER LEADING-EDGE AND SECONDARY STRUCTURES

Rather than primary spar caps, VOEVs could first target secondary parts — fairings, nacelle covers, leading-edge protection — where loads are lower and repairability and recyclability have clear value. Local heating (Chapter 7) could reshape or heal leading-edge damage in the field. Validation targets: rain-erosion resistance, UV and moisture ageing, creep at summer surface temperatures, and repair quality after field heating.

10.3 ELECTRONICS AND PRINTED CIRCUIT BOARDS

Printed circuit boards are glass-fibre/epoxy laminates (typically flame-retardant FR-4 grades) carrying copper circuitry and components. Their end-of-life value lies in metals and components, but separating these from the cured epoxy is difficult. Vitrimer-based PCBs (vPCBs) used a transesterification vitrimer matrix; at end of life the boards were swollen with small-molecule solvents, recovering 98 % of the polymer, 100 % of the glass fibre and 91 % of the solvent, and the recovered materials were used to make new boards. A cradle-to-cradle life-cycle assessment reported environmental impact reductions relative to conventional boards across 11 impact categories [63].

Electronics impose a flame-retardancy requirement that oil-based networks do not meet unaided. Phosphorus-containing vitrimers that combine reprocessability with fire protection [55] and intrinsically flame-retardant bio-based epoxy vitrimers [52] point toward a bio-based, flame-retardant, recyclable laminate. Additional requirements — low dielectric loss, low ionic contamination (including from exchange catalysts), dimensional stability through soldering temperatures, and copper adhesion — must be demonstrated for any VOV formulation.

Transient and recyclable electronics

Beyond conventional boards, dynamic networks enable electronics designed to be disassembled on demand: swelling or selective depolymerization releases components for reuse, and devices with planned short lives (sensors, disposable diagnostics) can be built for recovery rather than landfill.

10.4 SPORTING GOODS AND CONSUMER PRODUCTS

Skis, bicycle frames, rackets, helmets and boards are high-value, impact-loaded composite products that are frequently damaged in use and often discarded after a crack or delamination. They are attractive early markets for vitrimer composites because repairability has visible value to the user, production volumes are moderate, and branding can reward sustainability.

DESIGN SCENARIO · REPAIRABLE CARBON-FIBRE BICYCLE FRAME

A carbon-fibre frame with a transesterification vitrimer matrix suffers a small delamination from an impact. A service centre clamps the region and heats it locally (by heating blankets or Joule heating through the carbon fibres) above T_v , re-consolidating the plies by exchange-driven flow. Validation targets: recovery of interlaminar strength (ILSS before and after), inspection methods to confirm repair quality, fatigue performance after repair, and liability frameworks for repaired safety-critical products.

Table 10.2 Sector readiness for vegetable-oil vitrimer composites (evidence-based summary).

Sector	Most relevant documented evidence	Evidence level	Main barrier
Automotive interiors	Natural-fibre/ESO composites [57]; vitrimer adhesives [44, 65]	Material-level research	Qualification; emissions; cost
Automotive structural / under-hood	None specific to VOEVs	Concept	T_g , creep, fluid resistance
Wind energy	Separable-resin blade in industrial demonstration [1]	Industrial demo (resin chemistry not disclosed)	Fatigue, creep, scale
Printed circuit boards	vPCB with recovery and LCA data [63]	Laboratory demonstration	Flame retardancy; dielectric and soldering performance
Carbon-fibre composites generally	Closed-loop recycling [58]; bio-based vitrimer CF composites [52, 54]	Laboratory demonstration	Scale-up; property retention
Sporting goods	None specific to VOEVs	Concept	Repair validation; liability

CHAPTER SUMMARY

- Automotive interiors and bonded assemblies are the nearest-term automotive fits; structural and under-hood parts need higher T_g and creep resistance.
- Wind energy shows industrial interest in separable resins (RecyclableBlade, 2021), but VOEVs are better suited first to secondary blade structures.
- Vitrimer PCBs have demonstrated near-complete material recovery and LCA benefits in the laboratory; flame retardancy and electrical performance are the key gaps for bio-based versions.
- Sporting goods are attractive early markets because repairability is visible and valued; repair validation is the main hurdle.

TECHNO-ECONOMIC ANALYSIS (TEA) AND LIFE CYCLE ASSESSMENT (LCA)

A recyclable matrix earns its premium only if something valuable is recovered, and earns its environmental claim only if the recovery is counted honestly. Both questions require the whole life cycle, not just the resin.

IN THIS CHAPTER

- Which raw materials are commodities, which are specialties, and what that means for scale-up.
- A cost model for VOEV composites that includes recovery value — and a test for economic parity with DGEBA.
- Cradle-to-grave and multi-cycle LCA: functional units, allocation across lives, biogenic carbon and energy.

11.1 SUPPLY CHAIN AND SCALABILITY

The scalability of a vitrimer formulation is set by its least available ingredient. Epoxidized soybean and linseed oils are manufactured industrially against published specifications [11, 12]. Many of the hardeners, rigid co-monomers and catalysts that make VOEVs perform, by contrast, are specialty or research chemicals.

Table 11.1 Availability tiers for VEOV formulation components (qualitative assessment).

Component	Examples	Availability tier	Scale-up consideration
Epoxidized oils	ESO, ELO	Commodity	Specify hydroxyl and acid values for vitrimer use
Epoxidized specialty oils	Epoxidized hemp oil	Specialty	Small, less liquid oil markets
Aliphatic diacids	Sebacic, azelaic, dimer acids	Industrial	Solid handling (melting/dissolution)
Natural polyacids	Citric acid	Commodity	Water management in formulation
Lignin-derived aromatics	Vanillin derivatives, divanillic acid	Specialty / research	Synthesis steps; cost [43]
Bio-anhydrides	Maleinized oils, rosin anhydrides	Industrial / specialty	Moisture sensitivity
Exchange catalysts	Zinc salts; TBD; imidazoles	Commodity (Zn) to specialty (TBD)	Low loading but critical to performance
Fibres	Flax, hemp, glass, carbon	Industrial	Sizing compatibility; recovery value

A practical scale-up strategy is to anchor formulations on commodity oils and diacids, to add specialty rigid components only where performance demands them, and to qualify more than one source for each ingredient. Oil variability (Chapter 1) must be handled by specification rather than by assuming a fixed structure.

11.2 COST STRUCTURES

Feedstock and processing

For an epoxidized oil, raw materials dominate cost, and the oil dominates raw materials. A first mass balance shows the scale: one tonne of ESO at 6.8 % oxirane oxygen contains about 0.93 t of oil and 68 kg of oxirane oxygen, requiring about 145 kg of hydrogen peroxide (100 % basis) stoichiometrically, before excess and losses (calculated; see the companion volume). On top of the epoxidized oil, the vitrimer formulation adds hardener — often 30–40 % of resin mass — catalyst, and any rigid co-monomers, each with its own price and supply risk.

Processing overhead

Vitrimer composites can add processing costs: higher cure and reprocessing temperatures, longer dwell times for exchange-driven consolidation, inert atmospheres, and handling of solid diacids. They can also remove costs: scrap and off-spec parts become feedstock; misformed parts can be corrected; secondary bonding can be replaced by welding.

Economic parity with DGEBA

Comparing price per kilogram of resin is misleading for three reasons. Performance differs, so equal mass does not give equal function. The matrix is only part of a composite's cost. And the value of a recyclable matrix appears at end of life. A more useful comparison is life-cycle cost per functional unit:

$$LCC = C_{\text{materials}} + C_{\text{processing}} + C_{\text{use \& repair}} + C_{\text{end-of-life}} - V_{\text{recovered}} \quad (11.1)$$

where $V_{\text{recovered}}$ is the value of fibres, matrix chemicals and parts recovered, net of the cost of recovering them, and all terms refer to the same functional unit.

WORKED EXAMPLE · WHEN CAN FIBRE RECOVERY PAY FOR A MATRIX PREMIUM?

Use illustrative *ratios*, not market prices. Let a carbon-fibre composite be 65 % fibre and 35 % matrix by mass, and let virgin carbon fibre cost 10 times as much per kilogram as a conventional resin (cost unit c). Per kilogram of composite: fibre cost = 6.5c, resin cost = 0.35c. If chemical recycling recovers fibre worth 50 % of virgin value, net of processing, the recovered value is 3.25c per kilogram of composite — enough, in principle, to offset a matrix costing up to about ten times the conventional resin (3.25c/0.35 ≈ 9.3c per kg of matrix extra). For a natural-fibre composite, where fibre value is low, the same logic gives almost no allowance. All numbers are illustrative; the conclusion is structural: *recyclable matrices are easiest to justify where the fibre is expensive and recoverable*.

Table 11.2 Cost levers for VOEV composites relative to DGEBA-based composites (qualitative).

Lever	Direction	Notes
Oil price vs petrochemical price	Variable	Agricultural and biofuel-policy exposure
Hardener and co-monomer choice	Usually cost ↑	Specialty aromatics are the main premium
Catalyst	Small ↑	Low loading; specialty catalysts cost more
Processing time and temperature	↑ or ↓	Longer dwell vs scrap recovery and rework
Repair instead of replacement	↓ (life-cycle)	Requires validated repair procedures
Fibre and matrix recovery	↓ (life-cycle)	Strongest for carbon fibre
Avoided disposal costs and landfill restrictions	↓	Growing where landfill bans apply [1]

11.3 CRADLE-TO-GRAVE LIFE CYCLE ASSESSMENT

Scope and functional unit

Cradle-to-gate studies stop at the factory gate and cannot capture the benefits of repair or recycling. For vitrimer composites, a cradle-to-grave (or cradle-to-cradle) boundary is needed, including use-phase repair, reprocessing cycles and end-of-life recovery. The functional unit should be defined by performance over a service period — for example, a panel of specified stiffness for a stated life — so that a weaker matrix that requires more material, or a recyclable one that lasts multiple lives, is credited fairly.

Evidence so far

Two studies frame the current evidence. A cradle-to-gate assessment of bio-epoxies from bark extractives, lignin and triglycerides found triglyceride-based epoxy the most favourable of the three, identified electricity use in synthesis as the main hotspot, and cautioned that bio-based origin does not guarantee lower impact [17]. A cradle-to-

cradle assessment of vitrimer-based printed circuit boards reported environmental impact reductions relative to conventional boards across 11 impact categories [63]. Neither is a direct LCA of a vegetable-oil vitrimer composite; such studies are a priority for the field.

Allocating burdens across multiple lives

When a material is reprocessed several times, the burdens of virgin production and the benefits of recycling must be shared between life cycles. Common approaches include the *cut-off* method (each life bears only its own processing; recycled input arrives burden-free), the *avoided-burden* or end-of-life recycling method (recycling is credited with the virgin production it displaces), and formula-based compromises such as the Circular Footprint Formula used in EU Product Environmental Footprint guidance. The choice can change conclusions and must be stated and tested by sensitivity analysis.

Carbon footprint, GWP and energy

- **Biogenic carbon.** Carbon in the oil was absorbed from the atmosphere by the crop. Whether that uptake is credited at cradle-to-gate, and how its release at end of life is treated, must follow one declared convention.
- **Hardener and catalyst.** A fossil hardener can supply a third or more of the matrix carbon (companion volume, Chapter 9); its footprint is not offset by the oil's bio-origin.
- **Reprocessing energy.** Heating a composite to reprocessing temperature is energetically modest compared with producing new material, as the worked example shows — but solvent-based recycling adds solvent production and recovery energy, which is why high solvent recovery (91 % in the vPCB case [63]) matters.

WORKED EXAMPLE · SENSIBLE HEAT FOR ONE REPROCESSING CYCLE

Heating 1 kg of composite from 25 °C to 200 °C with an assumed average specific heat of $1.2 \text{ kJ kg}^{-1} \text{ K}^{-1}$ requires $1.2 \times 175 = 210 \text{ kJ} \approx 0.058 \text{ kWh}$ of heat, before press and furnace losses (which can be several times larger). Even multiplied by a realistic process inefficiency, this is small compared with the energy embodied in producing new fibres and resin, so the climate case for reprocessing is generally favourable — provided property retention (Chapter 8) allows the recycled material to replace virgin material. Inputs are illustrative.

Table 11.3 LCA checklist for vegetable-oil vitrimer composites.

Item	Requirement
Standards	ISO 14040 / 14044; state impact method
Boundary	Cradle-to-grave or cradle-to-cradle, including repair and reprocessing
Functional unit	Performance-based over a defined service life
Agricultural inventory	Land use, fertilizer N ₂ O, eutrophication, pesticides; allocation between oil and meal
Co-reactants	H ₂ O ₂ , hardener, catalyst, rigid co-monomers
Multiple lives	Declared allocation method + sensitivity analysis
Recycling	Property retention per cycle; solvent and energy use; recovered-material quality
Biogenic carbon	One declared convention throughout
Comparator	DGEBA-based composite modelled with the same data and method

CHAPTER SUMMARY

- ESO and ELO are commodities; many rigid co-monomers and some catalysts are specialties that limit scale and raise cost.
- Life-cycle cost per functional unit (Eq. 11.1), not resin price per kilogram, is the right parity test; recovered fibre value can justify a matrix premium for carbon-fibre composites but not for natural-fibre ones.
- LCA must cover repair and recycling, use performance-based functional units, declare allocation across lives and biogenic-carbon convention, and include hardeners and solvents.
- Current evidence (bio-epoxy cradle-to-gate; vPCB cradle-to-cradle) is encouraging but indirect; dedicated VOEV composite LCAs are needed.

FUTURE PERSPECTIVES AND REGULATORY LANDSCAPE

The chemistry works. The open questions are whether it can be made durable enough, fast enough and standardized enough – and whether regulation will reward materials designed for a second life.

IN THIS CHAPTER

- Regulatory drivers: REACH, the EU Circular Economy Action Plan, bisphenol A restrictions and bio-based content standards.
- The technical challenges that remain: creep, the speed–durability trade-off, shelf life, retention and standardization.
- Additive manufacturing with bio-based epoxy vitrimers.

12.1 REGULATORY DRIVERS

REACH

Under Regulation (EC) No 1907/2006 (REACH), substances manufactured in or imported into the EU at one tonne or more per year per manufacturer or importer must be registered [66]. Polymers are generally exempt from registration, but their monomers and reactants are not; epoxidized oils, diacids, specialty aromatics and catalysts must each be covered. Catalysts deserve particular attention: some organometallic compounds, including certain organotin, face restrictions, which is one reason zinc salts and organic catalysts are favoured in vitrimer research.

EU Circular Economy Action Plan

The European Commission's *A new Circular Economy Action Plan for a cleaner and more competitive Europe*, COM(2020) 98, published on 11 March 2020, is a main building block of the European Green Deal. It proposes a coherent sustainable-product policy framework intended to make sustainable products, services and business models the norm, and to address key product value chains as a priority [67]. For composites, the direction of travel is toward design for durability, repairability and recyclability — properties that vitrimers are designed to deliver — and away from landfill, which several European countries already prohibit for composite waste [1].

Bisphenol A and safer-chemistry pressure

The EU banned bisphenol A and other hazardous bisphenols from food-contact materials through Regulation (EU) 2024/3190, adopted in December 2024 [68]. Although composites are rarely food-contact materials, the ban reflects a broader regulatory pressure on BPA-based epoxies that strengthens the case for bisphenol-free alternatives, including vegetable-oil networks.

Bio-based content standards

Bio-based claims are verified by radiocarbon analysis. ASTM D6866 determines biobased carbon content (Methods B and C, by accelerator mass spectrometry and liquid scintillation counting), with results expressed as fraction of modern carbon and inter-laboratory uncertainty that can reach ± 3 % absolute [15]. EN 16785-1 combines radiocarbon and elemental analysis to determine bio-based content including biogenic hydrogen, oxygen and nitrogen [16]. Claims should state the standard, the metric (carbon or total content) and whether they refer to the resin or the whole composite — fibres can dominate the latter.

Canada

For Canadian producers, new substances not on the Domestic Substances List require notification under the New Substances Notification Regulations of the Canadian Environmental Protection Act, 1999, before manufacture or import above prescribed quantities; workplace hazard communication follows WHMIS 2015.

Table 12.1 Regulatory and standards landscape for VOEV composites.

Instrument	Relevance
REACH (EC 1907/2006) [66]	Registration of monomers, hardeners, catalysts; restrictions on hazardous substances
Circular Economy Action Plan, COM(2020) 98 [67]	Policy framework favouring durable, repairable, recyclable products
Regulation (EU) 2024/3190 [68]	BPA restriction in food contact; signal for BPA-free epoxies
ASTM D6866 [15]	Biobased carbon content
EN 16785-1 [16]	Bio-based content (radiocarbon + elemental analysis)
ISO 14040 / 14044	Life-cycle assessment framework
CEPA 1999 / NSNR; WHMIS 2015 (Canada)	New-substance notification; hazard communication

12.2 REMAINING TECHNICAL CHALLENGES

Reducing high-temperature creep

A network that can flow at 200 °C can also flow, more slowly, at 60 °C. The Arrhenius law makes the trade-off quantitative.

WORKED EXAMPLE · HOW ACTIVATION ENERGY PROTECTS AGAINST CREEP

Take $\tau^* = 300$ s at a processing temperature of 200 °C (473 K), and ask what τ^* is at a service temperature of 60 °C (333 K), assuming the network is above T_g at 60 °C so that the Arrhenius law still applies. With $E_a = 110$ kJ mol⁻¹, τ^* rises by a factor of $\exp[(E_a/R)(1/333 - 1/473)] \approx 1.3 \times 10^5$, to about 3.8×10^7 s — roughly 1.2 years. Stress would relax appreciably over a service life: the part would creep. With $E_a = 200$ kJ mol⁻¹, the factor is $\approx 1.9 \times 10^9$ and $\tau^* \approx 18\,000$ years. Calculated values; if T_g lies above service temperature, glassy immobility suppresses exchange further.

Strategies to suppress creep include:

- **High activation energies and latent catalysts**, including amines reversibly trapped until high temperature [10];
- **T_g above service temperature**, using rigid bio-based partners (Chapter 4), so that the network is glassy in use;
- **A fraction of permanent crosslinks**, accepting partial rather than full reprocessability;
- **Fibre reinforcement**, which carries most of the load in fibre-dominated directions and reduces matrix creep in those directions (but not in matrix-dominated shear and transverse directions).

Accelerating exchange without sacrificing durability

The ideal vitrimer switches sharply between an inactive and an active state. Beyond raising E_a , approaches include neighbouring-group participation that activates exchange only above a threshold mobility, dual dynamic networks in which a fast chemistry handles healing and a slow one governs load-bearing (Chapter 3), and external triggers — light or electric current through conductive fillers — that heat only where and when exchange is wanted (Chapter 7).

Long-term shelf life

Many exchange catalysts also catalyse cure, so one-component formulations have limited storage life; anhydrides are moisture-sensitive; imines hydrolyse; and solid diacids may phase-separate. Latent catalysts, two-component packaging, moisture-barrier storage and partially reacted, storage-stable prepolymers are the main responses. Shelf-life testing should track viscosity, gel time and — for vitrimers — relaxation behaviour after cure.

Retention across cycles and standardized testing

Property loss per reprocessing cycle compounds rapidly (Chapter 8). Lower-temperature exchange, antioxidant packages and catalyst stability are research priorities. At the same time, the field lacks standardized test methods for vitrimer-specific properties: stress-relaxation protocols, T_v determination, creep under defined conditions and multi-cycle retention are reported in many different ways, making comparison difficult. Agreeing on test protocols would accelerate both research and qualification.

Table 12.2 Research and development agenda for vegetable-oil vitrimer composites.

Challenge	Why it matters	Promising directions
Creep at service temperature	Dimensional stability; structural approval	High E_{α} ; trapped catalysts; higher T_g ; partial permanent networks
Speed vs durability	Economic processing without in-service relaxation	Switchable catalysis; dual networks; local triggers
Shelf life	Industrial handling and logistics	Latent catalysts; two-component systems
Low T_g of oil networks	Structural and hot-wet performance	Rigid bio-based aromatics; high-functionality oils
Multi-cycle retention	Credible circularity	Lower reprocessing T; stabilizers; catalyst replenishment
Fatigue and long-term durability data	Design allowables	Coupon and component fatigue programmes
Standardized vitrimer test methods	Comparability; qualification	Agreed protocols for relaxation, T_v , creep, retention
Dedicated LCAs	Evidence for environmental claims	Cradle-to-cradle studies with performance-based units

12.3 HORIZON TECHNOLOGIES

Additive manufacturing with bio-based epoxy vitrimers

Thermosets dominate high-resolution 3D printing because photopolymer resins cure quickly and precisely — but conventional printed thermosets cannot be reprocessed. A two-step polymerization strategy has been used to create reprocessable thermosets for 3D printing that can be reshaped, repaired and recycled [69]. On the bio-based side, photocurable acrylated epoxidized soybean oil has been printed into shape-memory (“4D”) biomedical scaffolds [29]. Combining the two ideas — oil-based photoresins containing exchangeable ester or disulfide links — points toward printed parts that can be welded together, repaired after damage, and returned to feedstock.

Several printing modes are relevant:

- **Vat photopolymerization (SLA/DLP)** of acrylated or hybrid acrylate–epoxy oil resins, with exchange enabled after printing by thermal post-cure.
- **Direct ink writing** of shear-thinning, filler- or fibre-loaded vitrimer pastes, followed by thermal cure; short carbon or natural fibres can align along the print path.
- **Welding of printed segments** into large structures by exchange at the interfaces, removing build-volume limits.

4D printing

Vitrimers add a second programmable dimension to printed objects: printed shapes can be programmed elastically (shape memory above T_g) and re-programmed permanently above T_v (Chapter 5). Adaptive tooling, deployable structures and personalized medical devices are natural targets.

Outlook

Vegetable-oil vitrimers sit at a rare intersection: an existing commodity feedstock, a chemistry that suits it naturally, and a circular-economy policy environment that increasingly rewards repair and recovery. The decisive work now lies less in discovering new exchange reactions than in engineering: suppressing creep, standardizing tests, demonstrating multi-cycle retention and producing honest life-cycle data. If those are achieved, the thermoset that could not be undone may become the composite designed to be remade.

CHAPTER SUMMARY

- REACH, the 2020 Circular Economy Action Plan, BPA restrictions and radiocarbon-based bio-content standards define the European policy context; Canadian producers must also address CEPA new-substance rules and WHMIS.
- Creep is the central technical risk: a calculated E_a of 110 kJ mol⁻¹ implies relaxation over about a year at 60 °C for a network relaxing in 5 min at 200 °C, versus millennia at 200 kJ mol⁻¹.
- Shelf life, multi-cycle retention, fatigue data and standardized vitrimer test methods are the remaining engineering gaps.
- Reprocessable 3D-printing thermosets and printed AESO structures point to additive manufacturing of repairable, recyclable bio-based parts.

KEY EQUATIONS, REPORTING CHECKLIST, AND TEST METHODS

A working toolkit gathered from the chapters: the equations used for design, a reporting checklist for vitrimer composite studies, and an index of test methods.

A.1 KEY EQUATIONS

Table A.1 Design equations used in this book.

Quantity	Relation	Chapter
Epoxide equivalent weight	$EEW = 1600 / OOC (\%)$	2
Epoxides per molecule	$f = M / EEW$	2
Relaxation time (Arrhenius)	$\tau^* = \tau_0 \exp(E_a/RT)$	1, 3
Viscosity (Maxwell)	$\eta \approx G \tau^*$; T_v where $\eta = 10^{12}$ Pa s	1, 3
Stress relaxation	$G/G_0 = \exp[-(t/\tau^*)^\beta]$	3
Activation energy from two points	$E_a = R \ln(\tau_1/\tau_2) / (1/T_1 - 1/T_2)$	3
Crosslink density	$\nu_e \approx E'_{rubbery} / 3RT$	5
Healing efficiency	$\eta_{heal} = P_{healed}/P_{virgin} \times 100 \%$	5
Shape fixity / recovery	$R_f = \epsilon_{fixed}/\epsilon_{prog}$; $R_r = (\epsilon_{prog} - \epsilon_{res})/\epsilon_{prog}$	5
Critical fibre length	$l_c = \sigma_f d / 2\tau$	6, 7
Infusion fill time (1-D)	$t_{fill} = \phi \mu L^2 / 2K\Delta P$	6
Gel point (Flory–Stockmayer)	$\alpha_{gel} = 1/\sqrt{r(f_e - 1)(f_a - 1)}$	6
Chemorheology (Castro–Macosko)	$\eta = \eta_0 e^{E_\eta/RT} [\alpha_{gel}/(\alpha_{gel} - \alpha)]^{A+B\alpha}$	6
Percolation	$\sigma \propto (\phi - \phi_c)^t$	7
Gauge factor	$GF = (\Delta R/R_0)/\epsilon$	7
Multi-cycle retention	$P_n = P_0 k^n$	8
Fickian half-uptake time	$t_{1/2} \approx 0.049 h^2/D$	9
Life-cycle cost	$LCC = C_{mat} + C_{proc} + C_{use} + C_{EoL} - V_{rec}$	11

A.2 REPORTING CHECKLIST FOR VTRIMER COMPOSITE STUDIES

Table A.2 Minimum information to report, so that results can be compared and reproduced.

Category	Report
Epoxidized oil	Source oil; OOC/EEW; hydroxyl, acid and residual iodine values; supplier or synthesis route
Formulation	Hardener(s), stoichiometric ratio, co-monomers, catalyst and loading (mol % relative to a stated group)
Cure	Schedule (T, time, pressure, atmosphere); conversion (DSC/FTIR); gel fraction
Thermal transitions	T_g by DSC and DMA with definitions; T_v and method
Exchange kinetics	Stress-relaxation protocol (strain, temperatures), τ^* definition, β , E_a with uncertainty
Creep	Stress, temperature, duration, strain–time curve
Composite	Fibre type, sizing, architecture, volume fraction, void content, process
Reprocessing / recycling	Method, conditions, number of cycles, property retention per cycle, recovered-fibre properties, solvent recovery
Durability	Hot–wet conditioning; UV; fluids; fatigue where relevant
Sustainability claims	Bio-based standard and metric; LCA boundary, functional unit, allocation, biogenic-carbon convention

A.3 TEST METHODS INDEX

Designations below are given for orientation; confirm scope and current edition with the issuing body. Standards cited as references in the chapters were checked against the issuing bodies' records [15, 16, 33, 34].

Table A.3 Test methods relevant to VOV composites.

Property	Method(s)
Oxirane oxygen / epoxy content	AOCS Cd 9–57; ASTM D1652
Iodine value	AOCS Cd 1–25 (Wijs); ISO 3961
DSC transitions and cure	ASTM D3418; ISO 11357
Dynamic mechanical properties	ASTM D4065; ASTM D7028 (composites)
Thermogravimetry	ASTM E1131; ISO 11358
Tensile / flexural	ASTM D638, D790; ISO 527, 178; ASTM D3039 (composites)
Interlaminar shear (short beam)	ASTM D2344
Fracture toughness	ASTM D5045; ASTM D5528 (mode I delamination)
Flammability	Limiting oxygen index (ISO 4589); UL 94; cone calorimetry (ISO 5660)
Biodegradation	ISO 14855 (composting); ISO 17556 (soil)
Bio-based content	ASTM D6866; EN 16785–1
Life-cycle assessment	ISO 14040; ISO 14044

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GLOSSARY OF ABBREVIATIONS AND TERMS

AESO

Acrylated epoxidized soybean oil.

AFP

Automated fibre placement.

Associative exchange

Bond exchange in which a new bond forms as an old one breaks; crosslink count is conserved.

β (stretch exponent)

Breadth parameter in stretched-exponential relaxation; $\beta = 1$ is single-exponential.

CAN

Covalent adaptable network.

CNT

Carbon nanotube.

Dissociative exchange

Bond exchange in which bonds break before re-forming; crosslink density falls on heating.

DCC

Dynamic covalent chemistry.

DGEBA

Diglycidyl ether of bisphenol A.

DLP / SLA

Digital light processing / stereolithography.

DMA

Dynamic mechanical analysis.

E_a

Activation energy of the exchange reaction (from Arrhenius analysis of τ^*).

EEW

Epoxide equivalent weight (g eq^{-1}).

EHO / MHO

Epoxidized / maleinized hemp oil.

ELO / ESO

Epoxidized linseed / soybean oil.

EVO

Epoxidized vegetable oil.

GF

Gauge factor (piezoresistive sensitivity).

GO

Graphene oxide.

ILSS

Interlaminar shear strength.

IV

Iodine value (g I_2 per 100 g).

LCA / LCC

Life-cycle assessment / life-cycle cost.

MALDI-TOF MS

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry.

OOC

Oxirane oxygen content (wt %).

RIM

Reaction injection moulding.

RTM / VARTM

Resin transfer moulding / vacuum-assisted RTM.

TBD

1,5,7-Triazabicyclo[4.4.0]dec-5-ene, a guanidine organocatalyst.

TEA

Techno-economic analysis.

T_g

Glass transition temperature.

T_v

Topology-freezing temperature ($\eta = 10^{12}$ Pa s).

τ^*

Characteristic stress-relaxation time.

VOEV

Vegetable oil epoxy vitrimer.

vPCB

Vitrimer-based printed circuit board.

Vitrimer

Permanently crosslinked network that flows by associative exchange above T_v .

$\text{Zn}(\text{acac})_2$

Zinc acetylacetonate, a common transesterification catalyst.

ABOUT THE AUTHOR

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VEGETABLE OIL BIOEPOXY VITRIMERS FOR COMPOSITE MATERIALS

Thermoset composites are strong, durable — and notoriously hard to repair or recycle. Vitrimers keep a permanent covalent network yet let it rearrange, so parts can be healed, reshaped and recovered. This reference shows how epoxidized plant oils, whose natural hardeners create exactly the bonds that vitrimers exchange, can form the matrix of recyclable fibre-reinforced composites.

- Vitrimer physics: T_g , T_v , stress relaxation and Arrhenius flow
- Epoxidation, characterization and dynamic covalent chemistries
- Formulation, catalysts, self-healing, shape memory and welding
- Fibres, interfaces, processing windows and functional nanocomposites
- Thermoforming, remoulding, chemical recycling and biodegradation
- Applications, techno-economics, LCA, regulation and 3D printing

With worked examples throughout, an evidence-graded view of applications, and a reference list verified against bibliographic databases.